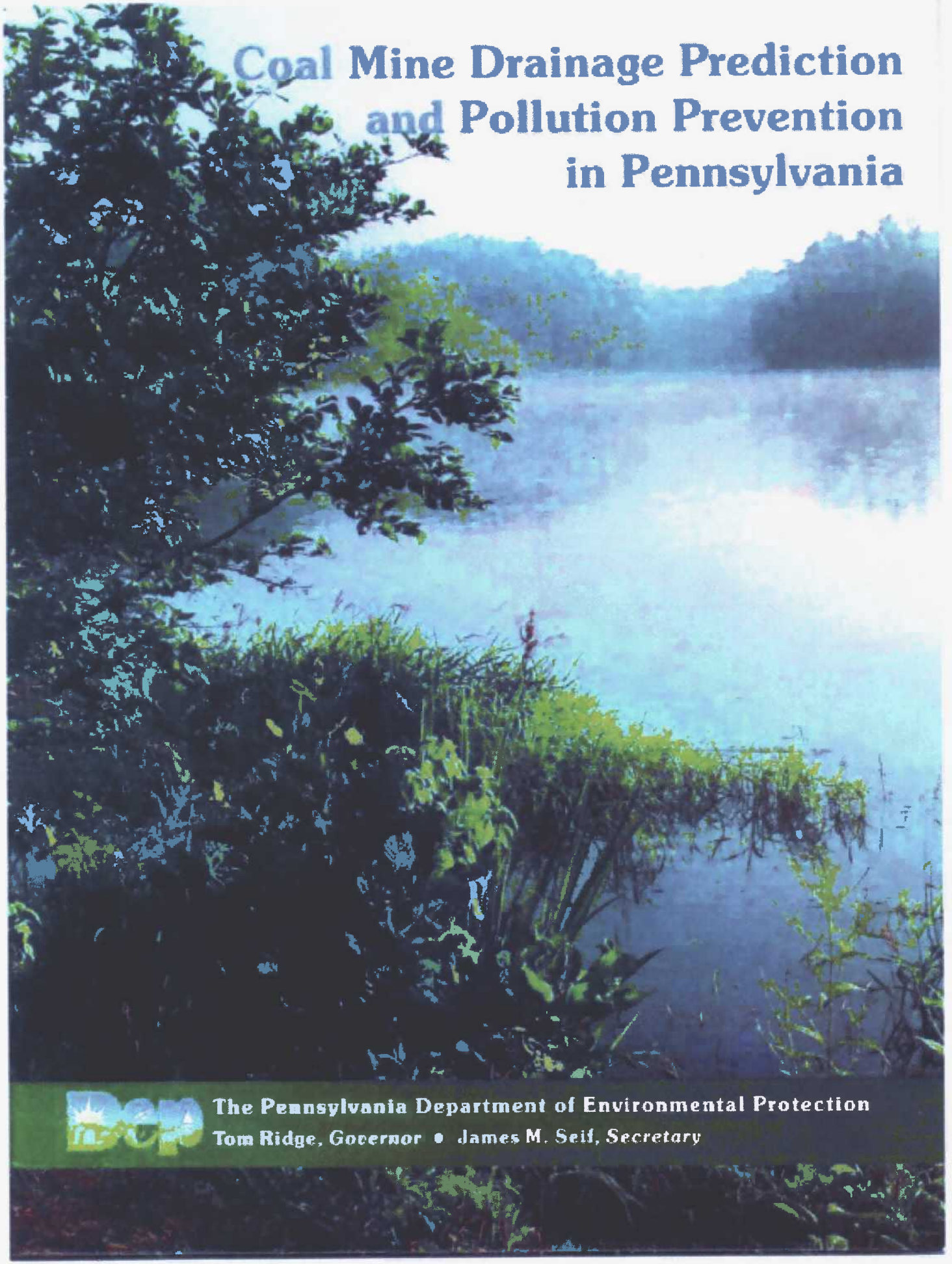
Coal Mine Drainage Prediction and Pollution Prevention in Pennsylvania



The Pennsylvania Department of Environmental Protection
Tom Ridge, *Governor* • James M. Seif, *Secretary*

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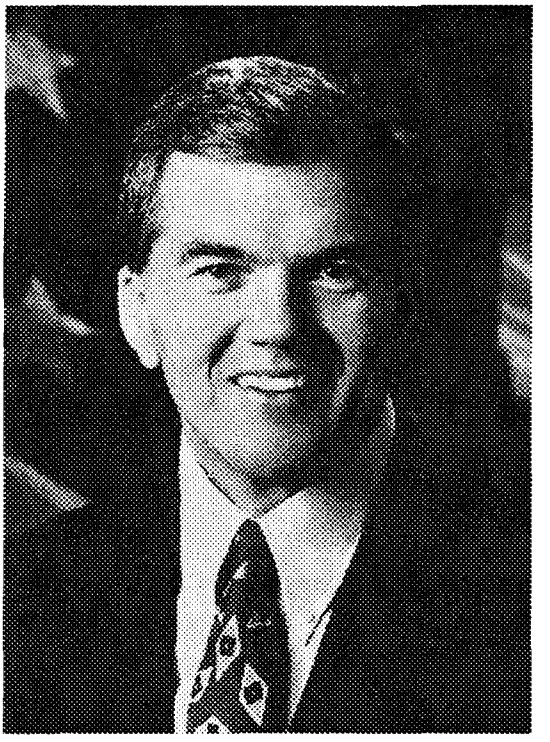

When I took office in January 1995, I called for a partnership--the most advanced partnership in the nation--to promote and enhance our natural resources. I called for Pennsylvania to showcase inspired, common-sense environmental leadership.

Pennsylvania's coal mining industry, Department of Environmental Protection scientists, Penn State researchers and federal officials answered that call by working together to produce this volume. These chapters contain the most current, statewide and research-based information available on acid mine drainage, overburden analysis and techniques to prevent pollution from coal mining. Much of the content of this report is being presented here for the first time and represents data available nowhere else.

Acid mine drainage, the single, largest water pollutant in the state, affects 2,400 miles of Pennsylvania streams. We are leading the nation in developing creative ways to predict and combat mine drainage. I am proud to say this environmentally innovative book, written in the spirit of pollution prevention, contributes to Pennsylvania's internationally recognized 'green technology' efforts.

I invite you to use this book as a technical reference, but also to acknowledge that mining and reclamation technology is still evolving. DEP will continue to work with all partners toward full understanding of mine drainage issues as the new century approaches.

Armed with this knowledge, we can now more clearly evaluate our mining practices. Remember, considering the environmental impact of our decisions is not only the right thing to do, it is the smart thing to do.

Sincerely,

Tom Ridge

TOM RIDGE, Governor
Commonwealth of Pennsylvania

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Acknowledgments

This report represents the combined efforts of many individuals from not only the Pennsylvania Department of Environmental Protection, but also from other government agencies, academia and industry. Chapter authors graciously donated their time and knowledge to this effort. In addition to the authors of each chapter, many individuals worked on the preparation and editing of this report. Tim Kania and Scott Barnes of the Bureau of District Mining Operations assisted with technical review and editing. Additional editing of references and format was done by William Hellier, Charles Miller and Joe Tarantino of District Mining Operations. Members of the Pennsylvania Mining Professionals and the Pennsylvania Coal Association reviewed the text and provided many useful suggestions and constructive criticisms.

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PREFACE

A short history of mine drainage prediction and overburden analysis is appropriate. The Surface Mining Conservation and Reclamation Act of 1971 required that "(n)o approval shall be granted [for a permit] unless the plan provides for a practicable method of avoiding acid mine drainage...or other stream pollution." This requirement implied the obvious need for the development of techniques to predict mine water quality and an understanding of methods to prevent mine drainage pollution. As is often true, the law was ahead of the science; as is sometimes true, the law drove the science, in this case, to develop techniques that could fulfill the aims of mine drainage prediction and pollution prevention. New prediction tools were being developed, but interpretation of their results was in its infancy.

In the early 1970s, two laboratory methodologies- simulated weathering tests and acid-base accounting were being investigated. Pennsylvania's Department of Environmental Protection (DEP) felt a need to explain to the mining community which overburden analysis methods were acceptable to the department and the requirements for submittal of data. This explanation took the form of a three-page letter to mine operators which accompanied permit application review letters from 1979 through 1981. As the science of mine drainage prediction developed, the department attempted to keep pace in its guidance documents. In 1980, the department developed an eight-page internal guidance memorandum to assist permit reviewers. A thirty-four page draft "Overburden Manual" followed in 1984. Concurrently, during the early 1980s, the Environmental Hearing Board upheld several permit denials based on the use of acid-base accounting. In 1989, in response to a much better understanding of the science, a revised draft manual was developed that was twice the length of the 1984 version. The revised manual included discussions of acid-base accounting and some other prediction techniques. The mining industry was concerned that acid base accounting was becoming the dominant decision-making tool for reviewing coal surface mine permit applications and that other techniques and pollution prevention measures were not being given more consideration. The Pennsylvania Coal Association (PCA) filed an action in Commonwealth Court, asserting, among other things, that the manual was either an invalid regulation or an improper policy. Settlement discussion ensued and a more cooperative atmosphere prevailed. It also became apparent, as time went by, that the 1989 manual was quickly becoming outdated because of progress in the science.

The settlement discussions provided both an impetus and a mechanism to begin what has turned out to be a lengthy revision. The 1989 volume had two authors, the present work has more than 20. A work with two parts has expanded to 18 chapters. The current work addresses industry concerns by the inclusion of numerous topics not discussed in the earlier work, such as discussions on geology and groundwater hydrology and simulated weathering tests. Other important additions are greatly expanded discussions of prediction methods other than acid-base accounting and a discussion of various pollution prevention techniques and the benefits of remining.

Throughout, both the DEP and the PCA, for similar and different reasons, saw for the need for an introduction which would clarify the purpose(s) of the manual which is no longer a manual. Certainly the book has more authors, covers more subjects, is longer and has a new title. More important, it has a new purpose, a new focus. It is now a technical reference document: the 1997 version of the latest scientific research and the most advanced scientific thinking about predicting mine drainage quality and preventing mine drainage pollution. It is not a regulation. It is not a policy. It should not be used as either. Inclusion of information or methodologies in the book does not guarantee applicability to a particular situation or assure permit issuance or denial. Absence of information or a methodology from the book does not mean that the information or methodology is inapplicable or that a site may or may not be mined.

Even a cursory review of the current version shows that scientific research and thinking have evolved greatly since 1977, since 1984, and since 1989. More importantly, our knowledge will continue to grow. This version of the book is meant to spur innovation, not to freeze thinking. New tests, practices, and ideas are sure to appear eventually, perhaps soon. The reader, whether in the department, in industry, or in the environmental community, should be vigilant for new material relevant to a particular site or situation which has developed after publication of this book.

One final caveat: Nothing in the book is a substitute for thoughtful and thorough decision making on each permit. Decision making should be based on site-specific information, application of any scientifically valid and appropriate methodology, and the exercise of common sense.

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Coal Mine Drainage Prediction and Pollution Prevention in Pennsylvania

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Biographical Sketches of Authors

Chapter 1
GEOCHEMISTRY OF COAL MINE DRAINAGE

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Summary

Coal mine drainage ranges widely in composition, from acidic to alkaline, typically with elevated concentrations of sulfate (SO_4), iron (Fe), manganese (Mn) and aluminum (Al) as well as common elements such as calcium, sodium, potassium and magnesium. The pH is most commonly either in the ranges 3 to 4.5 or 6 to 7, with fewer intermediate or extreme values. A key parameter is the acidity, which is the amount of base required to neutralize the solution. In coal mine drainage, major contributors to acidity are from ferrous and ferric Fe, Al, and Mn, as well as free hydrogen ions. The acidity should be determined by a "hot acidity procedure", so that ferrous iron is oxidized and its acidic properties properly measured.

Acidic mine drainage (AMD) is formed by the oxidation of pyrite to release dissolved Fe^{2+}, SO_4^{2-} and H^+, followed by the further oxidation of the Fe^{2+} to Fe^{3+} and the precipitation of the iron as a hydroxide ("yellow boy") or similar substance, producing more H^+. Neutralization of the acidic solution by limestone or similar materials can form neutral mine drainage with high SO_4, and possibly elevated Fe and Mn. If appreciable Fe or Mn is present, these neutral solutions can become acid on oxidation and precipitation of the Fe and Mn.

Many factors control the rate and extent of AMD formation in surface coal mines. More abundant pyrite in the overburden tends to increase the acidity of drainage, as does decreasing grain size of the pyrite. Iron-oxidizing bacteria and low pH values speed up the acid-forming reaction. Rates of acid formation tend to be slower if limestone or other neutralizers are present. Access of air containing the oxygen needed for pyrite oxidation is commonly the limiting factor in rate of acid generation. Both access of air and exposure of pyrite surfaces are promoted by breaking the pyrite-bearing rock. The oxygen can gain access either by molecular diffusion through the air-filled pore space in the spoil, or by flow of air which is driven through the pore space by temperature or pressure gradients.

Because of the complex interactions of all these and other factors, prediction and remediation of AMD is site specific. An evaluation of a given site or proposed procedure can be aided by understanding the processes and concepts discussed in this chapter.

Introduction

Coal mine drainage can be acidic or alkaline and can seriously degrade the aquatic habitat and the quality of water supplies because of toxicity, corrosion, incrustation and other effects from dissolved constituents.

Acidic mine drainage (AMD), in which mineral acidity exceeds alkalinity, typically contains elevated concentrations of SO_4, Fe, Mn, Al and other ions. AMD may or may not have a low pH (high concentration of H^+ ions), since the presence of dissolved Fe, Al and Mn can generate hydrogen ions by hydrolysis. The major source of acidity is oxidation of pyrite (FeS_2) in freshly broken rock that is exposed by mining. Pyrite oxidation can be rapid upon exposure to humid air or aerated water, particularly above the water table.

In contrast, neutral or alkaline mine drainage (NAMD) has alkalinity that equals or exceeds acidity but can still have elevated concentrations of SO_4, Fe, Mn and other solutes. NAMD can originate as AMD that has been neutralized by reaction with carbonate minerals, such as calcite and dolomite, or can form from rock that contains little pyrite. Dissolution of carbonate minerals produces alkalinity, which promotes the removal of Fe, Al and other metal ions from solution, and neutralizes acidity. However, neutralization of AMD does not usually affect concentrations of SO_4.

Sample		Measured water-quality constituent										
Site name[1]	Depth, meters	Conductance, mS/cm	Oxygen, dissolved	Eh, mV	pH	Acidity, $CaCO_3$	Alkalinity, $CaCO_3$	SO_4	Ca	Mg	Fe	Mn
Mine 1, Clarion County, C & K Mines 18, 19, and 20 (lat 41°04'15" N, long 79°26'45" W)												
LMS N2-S	1.5	3,230	--	--	6.8	0	280	2,300	470	270	0.05	7.40
LMS N2-15	4.5	--	--	--	4.0	--	0	7,600	490	1,200	1.30	260.00
WMS N2-1	17.4	2,900	.17	358	6.1	64	120	2,200	320	242	30.00	58.00
WMS N3-1	19.2	1,270	.20	376	6.1	0	170	680	180	94	2.00	3.60
WMS N4-1	11.5	1,690	.19	433	5.5	31	51	1,150	306	145	3.30	18.50
LMS S1-S	1.5	3,400	--	--	6.9	0	560	2,100	680	240	.09	13.00
LMS S1-15	4.6	3,550	--	--	6.9	0	600	1,800	610	220	1.80	19.00
WMS S1-1	28.9	2,330	.35	398	6.7	0	500	1,300	380	130	.78	5.10
LMS S2-S	1.5	4,370	--	--	7.0	0	750	2,300	560	210	.04	6.80
LMS S2-15	4.6	3,890	--	--	6.9	0	700	1,900	650	230	5.70	7.50
WMS S2-1	17.2	1,950	.38	431	6.3	0	230	1,200	290	140	8.20	17.00
WMS S4-1	20.1	2,310	.28	423	6.3	30	360	1,400	410	180	.70	16.00
Mine 2, Clarion County, Old Forty Mine (lat 41°09'50" N, long 79°25'30" W)												
WMB A1	10.0	2,120	--	--	2.6	688	0	913	83	74	174.00	26.50
WMS A2	10.2	2,980	--	--	2.4	1,080	0	1,350	97	102	162.00	38.70
WMB B1	10.9	3,400	--	--	3.1	1,106	0	1,904	253	169	472.00	79.30
WMS B2	7.4	2,710	--	--	2.4	1,020	0	988	62	58	140.00	28.70
WMB C1	8.4	5,270	--	--	2.3	2,380	0	2,844	131	138	566.00	47.60
WMS C2	7.1	5,110	--	--	4.3	3,060	0	4,034	205	198	1,560.00	84.40
OMS Dm	0	4,700	--	--	2.2	2,160	0	2,444	82	105	433.00	36.10
Mine 3, Clarion County, C & K Mine #69 (lat 41°09'15" N, long 79°29'30" W)												
WMS 14B	33.6	2,870	.16	234	5.7	50	81	2,185	384	250	48.10	24.80
WUB 14A	33.2	2,960	.20	269	5.4	122	54	2,251	325	229	62.80	24.10
WUB 14	33.3	3,030	.20	294	5.2	138	33	2,049	306	215	63.40	26.60
WMS 15B	16.3	5,030	2.70	599	2.8	1,660	0	3,457	331	287	375.00	36.10
WMB 15A	24.8	6,040	1.90	577	2.5	2,680	0	4,404	279	234	583.00	41.10
WMB 15	36.4	4,840	1.85	558	3.4	1,604	0	3,675	353	270	477.00	48.30
OMS 15	0	3,280	.63	373	5.2	22	56	2,352	311	288	18.80	22.80
Mine 4, Clearfield County, J.A. Thompson Mine (lat 40°55'30" N, long 78°22'30" W)												
WUB 1K	20.3	140	.88	275	6.4	0	54	32	24	6	.80	.80
WUB 1C	25.4	186	1.00	315	6.6	0	61	54	33	6	<.01	1.10
WMS 2K	19.4	1,860	.63	485	4.2	270	0	1,600	270	280	34.00	67.00
WMB 2C	24.5	2,340	.82	485	3.8	450	0	2,100	250	230	120.00	71.00
LMS 3	1.2	836	--	--	8.3	0	98	370	57	36	.14	.03
WMS 3K	20.9	1,800	4.40	--	3.6	120	0	1,200	200	130	12.00	56.00
WMB 3C	33.8	926	1.10	217	5.8	28	37	660	240	55	40.00	7.80
WMS 4K	18.5	2,640	.58	545	3.6	570	0	2,300	230	260	87.00	93.00
WMB 4C	23.4	3,110	.68	430	4.4	840	0	3,300	540	440	500.00	140.00
WMS 5K	6.2	1,810	1.60	562	2.9	510	0	1,200	230	210	190.00	74.00
WMB 5C	19.2	1,920	1.10	--	5.6	170	28	1,400	450	100	96.00	10.00
LMS 6	1.2	454	--	--	5.7	0	24	230	34	19	.04	4.90
WMS 6K	16.6	4,130	1.20	528	3.2	550	0	4,600	850	920	160.00	400.00
WMB 6C	29.5	2,550	.73	313	3.8	280	0	2,200	380	130	180.00	41.00
WMS 7K	17.5	1,840	.85	510	4.0	130	0	1,400	280	240	12.00	70.00
WMB 7C	31.5	2,150	1.20	280	5.8	390	36	1,800	400	120	220.00	28.00
OMS N1	0	2,820	--	--	3.4	330	0	3,300	340	210	52.00	54.00
Mine 5, Clearfield County, Kauffman Mine (lat 40°55'45" N, long 78°23'30" W)												
OUB 4-3	0	34	9.50	--	5.6	10	9	17	5	3	<.01	.03
WUB W3A	30.3	241	.56	--	7.1	0	126	13	38	5	1.10	.28
WUB W5A	25.3	256	.84	--	7.3	0	134	18	39	4	.12	.15
WUB W1A	14.0	10	--	--	5.9	15	16	8	--	--	.13	.62
Bulk Precipitation, Centre, Clinton, Somerset, and Union												
CEN PA11	--	26	--	--	4.1	4	0	2.7	3	< 1	.03	< 01
CLI PA08	--	24	--	--	4.1	4	0	1.6	3	<.1	.03	< 01
SOM PA04	--	38	--	--	4.0	5	0	3.8	5	< 1	.06	.01
UNI PA13	--	23	--	--	4.2	3	0	2.2	3	<.1	.02	.08

Table 1.1 Measured composition and computed CO_2 and saturation indices for water and associated gas samples collected from surface coal mines in western Pennsylvania [water-quality constituents in milligrams per liter, except as noted; oxygen isotope composition ($\delta^{18}O$) in per mil; gas composition in volume percent; saturation index unitless ; <, less than; --, no data; . , value <-10]

				Oxygen isotope[2]			Gas composition[3]			Saturation index[4]			
Al	Cu	Ni	Zn	H_2O	SO_4	$\Delta^{18}O$	O_2 mea-sured	CO_2 mea-sured	CO_2 com-puted	Calcite	Siderite	$Fe(OH)_3$	Gypsum
middle and lower Kittanning coal seams (mined 1980-86; sampled December 1992)													
0.17	<0.01	0.06	0.14				14.8	5.8	3.5	-0.1	-2.3	-0.8	-0.0
26.00	.09	1.70	2.50									-5.3	.1
.27	<.01	.30	.21				3.2	13.6	7.9	-1.3	-0.4	2.7	-0.2
<.14	<.01	.03	.08						12.5	-1.3	-1.4	1.9	-0.7
1.10	<.01	.23	.22						14.4	-2.3	-2.3	1.3	-0.5
<.14	<.01	.07	.20				14.6	6.2	5.9	.4	-1.7	-0.7	.0
<.14	<.01	.04	.08				3.4	12.7	6.4	.4	-0.3	.7	-0.1
<.14	<.01	<.02	.03				4.3	15.7	8.9	.1	-1.5	2.9	-0.2
<.14	<.01	.04	.12				12.6	6.3	6.3	.5	-1.8	-0.6	-0.0
<.14	<.01	.04	.04				11.1	8.4	7.7	.5	.2	1.2	.0
<.14	<.01	.04	.03				3.3	16.4	10.3	-0.7	-0.9	3.5	-0.3
<.14	.01	.04	.03				13.0	8.6	7.0	-0.4	-1.7	2.3	-0.2
Clarion coal seam (mined 1961-75; sampled September 1990)													
58.90	.08	1.56	2.25		-0.9	9.9						-2.4	-1.0
91.50	.20	1.89	3.56		1.0	11.4						-2.4	-0.9
190.00	.38	3.47	3.96	-10.6	-1.8	9.0						-0.5	-0.4
93.40	.29	1.66	4.75	-10.2	-0.1	10.3						-2.4	-1.1
134.00	.02	3.66	4.49		-0.2	10.2						-6.0	-0.6
39.50	.06	6.35	8.31		1	10.5						-0.3	-0.3
141.00	.24	2.61	4.12		-1.4	9.0						-2.6	-0.8
lower Kittanning and Clarion Coal seams (mined 1978-81; sampled September 1990)													
.27	.04	.54	.27	-10.6	-4.3	6.0			15.5	-1.7	-0.7	-0.1	-0.1
.83	.05	.71	.36	-10.4	-4.4	5.9			23.5	-2.2	-1.0	-0.2	-0.2
.93	.05	.75	1.29	-10.0	-0.2	10.1			24.9	2.6	-1.4	-0.4	-0.2
72.20	.22	3.02	1.95	-10.3	-3.6	8.7						-5.3	-0.1
98.00	.25	2.74	2.50	-10.6	-3.7	6.6						-5.3	-0.1
87.80	.13	2.67	2.48	-10.3	-4.0	8.3						-2.8	-0.1
1.46	.05	.58	.31	-10.2	-1.7	8.6			37.2	-2.4	-1.7	-1.0	-0.2
lower Kittanning coal seam (mined 1968-85; sampled September 1990)													
<.14	<.01	<.02	.02		-.5	11.5			1	-1.9	-1.5	-1.0	-2.4
<.14	<.01	<.02	.01		-0.8	10.2			1.7	-1.6	-3.6	-1.2	-2.0
26.00	.07	1.80	2.50				20.9	.03				-2.1	-0.4
26.00	.06	2.10	2.20									-2.3	-0.3
<.14	.04	<.02	.12				20.9	.03	5.0	-1.8	-2.9	1.6	-1.2
8.20	.06	2.50	3.30				20.9	.05				-3.7	-0.5
.31	<.01	.18	.09						3	-2.1	-1.1	3.3	-0.5
63.00	.10	3.30	4.10		-2.5	8.5	20.7	.03				-3.0	-0.3
32.00	.05	3.50	5.20	-10.7	-3.9	7.1						2.5	.0
58.00	.29	1.80	2.00				20.8	.05				-1.0	-0.5
.28	.03	.35	.13						3	-2.3	-1.1	1	-0.1
<.14	.03	.20	.32						2	-2.9	-4.0	-2.5	-1.5
77.00	.22	10.00	15.00		-4.8	6.2						-0.8	.1
.53	.03	1.20	.55	-11.9	-2.6	8.4						.6	-0.1
13.00	.05	1.90	1.80	-10.9	-4.3	6.8	20.8	.05				-4.3	-0.4
.28	.01	1.00	.51		-0.2	10.8			3.7			-2.6	-0.1
25.00	.07	1.40	1.50		-5.0	6.0						3.7	-0.2
lower Kittanning coal seam (mined 1992-95; sampled May 1992, before mining)													
<.13			.08						2.4	-4.2	-5.3	-2.7	-3.2
<.13			.05						1.1	-0.8	-0.5	-3.5	-2.6
<.13			.01						3	-0.5	-1.3	-1.4	-2.3
Counties (sampled December 1980-February 1981)													
	<.01	<.01	<.01										
	<.01	<.01	<.01										
	<.01	<.01	.02										
	<.01	<.01	<.01										

[1] Three-letter prefix of sample site name sequentially indicates sample type (W=well, L=lysimeter, D=discharge), mined condition (U=unmined, M=mined), and lithology of sampled interval (B=bedrock, S=spoil). Descriptions and complete data collected at the above mines have been reported: Site 1 – Lescansky et al. (1993), Cravotta et al. (1994a,b), Site 2—Brady et al. (1990, site9), Dugas et al. (1993), Williams et al. (in press), Site 3—Dugas et al. (1991), Cravotta (1994), Site 4—Loper et al. (1991), Durkin and Schaffstall (1992, 1993), Guo et al. (1994), Cravotta (1992) Site 5—Rose et al. (1995), Brady et al. (1996), Bulk Precipitation—Peters and Bonelli (1982)

[2] Isotope composition of oxygen in water ($\delta^{18}O_{H2O}$) and sulfate $\delta^{18}O_{SO4}$) reported as per mil relative to SMOW standard. $\Delta^{18}O = \delta^{18}O_{SO4} - \delta^{18}O_{H2O}$.

[3] Gas composition for unsaturated-zone air samples nearest to water sampling locations. Data for site 1 is average value from Cravotta et al. 1994a; data for site 4 September 1990 value from W. Guo (written commun., 1995).

[4] Saturation index and partial pressure of CO_2 calculated with WATEQ4F (Ball and Nordstrom, 1991) and reported measured data (above, adjusted to balanced ionic charge), additional constituents (including F, NO_3, NH_4, PO_4, SiO_2, and Sr), temperature (values ranged from 9.4° to 14°C), measured Eh or computed Eh from Fe_{tot} or ratio of Fe^{3+}/Fe^{2+}

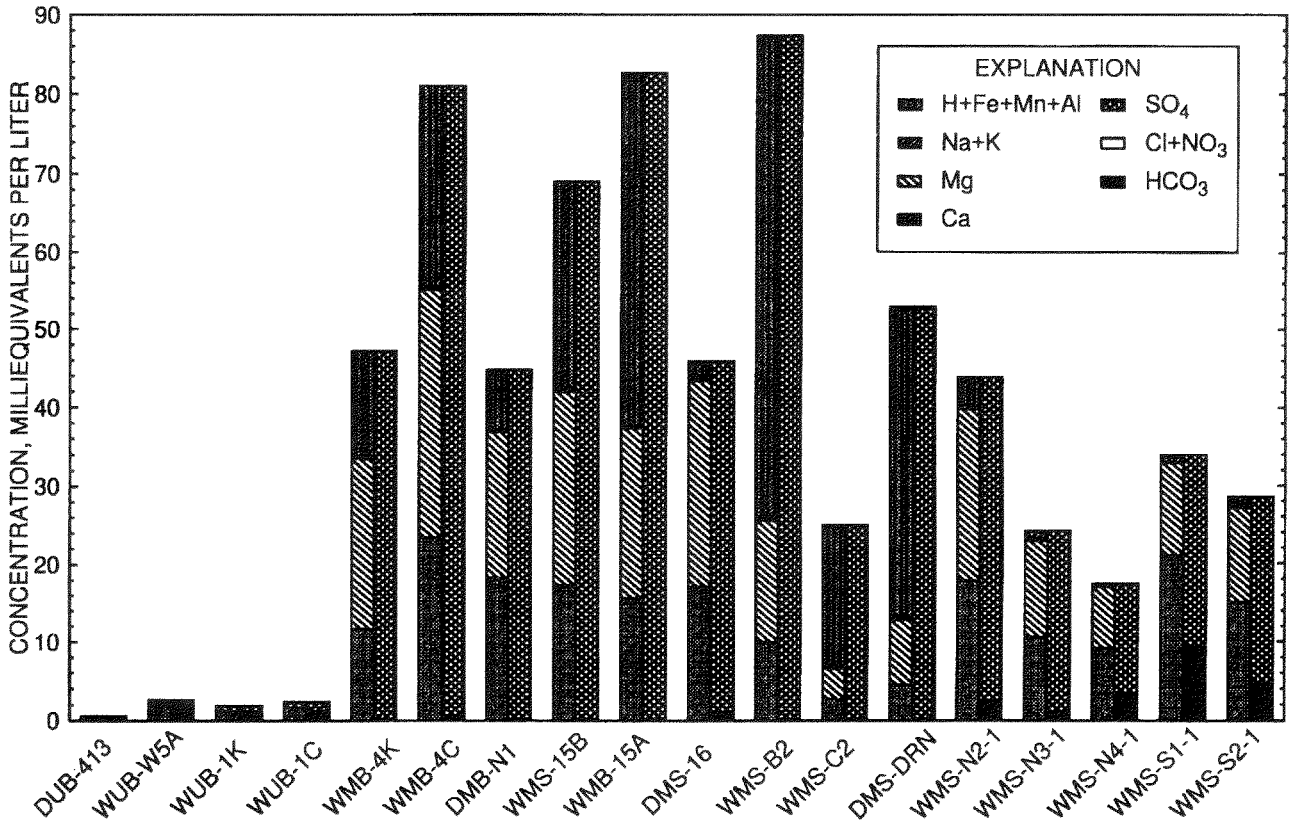


Figure 1.1 Major ions in water samples from surface-coal mines in western Pennsylvania (selected data from table 1.1). The first four samples on the left are characteristic of conditions unaffected by mining; the other samples are characteristic of conditions affected by mining, which include elevated concentrations of sulfate (SO_4) and metals (Fe, Mn, Al). Note that acidity (computed as H+Fe+Mn+Al and expressed in millequivalents) commonly exceeds alkalinity (as HCO_3). See text for discussion of acidity.

Chemistry of Coal Mine Drainage

The chemistry of water samples from unmined, surface-mined or underground-mined areas in the coalfields of western Pennsylvania is extremely variable (Table 1.1, Figure 1.1). Rain in Pennsylvania is generally acidic (Peters and Bonelli, 1982; Lynch et al., 1990) but is typically much more dilute than spring water or ground water (Table 1.1). In unmined areas, spring water and ground water are typically alkaline or only slightly acidic and contain much lower concentrations of dissolved solutes than water from mined areas. In unmined areas, spring water commonly is only slightly more mineralized than rainfall, and is dilute relative to nearby ground water at depth beneath hills (Chapter 10).

Under mined conditions, ground water ranges from alkaline to acidic. For example, samples reported in Table 1.1 have pH ranging from 2.2 to 7.0. Compilations of data show that pH values commonly have a bimodal frequency distribution; most samples are either distinctly acidic (pH 2.5 to 4) or near-neutral (pH 6 to 7), with relatively few samples having pH values between 4 and 6 (Figures 1.2a, 1.3a) (Brady et al., 1997). In contrast, the acidity (or net alkalinity, equal to alkalinity - acidity) is unimodal, with a peak between -100 and +100 mg/L $CaCO_3$ (Figure 1.2b). The net alkalinity generally decreases with decreasing pH, with few exceptions, but in a non-linear manner (Figure 1.2c, 1.3b). In the acidic waters, SO_4 is the principal anion, and Fe, Mn and Al are major cations (Figure 1.1). In alkaline waters, HCO_3 is a significant anion along with SO_4, and concentrations of Ca, Mg, and Na are generally elevated relative to Fe and Al.

Characteristically, the quantity and quality of discharge from coal mines in Pennsylvania varies widely with time (Brady et al., 1990, 1994; Hornberger et al., 1990). In the extreme, at a single sampling site, net alkalinity can alternate from alkaline to acidic at different times (Figure 1.4). Specific factors that cause water-quality variations at surface mines are discussed in subsequent sections.

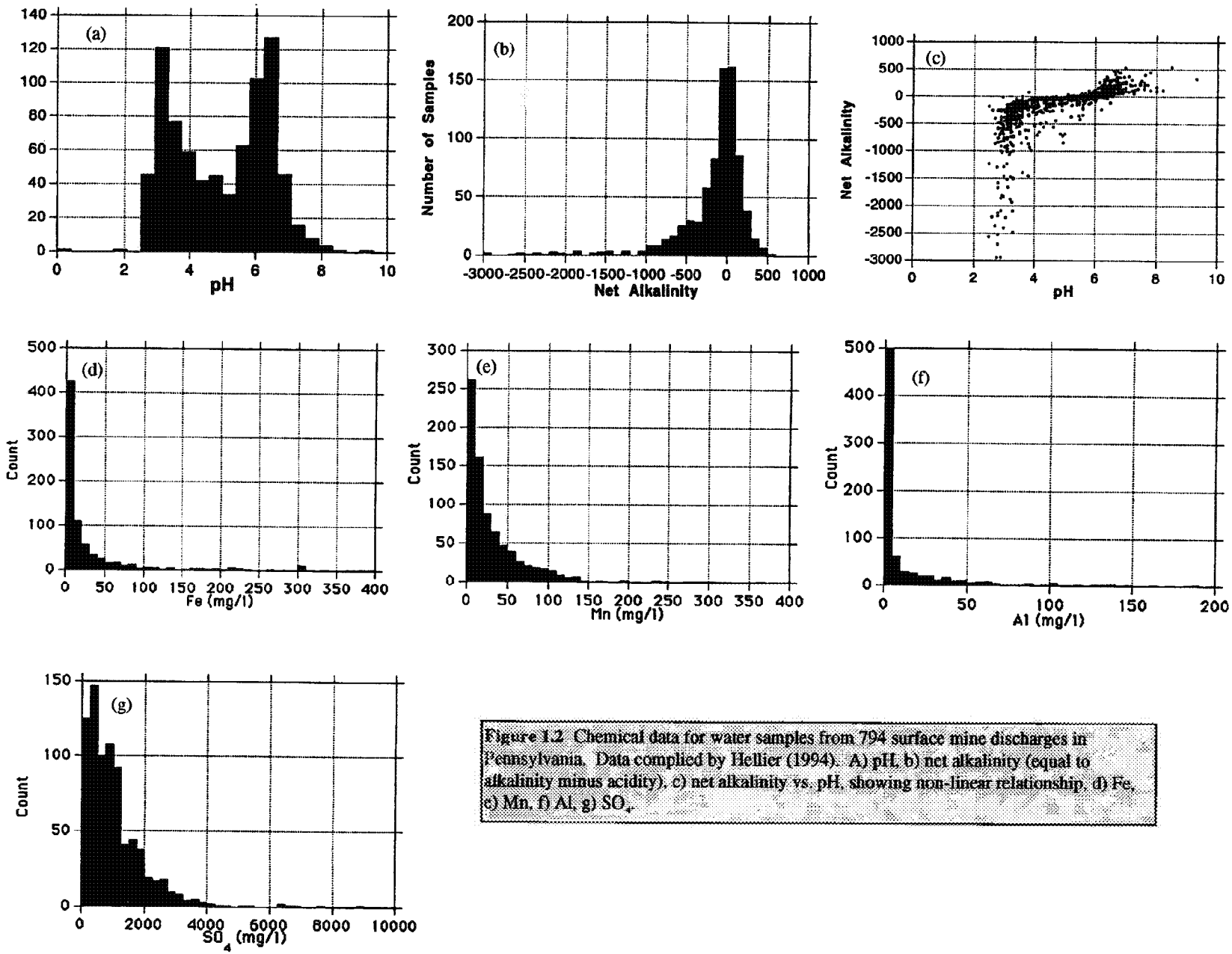


Figure 1.2 Chemical data for water samples from 794 surface mine discharges in Pennsylvania. Data complied by Hellier (1994). A) pH, b) net alkalinity (equal to alkalinity minus acidity), c) net alkalinity vs. pH, showing non-linear relationship, d) Fe, e) Mn, f) Al, g) SO_4.

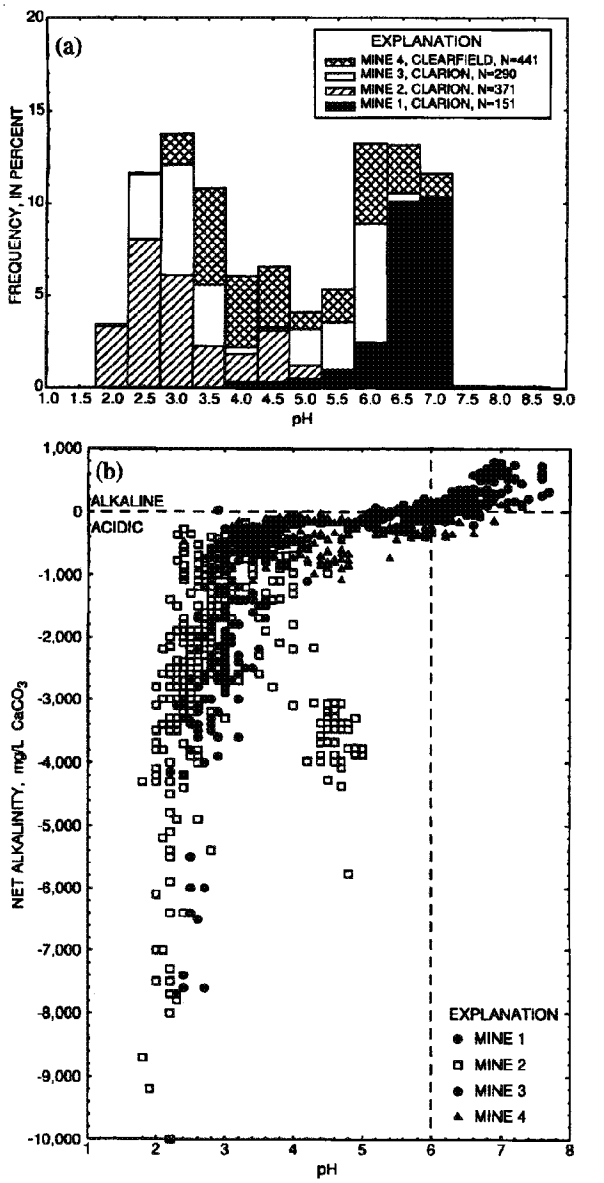


Figure 1.3 (a) Frequency distribution of pH, showing bimodal pattern similar to Figure 1.2a. Acidity, alkalinity, and pH data for 1253 water samples from the four coal mines contributing data to Table 1.1, weighted to 25% from each mine. (b) Net alkalinity (alkalinity - acidity) relative to pH of the same water samples.

Production of Acidity

The geochemistry of AMD has been the subject of numerous investigations. Some general references on the subject include publications by Temple and Koehler (1954), Singer and Stumm (1970), Kleinmann et al. (1981), Nordstrom (1982), Williams et al. (1982), Hornberger et al. (1990), Alpers and Blowes (1994), Blowes and Jambor (1994), Evangelou (1995), and Nordstrom and Alpers (1996).

AMD results from the interactions of certain sulfide minerals with oxygen, water, and bacteria (Figure 1.5). The iron disulfide minerals pyrite (FeS_2) and, less commonly marcasite (FeS_2), are the principal sulfur-bearing minerals in bituminous coal (Davis, 1981; Hawkins, 1984). Pyrrhotite (FeS), arsenopyrite (FeAsS), chalcopyrite ($CuFeS_2$) and other sulfide minerals containing Fe, Cu, As, Sb, Bi, Se and Mo also can produce acidic solutions upon oxidation, but these minerals are uncommon in coal beds. Hence, because of its wide distribution in coal and overburden rocks, especially in shales of marine and brackish water origin, pyrite is recognized as the major source of acidic drainage in the eastern United States.

The overall stoichiometric reaction describing the oxidation of pyrite and marcasite is commonly given as:

$$FeS_2(s) + 3.75\ O_2 + 3.5\ H_2O = Fe(OH)_3(s) + 2\ SO_4^{2-} + 4\ H^+ + \text{heat} \qquad (1.1)$$

In reaction 1.1, solid pyrite, oxygen (O_2) and water (H_2O) are reactants, and solid ferric hydroxide ($Fe(OH)_3$), sulfate (SO_4^{2-}), hydrogen ions (H^+) and heat energy are products. The heat energy produced in this reaction for complete conversion of one mole of pyrite to ferric hydroxide amounts to about 1490 kilojoules at 25°C, based on enthalpies in Robie et al. (1978) and Naumov et al. (1974).

In most samples of coal mine drainage, an abundance of dissolved ferrous iron (Fe^{2+}) (Table 1.1) indicates that the chemical reactions are at an intermediate stage in the series of reactions that together represent pyrite oxidation (reaction 1.1). The following reactions characterize various stages in the complete reaction (Stumm and Morgan, 1981, pp. 470):

$$FeS_2(s) + 3.5\ O_2 + H_2O = Fe^{2+} + 2\ SO_4^{2-} + 2H^+ \qquad (1.2)$$

$$Fe^{2+} + 0.25\ O_2 + H^+ = Fe^{3+} + 0.5\ H_2O \qquad (1.3)$$

$$FeS_2(s) + 14\ Fe^{3+} + 8\ H_2O = 15\ Fe^{2+} + 2\ SO_4^{2-} + 16\ H^+ \qquad (1.4)$$

$$Fe^{3+} + 3\ H_2O = Fe(OH)_3(s) + 3\ H^+ \qquad (1.5)$$

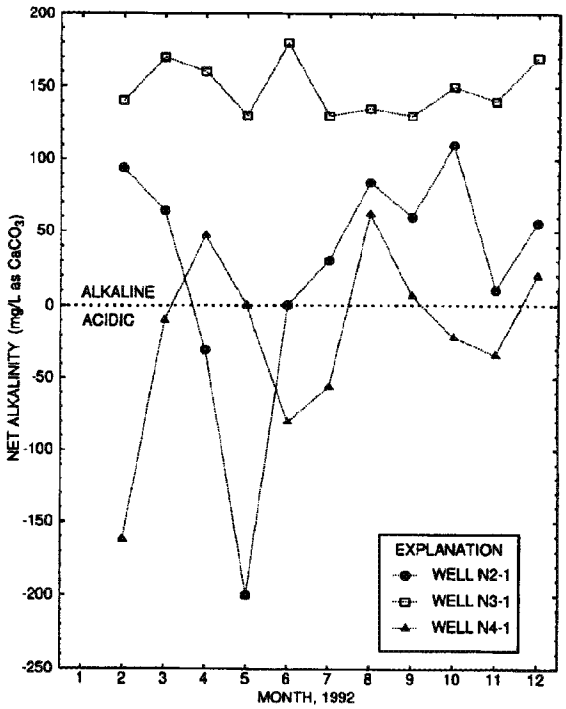
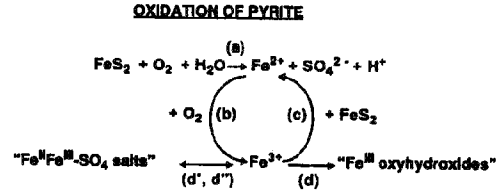


Figure 1.4 Temporal variations in net-alkalinity data for groundwater samples from three sites at a reclaimed surface coal mine in western Pennsylvania (mine 1 in table 1.1; data from Lescinsky et al., 1993, and Cravotta et al., 1994 a, b).

OXIDATION OF PYRITE



OVERALL: $FeS_2 + 3.75\ O_2 + 3.5\ H_2O \rightarrow Fe(OH)_3 + 2\ SO_4^{2-} + 4\ H^+$

STEPS:

(a) $FeS_2 + 3.5\ O_2 + H_2O \rightarrow Fe^{2+} + 2\ SO_4^{2-} + 2\ H^+$

(b) $Fe^{2+} + 0.25\ O_2 + H^+ \rightarrow Fe^{3+} + 0.5\ H_2O$

(c) $FeS_2 + 14\ Fe^{3+} + 8\ H_2O \rightarrow 15\ Fe^{2+} + 2\ SO_4^{2-} + 16\ H^+$

(d) $Fe^{3+} + 3\ H_2O \rightarrow Fe(OH)_3 + 3\ H^+$

(d') $2\ Fe^{3+} + Fe^{2+} + 4\ SO_4^{2-} + 14\ H_2O \rightarrow Fe^{II}Fe_2^{III}(SO_4)_4 \cdot 14H_2O$

(d") $3\ Fe^{3+} + K^+ + 2\ SO_4^{2-} + 6\ H_2O \rightarrow KFe_3^{III}(SO_4)_2(OH)_6 + 6\ H^+$

Figure 1.5 Model for the oxidation of pyrite (modified from Stumm and Morgan, 1981, p. 470). Steps a through d correspond with reactions 1.2-1.5, respectively, in the text. Steps d' and d" represent the formation of iron-sulfate minerals, which can be stores of acidity, ferric ions, and sulfate.

Reactions 1.2 and 1.3, which involve the oxidation of sulfur and iron, respectively, by gaseous or dissolved O_2, can be mediated by various species of sulfur and iron-oxidizing bacteria, notably those of the genus *Thiobacillus*. These bacteria, which require only dissolved CO_2, O_2, a reduced form of Fe or S and minor N and P for their metabolism, produce enzymes which catalyze the oxidation reactions, and use the energy released to transform inorganic carbon into cellular matter (Temple and Delchamps, 1953; Kleinmann et al., 1981; Nordstrom, 1982; Ehrlich, 1990).

In reaction 1.4, dissolved ferric iron (Fe^{3+}) produced by reaction 1.3 is the oxidizing agent for pyrite (Figure 1.5). Kinetic studies (Garrels and Thompson, 1960; McKibben and Barnes, 1986; Moses et al., 1987; Moses and Herman, 1991; Williamson and Rimstidt, 1994) show that at acidic pH, rates of pyrite oxidation by Fe^{3+} are much faster than oxidation by O_2 (reaction 1.2; see Figure 1.9). Therefore, in well-established acid-generating environments, the typical sequence is pyrite oxidation by reaction 1.4 to produce Fe^{2+}, which is then oxidized to Fe^{3+} by bacteria via reaction 1.3; the Fe^{3+} is then available for further pyrite oxidation. Although O_2 is not directly consumed in the pyrite-oxidizing step, it is necessary for the regeneration of Fe^{3+} to continue the pyrite-oxidation cycle.

As a final step, part or all of the Fe may precipitate as $Fe(OH)_3$ or related minerals (reaction 1.5). Because of the relative insolubility of Fe^{3+}, most dissolved Fe in solutions with pH greater than about 3.5 occurs as Fe^{2+}. AMD solutions commonly have pH and Eh (oxidation potential) plotting along or near the Fe^{2+}-$Fe(OH)_3$ boundary on an Eh-pH diagram (Figure 1.6; also see Figure 1.10; Langmuir and Whittemore, 1971). Near-neutral Fe-bearing solutions (pH 5-6) are normally relatively reduced, while more acidic solutions are more oxidizing. At pH less than about 3 (the exact value depending on Fe and SO_4 content), major amounts of dissolved Fe^{3+} can be present.

The oxygen isotopic composition of dissolved SO_4^{2-} in mine drainage varies in relation to the source of oxygen ($\delta^{18}O$ of O_2 in air is 23 permil, $\delta^{18}O$ of H_2O= -9.5 to -11.5 permil in the sampled area) (Table 1.1), so that the oxygen in the SO_4 can indicate whether reaction 1.2 or 1.4 is dominant (Taylor et al., 1984a,b; van Everingden and Krouse, 1985; Taylor and Wheeler, 1994; Reedy et al., 1991). In reaction 1.2, where O_2 is the oxidant, most of the oxygen in the SO_4 is derived from molecular O_2; in reaction 1.4 where

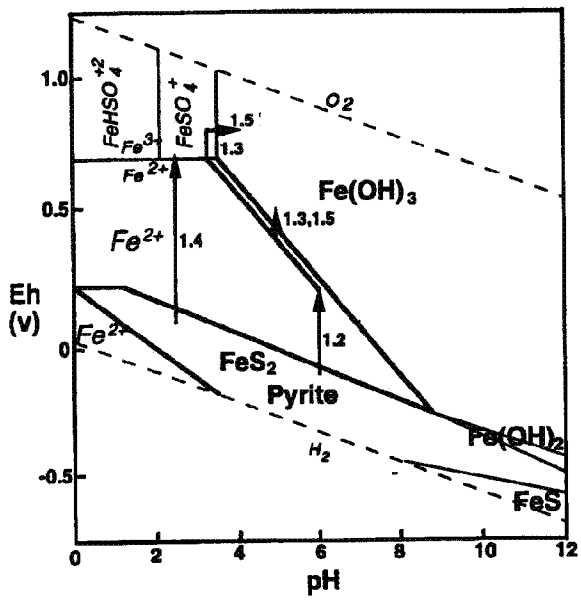


Figure 1.6 Eh-pH diagram showing theoretical stability fields for system Fe-O-H-S. Boundaries for stability fields of solid phases (vertical letters) and dissolved species (slanted letters) calculated for activities of $Fe=2x10^{-5}$ (~1 mg/L) and $S = 3 \times 10^{-3}$ (~300 mg/L as SO_4), and with pK=37.5 for $Fe(OH)_3$. Boundary near Eh=0.7 separates ferrous (Fe^{2+}) from ferric (Fe^{3+}) species. Arrows with numbers refer to oxidation reactions in the text. Note that boundaries shift with concentrations of Fe or S.

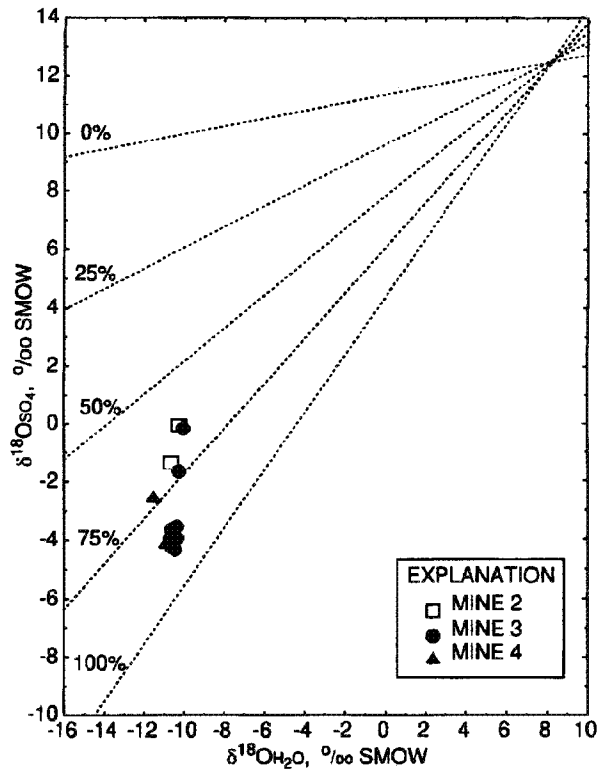


Figure 1.7 Isotopic composition of oxygen in dissolved sulfate ($\delta^{18}O_{SO4}$) of water samples from surface coal mines in western Pennsylvania (data from table 1.1) vs. isotopic composition of oxygen in associated groundwater ($\delta^{18}O_{H2O}$) originating from local precipitation, relative to SMOW standard, plotted after Van Everingden and Krouse (1985). Dotted lines indicate % contribution by reaction 1.4 (Fe^{3+} as oxidant) in contrast to reaction 1.2 (O_2 oxidant). The data indicate that Fe^{3+} is the dominant oxidant.

Fe^{3+} is the oxidant, all oxygen in the SO_4 is derived from H_2O (Figure 1.7). Oxygen isotopic data for dissolved SO_4 and H_2O of drainage from surface mines in Pennsylvania indicate that pyrite oxidation by both reactions 1.2 and 1.4 is important (Table 1.1, Figure 1.7).

Hydrolysis and precipitation of iron solids, denoted as $Fe(OH)_3$ in reactions 1.1 and 1.5, generally do not take place until the water is aerated and/or the acid is neutralized. The iron solids, which commonly form a reddish-yellow to yellowish-brown coating on rocks and other surfaces, can consist of a variety of amorphous or poorly crystalline ferric oxides, hydroxides or oxyhydroxysulfate minerals including ferrihydrite (variously given as $Fe_3(OH)_4$, $Fe_5HO_8 4H_2O$, or $Fe_5O_3(OH)_9$), goethite (FeOOH) and schwertmannite ($Fe_8O_8(OH)_6SO_4$) (Chukhrov et al., 1973; Eggleton and Fitzpatrick, 1988; Brady et al., 1986, Murad et al., 1994; Bigham et al., 1996). Ferrihydrite and schwertmannite are metastable and may ultimately dehydrate and recrystallize forming hematite (Fe_2O_3) or goethite. In acidic weathering environments, ferric sulfate compounds may form metastable intermediates prior to or in addition to ferric oxyhydroxide compounds (Nordstrom et al., 1979; Nordstrom, 1982). Because the ferric sulfate minerals tend to be soluble and typically form under evaporating conditions, they can be significant sources of acidity and sulfate when later dissolved by runoff or recharge water at surface mines (Nordstrom and Dagenhart, 1978; Olyphant et al., 1991; Cravotta, 1994). Furthermore, other forms of sulfur, such as native S and $S_2O_3^{2-}$, can be intermediate products in the oxidation of pyrite (Nordstrom, 1982; Goldhaber, 1983; Moses et al., 1987), but these tend to oxidize to SO_4^{2-} under surface conditions.

Measurement of Acidity

The acidity or net alkalinity of a solution, not the pH, is probably the best single indicator of the severity of AMD. Acidity is the total base requirement for

neutralization of a solution, and includes the base needed to neutralize acid produced by hydrolysis of Fe, Al and Mn (reactions 1.3, 1.5, 1.6, 1.7).

$$Al^{3+} + 3\ H_2O = Al(OH)_3(s) + 3\ H^+ \qquad (1.6)$$

$$Mn^{2+} + 0.5\ O_2 + H_2O = MnO_2(s) + 2\ H^+ \qquad (1.7)$$

In this chapter, acidity refers to a hot acidity in which hydrogen peroxide and heating are used to oxidize Fe and Mn, followed by titration with base to a pH of 8.2 or 8.3 (U. S. Environmental Protection Agency (EPA), 1979; American Public Health Association (APHA), 1980; ASTM, 1994). Note that the various methods differ slightly: the EPA, APHA and ASTM (Method C) procedures eliminate HCO_3 alkalinity prior to the titration, whereas a U.S. Geological Survey method (Fishman and Friedman, 1989) does not eliminate HCO_3 and does not oxidize iron. Some differences also exist among laboratories in reporting negative or zero acidity for samples with alkalinity exceeding acidity.

Alone, pH can be a misleading characteristic, because water that has near-neutral pH and elevated concentrations of dissolved Fe^{2+} can become acidic after complete oxidation and precipitation of the iron (reactions 1.3 and 1.5). For example, in Figure 1.3, many samples with pH of 5 to 6 and with measurable alkalinity actually have significant acidity (net alkalinity <0).

Although Fe^{3+}, Fe^{2+}, Mn^{2+}, Al^{3+}, and H^+ are the major components of acidity in coal-mine drainage (Ott, 1986), other dissolved species that precipitate as hydroxides or oxides or change form during the acidity titration, including Mg^{2+}, H_2CO_3, or H_2S, can contribute to acidity (Payne and Yeates, 1970).

Acidity is commonly expressed as milligrams of $CaCO_3$ per liter of solution (mg/L as $CaCO_3$) on the basis of the following stoichiometric relation:

$$2\ H^+ + CaCO_3 = Ca^{2+} + CO_2 + H_2O \qquad (1.8)$$

In accordance with reaction 1.8, 2 moles (2.0 g) of H^+ are neutralized by 1 mole (100.1 g) of $CaCO_3$. On this basis, acidity (and alkalinity) can also be expressed as milliequivalents per liter (meq/L), where 1 meq/L equals 50 mg/L as $CaCO_3$.

The acidity, in mg/L as $CaCO_3$, of acidic coal mine drainage can also be approximated by the following equation:

$$Acidity = 50\left[\frac{3C_{Fe^{3+}} + 2C_{Fe^{2+}}}{55.85} + \frac{3C_{Al^{3+}}}{26.98} + \frac{2C_{Mn^{2+}}}{54.94} + 10^{(3-pH)}\right] \qquad (1.9)$$

where C is the concentration in mg/L of the subscripted species and the divisor is the molecular weight of the subscripted species. On the basis of equation 1.9 and data in Table 1.1, calculated acidities generally are comparable with measured acidities (Figure 1.8). For the alkaline samples, however, because of the presence of dissolved HCO_3^- as free anions and complex ions, and OH^- as complex ions, calculated acidities typically exceed measured values. In acidic samples, the presence of HSO_4^- and OH^- complexes of Fe may cause discrepancies.

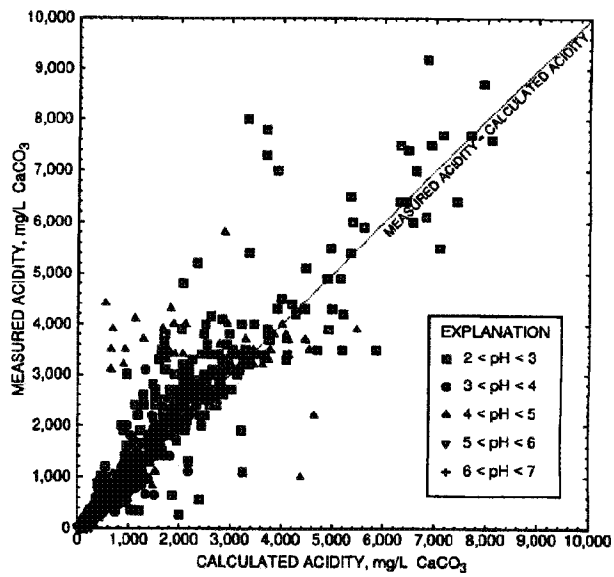


Figure 1.8 Comparison of measured acidity and calculated acidity. Acidity is calculated using equation 1.9 in text and data from sites in table 1.1. Causes for deviations from the line include hydroxyl complexing and HSO_4.

Factors Controlling The Rate of AMD Generation

Many factors determine the rate of AMD generation from pyrite oxidation, including the activity of bacteria, pH, pyrite chemistry and surface area, temperature, and O_2 concentration. The interactions of these factors are complex.

Bacteria - In many situations, the most important control on rate of AMD generation is bacterial oxidation of Fe^{2+} to Fe^{3+} by reaction 1.3. The resultant Fe^{3+} can oxidize pyrite by reaction 1.4 (Figure 1.5).

Figure 1.9 illustrates the rates of various reactions involved in AMD generation, including oxidation of Fe^{2+} by O_2 in the absence of bacteria or other catalysts.

At pH 6 the "half-life" of Fe^{2+} in an aerated solution at 25°C is about 7 hours, but at pH 4 or less the abiotic "half-life" is about 8 years (Singer and Stumm, 1970). Although Fe^{3+} is formed rapidly at pH>4, Fe^{3+} is relatively insoluble under these conditions and tends to form $Fe(OH)_3$ or other solids (Figures 1.4 and 1.5), so that little Fe^{3+} remains in solution to oxidize pyrite. The net effect is that in the absence of bacteria, Fe^{3+} is either not produced at a significant rate (pH<4) or is so insoluble that its dissolved form is relatively unimportant as an oxidant of pyrite (pH>4). However, Moses and Herman (1991) suggest that even when Fe^{3+} is negligible in solution, the reaction involves oxidation of adsorbed Fe^{2+} to Fe^{3+} at the pyrite surface, with the adsorbed Fe^{3+} in turn oxidizing the pyrite.

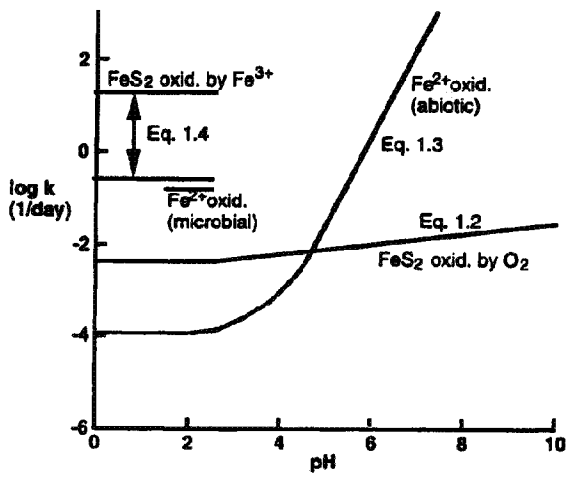


Figure 1.9 Comparison of rate constants as a function of pH for: I. The oxidation of pyrite by oxygen (reaction 1.2); II. The oxidation of ferrous iron by oxygen (reaction 1.3); and III. The oxidation of pyrite by ferric iron (reaction 1.4). Modified from Nordstrom (1982); bacterial oxidation of Fe based on Chavarie et al. (1993).

The bacterium *Thiobacillus ferrooxidans* and several similar species have the capability of catalyzing Fe^{2+} oxidation (reaction 1.3) under acidic, aerobic conditions, and obtain the energy for their metabolism from this reaction. In the process, these bacteria greatly speed up the reaction, so that under optimum conditions the "half-life" of Fe^{2+} is decreased to about 2 hr in an aerated solution with pH about 2.0 and Fe concentration of about 2.5 g/L (Chavarie et al., 1993). Because the rate of pyrite oxidation by Fe^{3+} is generally fast relative to the rate of oxidation by O_2 or the rate of inorganic Fe^{2+} to Fe^{3+} oxidation, the Fe^{2+}-Fe^{3+} oxidation is commonly rate-controlling (Singer and Stumm, 1970), and the bacteria are crucial in determining the rate of acid formation. In addition to oxidation of dissolved Fe^{2+}, Thiobacilli also have the ability to oxidize pyrite directly, i.e., they can accomplish reaction 1.2 while directly attached to the pyrite surface (Ehrlich, 1990).

Effect of pH - As indicated above, at pH values of 4 to 7 the rate of pyrite oxidation by O_2 is slow, and Fe^{3+} concentration is limited by the low solubility of $Fe(OH)_3$. In increasingly acidic systems, Fe^{3+} is increasingly soluble (Figures 1.5, 1.9). Since Fe^{3+} can rapidly oxidize pyrite, the oxidation of pyrite can be greatly accelerated at low pH. However, below about pH 1.5 to 2 the effectiveness of *Thiobacillus ferrooxidans* as a catalyst of Fe^{2+} oxidation decreases (Silverman and Lundgren, 1959; Schnaitman et al., 1969). Although pH values as low as negative 1.4 have been observed for AMD, these low values seem to require special circumstances (Nordstrom et al., 1991).

Kleinmann et al. (1981) and Nordstrom (1982) have suggested that the generation of AMD can be understood as three sequential stages. In stage I, while the pH is near-neutral or only slightly acidic, pyrite oxidation by reaction 1.2 proceeds by a combination of abiotic and bacterial mechanisms, and Fe^{2+} oxidation is primarily abiotic. Any biotic oxidation of pyrite is dominantly by bacteria attached to the surface of pyrite grains. In stage II, pH is generally in the range 3 to 4.5, and Fe^{2+} oxidation is mainly by *T. ferrooxidans*, because abiotic oxidation is so slow. Pyrite oxidation in this transition stage occurs by a combination of reactions 1.2 and 1.4, both abiotically and bacterially. In stage III, at pH less than about 3, the concentration of Fe^{3+} becomes high enough that reaction 1.4 becomes the main mechanism for acid production, with bacterial reoxidation of Fe^{2+} furnishing the Fe^{3+}. In stages I and II, the rate of AMD generation is relatively slow, but in stage III the rate becomes very rapid. This stage is responsible for production of the most acidic AMD. It should be noted that this sequence is based on processes in unsaturated systems with an adequate supply of O_2 and negligible alkaline material; in environments of limited O_2 and/or significant carbonate or other alkaline material, a different sequence of processes may occur.

Effect of Pyrite Surface Area and Crystallinity - Kinetic studies indicate that the rate of acid generation depends on the surface area of pyrite exposed to solution, and on the crystallinity and chemical properties of the pyrite surface (McKibben and Barnes, 1986). This dependence will be most important in initial stages while pH is greater than about 2.5. In general, rock

with a high percentage of pyrite will produce acidity faster than rock with a low percentage of pyrite. Also, a given mass of pyrite in small particles with high surface area will tend to oxidize more rapidly than the same mass composed of coarse smooth-surfaced grains. The high surface area of framboidal pyrite at least partly accounts for its observed high reactivity (Caruccio, 1975; Caruccio et al., 1976).

McKibben and Barnes (1986) observed that pyrite surfaces were pitted after reaction and suggested that the abundance of defects might be crucial in determining the reaction rate, but kinetic experiments on a variety of pyrite samples using Fe^{3+} at pH 2 show similar rates (Wiersma and Rimstidt, 1984), so the importance of this effect under strongly acid conditions remains to be demonstrated. Kitakaze et al. (1990), Graham (1991), and Mishra and Osseo-Asare (1988) have shown that pyrite can have vacant positions in its crystal lattice and correlated variations in atomic spacing and physical properties, suggesting another possible cause for different oxidation rates for different pyrite samples. Hammack et al. (1988) also found that sedimentary pyrites were more reactive than could be explained by surface area alone, and suggested that the cause was a difference in crystal structure between sedimentary and hydrothermal pyrite. Another possible variable is the content of trace elements in the pyrite, especially elements such as As that are clearly related to non-stoichiometry. The importance of these factors remains to be demonstrated, though the experiments of Wiersma and Rimstidt (1984) indicate that large effects are probably not common.

Effect of Oxygen - Atmospheric O_2 is required for the direct oxidation of pyrite and for regeneration of Fe^{3+}. Thus, if air and oxygenated or Fe^{3+}-rich waters can be excluded from pyritic material, pyrite oxidation can be inhibited and little or no acid will be generated.

Pure water in equilibrium with air at a total pressure of 1 atmosphere contains relatively low concentrations of dissolved O_2 ranging from 7.5 mg/L at 30°C to 12.4 mg/L at 5°C (Truesdale et al., 1955). On the basis of reaction 1.1, the complete oxidation of pyrite by 10 mg/L dissolved O_2 will produce acidic water with pH of 3.2 ($H^+ = 6.4 \times 10^{-4}$ mol/L) and concentrations of acidity and SO_4 of 32 mg/L as $CaCO_3$ and 31 mg/L, respectively. Higher concentrations of the products require additional O_2 transfer from the air, or a more complex mechanism, such as oxidation by previously generated Fe^{3+}.

Because the diffusion of O_2 in water is a slow process, and the solubility of O_2 in water is low, the effective exclusion of atmospheric O_2 from pyritic spoil can be achieved by perpetual immersion of the spoil in stagnant ground water (Watzlaf, 1992). Conversely, most AMD is generated in unsaturated mine spoil or other environments where air is in contact with moist pyrite-bearing rock.

Exclusion of O_2 by construction of "impermeable" or organic-rich covers has not generally been successful in preventing AMD generation in unsaturated spoil or mine workings. Covers may fail to stop or slow AMD formation because O_2 transfer is difficult to eliminate and because the rate of pyrite oxidation is independent of O_2 concentrations over the range 21 to 0.5 volume percent (Hammack and Watzlaf, 1990). In the unsaturated zone, O_2 can be supplied relatively rapidly by advection of air resulting from barometric pumping or differences in temperature and by molecular diffusion through air-filled pores (Guo, 1993; Guo et al., 1994a,b).

Effect of Microenvironments - Within unsaturated spoil, water typically fills small pores and occurs as films on particle surfaces. Flow rates of the water vary from relatively rapid movement through interconnected large pores, fractures, and joints to slow movement or nearly stagnant conditions in water films or small pores. Also, the abundance and distribution of pyrite and other minerals varies from one particle to another. Volumes with abundant pyrite, free movement of air, and impeded movement of water are expected to develop higher acidities than equal volumes that contain less pyrite or that are completely saturated with water. In addition, *T. ferrooxidans* may attach directly to pyrite surfaces and create its own microenvironment favorable to oxidation.

Because of these factors, the chemical environment within spoil, and consequently, water quality in unsaturated and saturated spoil commonly exhibit spatial and temporal variability (Table 1.1, Figures 1.1 to 1.4). Because of the small dimensions of the varying chemical environments, thorough characterization of chemical conditions (pH, O_2, Fe^{3+}, etc.) in unsaturated spoil may not be possible. The resulting coal-mine drainage generally is a mixture of fluids from a variety of dynamic microenvironments within the spoil, so that prediction of discharge water quality is difficult and imprecise. Evans and Rose (1995) discuss experiments that indicate the importance of microenvironments in coal-mine spoil.

Effect of Temperature - In general, the rates of reactions that form AMD increase with increasing temperature, so that AMD is formed faster if the pyritic material is warm. An exception to this trend is the rate of Fe oxidation by *T. ferrooxidans* above about 35°C. These bacteria thrive at optimum temperatures of 25 to 35°C, but they become inactive or die as temperatures increase to about 55°C (Cathles, 1979). Measurements indicate that oxidizing sulfide-rich material can warm internally to temperatures at least as high as 60°C because of the heat released by the oxidation reactions (Cathles and Apps, 1975). Some sulfide-rich material actually undergoes spontaneous combustion.

Formation of Secondary Minerals

Diagrams illustrating redox and pH conditions for the Fe-S-O-H and Fe-S-O-H-K systems for conditions similar to many AMD-generating environments are shown on Figures 1.6 and 1.10. Pyrite is clearly not stable in the presence of oxygenated air or measurable Fe^{3+}. Solutions with Fe dominantly as Fe^{2+} can exist at pH values up to about 8 (but these solutions become acidic on oxidation and precipitation of the Fe). At pH values higher than about 3.5, oxidation of Fe^{2+} precipitates Fe as an oxide or hydroxide. At pH values below about 3.5, appreciable concentrations of dissolved Fe can occur in the ferric state, as long as K is low enough that jarosite does not precipitate. Note that $FeSO_4^+(aq)$ and $FeHSO_4^{2+}(aq)$ actually dominate over $Fe^{3+}(aq)$ even at the relatively low SO_4 concentrations assumed for these diagrams. Plotted on Figure 1.10 are a variety of observed values of Eh and pH for AMD.

In addition to the Fe oxides and hydroxides (hematite, goethite, amorphous $Fe(OH)_3$), several other solid products are possible (Nordstrom, 1982). If appreciable K^+ or Na^+ is present, jarosite ($KFe_3(OH)_6(SO_4)_2$) or natrojarosite ($NaFe_3(OH)_6(SO_4)_2$) becomes stable under relatively acid conditions (Figures 1.6, 1.10). Also, hydronium jarosite ($(H_3O)Fe_3(OH)_6(SO_4)_2$) of poorly defined character may occur in solid solution with K- or Na-jarosite (Alpers et al., 1994). At the higher Fe^{2+} and SO_4^{2-} activities used for these diagrams, $FeSO_4(aq)$ dominates over Fe^{2+}. In a diagram plotting hematite which is more stable than the $Fe(OH)_3$ assumed for Figures 1.6 and 1.10, the ferrous ($FeSO_4^\circ$) field is limited to pH values lower than about 3.3. Nevertheless, newly precipitated Fe is most likely to be ferrihydrite (Langmuir and Whittemore, 1971), schwertmannite (Bigham et al., 1996), or some other poorly crystalline phase, so Figures 1.6 and 1.10 are generally relevant.

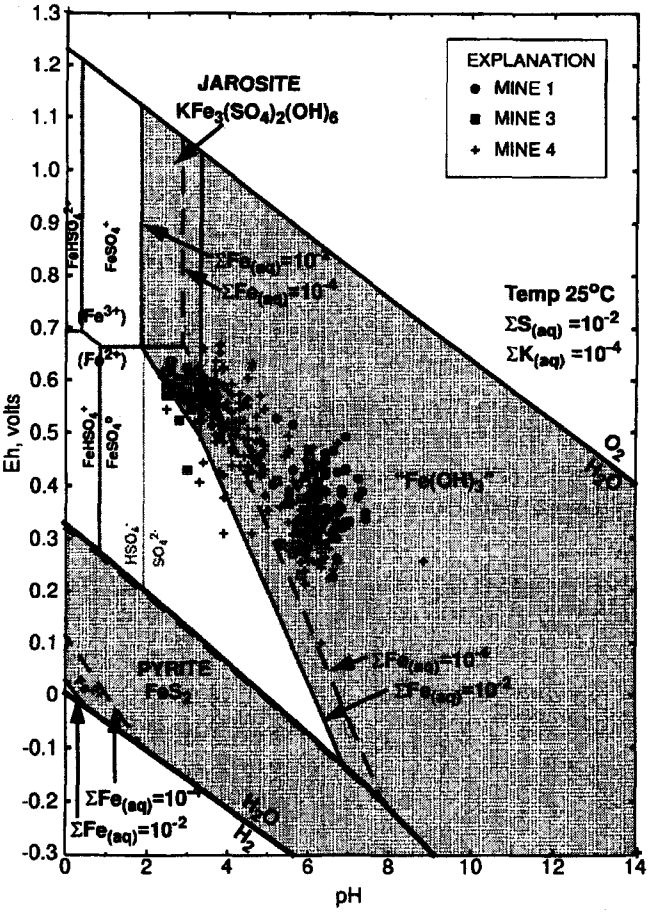


Figure 1.10 Eh-pH diagram for the system Fe-O-H-S-K and data points for measured Eh and pH of water samples from selected coal mines (Table 1.1). Boundaries for stability fields of solid phases (shaded pattern) and dissolved species calculated for activities of Fe = 10^{-2} (~560 mg/l) and 10^{-4} (~5.6 mg/l), S = 10^{-2} (~1000 mg/L as SO_4) and K^+ = 10^{-4} (~4 mg/l), and with pK = 39 for solid $Fe(OH)_3$. Boundary near Eh=0.7 divides dissolved ferrous (Fe^{2+}) from ferric (Fe^{3+}) species. See Cravotta (1996) for thermodynamic data. Note that boundaries shift with changes in concentrations of Fe, S and K.

At high Fe concentrations in solution, particularly under evaporating conditions, several secondary sulfate phases can precipitate from solution or form on the surface of oxidizing pyrite in near-surface rock or mine spoil. Some of the commonly observed phases include melanterite ($FeSO_4 \cdot 7H_2O$), rozenite ($FeSO_4 \cdot 4H_2O$), szomolnikite ($FeSO_4 \cdot H_2O$), copiapite ($Fe^{II}Fe^{III}_4(SO_4)_6(OH)_2 \cdot 20H_2O$), and coquimbite ($Fe_2(SO_4)_3 \cdot 9H_2O$) (Nordstrom, 1982; Alpers et al., 1994; Dixon et al., 1982; Bayless and Olyphant, 1993). Evaporation of AMD or oxidation of pyrite under humid conditions are usually the mechanisms

that form these phases. Cravotta (1991, 1994) has observed the above phases plus roemerite ($Fe^{II}Fe^{III}_2(SO_4)_4 \bullet 14H_2O$), pickeringite ($MgAl_2(SO_4)_4 \bullet 22H_2O$) and halotrichite ($Fe^{II}Al_2(SO_4)_4 \bullet 22H_2O$) in coal mine spoil in Pennsylvania.

The formation of these hydrous sulfate minerals can be significant because they represent "stored acidity" (Alpers et al., 1994). The "stored acidity" is released when the minerals are dissolved by recharge or runoff, and when the Fe or Al undergoes hydrolysis. For example, the dissolution of halotrichite

$$FeAl_2(SO_4)_4 \bullet 22H_2O + 0.25\ O_2 = Fe(OH)_3 + 2\ Al(OH)_3 + 4\ SO_4^{2-} + 8\ H^+ + 13.5\ H_2O \quad (1.10)$$

or coquimbite

$$Fe_2(SO_4)_3 \bullet 9H_2O = 2\ Fe(OH)_3 + 3\ SO_4^{2-} + 6\ H^+ + 3\ H_2O \quad (1.11)$$

shows this effect. The storage and release of acidity by these mechanisms can cause considerable temporal variability in water quality, or alternatively, can cause acid drainage to continue even after pyrite oxidation has been curtailed.

Neutralization of Acidity and Production of Alkalinity

Limestone and other materials that produce alkalinity can affect the generation of AMD in two ways. If water flowing into pyritic materials is alkaline, or alkaline conditions can be maintained in the pyritic material, the acid-generating reactions may be inhibited so that little or no AMD forms (i.e., bacterial oxidation of Fe^{2+} is minimal). Alternatively, once AMD has formed, its interaction with alkaline materials may neutralize the acidity and promote the removal of Fe, Al and other metals. Hence, water with high SO_4 and low Fe may be indicative of earlier AMD generation.

The carbonate minerals calcite ($CaCO_3$) and dolomite ($CaMg(CO_3)_2$) are the main minerals providing alkalinity. Siderite ($FeCO_3$) is also a possible source, with qualifications discussed later. The carbonate minerals may occur as layers of limestone or dolostone in the overburden above coal, as cement in sandstone or shale, or as small veins cutting the rock. The initial reaction with an acid solution (using calcite as an example) is:

$$CaCO_3 + 2\ H^+ = Ca^{2+} + H_2CO_3(aq) \quad (1.12)$$

If a gas phase is present, the H_2CO_3 may partly decompose and exsolve into the gas phase, i.e.:

$$H_2CO_3(aq) = CO_2(g) + H_2O_{(l)} \quad (1.13)$$

Upon further neutralization of AMD with carbonate to pH values greater than 6.3, the product is bicarbonate (HCO_3^-):

$$CaCO_3 + H^+ = Ca^{2+} + HCO_3^- \quad (1.14)$$

In contrast with oxidation reactions, which are mainly significant under unsaturated conditions, carbonate dissolution and production of alkalinity are significant under both water-saturated conditions and unsaturated conditions.

For a dilute water encountering limestone, Figure 1.11 indicates the approximate equilibrium concentration of HCO_3^- (alkalinity) in the aqueous phase as a function of the pH and P_{CO_2}, in the presence of calcite. Waters containing significant concentrations of other elements (Fe, Mg, SO_4) may deviate from the concentrations on this diagram. This diagram also indicates the approximate maximum amounts of dissolved alkalinity that may be carried into pyritic spoils by groundwater that has contacted carbonates, and the amounts of alkalinity that may be generated in systems such as anoxic limestone drains.

If one is concerned with the amount of calcite required to neutralize AMD of a given quality, as in the calculation of Neutralization Potential (Sobek et al., 1978) or the addition of alkaline materials to pyritic spoil in order to prevent AMD formation, reactions 1.12 and 1.14 are also relevant. The amount of calcite required to neutralize a given amount of acid mine drainage depends on the behavior of CO_2 during neutralization and on the pH reached. If the AMD is to be neutralized to pH 6.3 or above (i.e., HCO_3^- is the main carbonate species produced) and no CO_2 is allowed to exsolve to the gas phase, then the reaction may be written (Cravotta et al., 1990):

$$FeS_2 + 4\ CaCO_3 + 3.75\ O_2 + 3.5\ H_2O = Fe(OH)_3 + 2\ SO_4^{2-} + 4\ Ca^{2+} + 4\ HCO_3^- \quad (1.15)$$

Under these conditions, neutralization of the products of oxidizing 1 mole of pyrite requires 4 moles of $CaCO_3$, or 400 g of $CaCO_3$ to 64 g of pyritic sulfur, or 62.5 tons of $CaCO_3$ per 1000 tons of material with 1% S as pyrite.

In contrast, if all CO2 escapes to the gas phase and/or the AMD is only neutralized to about pH 5, then the reaction may be written:

$$FeS_2 + 2\ CaCO_3 + 3.75\ O_2 + 1.5\ H_2O = Fe(OH)_3 + 2\ SO_4^{2-} + 2\ Ca^{2+} + 2\ CO_2(g) \quad (1.16)$$

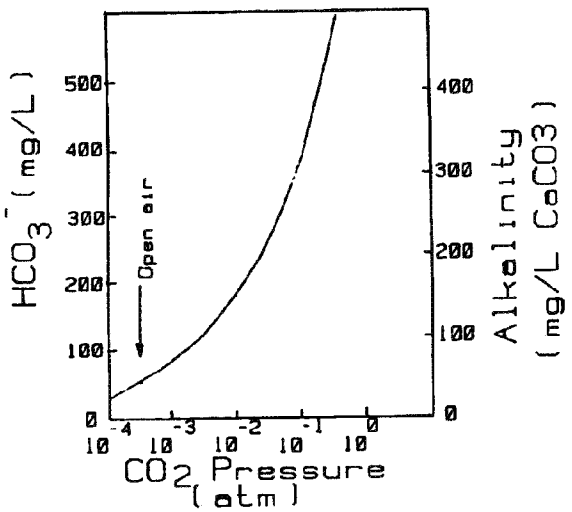


Figure 1.11 Equilibrium concentration of HCO_3^- (alkalinity) from dissolution of calcite ($CaCO_3$) by pure water at various partial pressures of carbon dioxide (P_{CO2}) at 25°C. Calculated after Garrels and Christ (1965).

Under these conditions, neutralization of AMD generated by oxidation of 1 mole of pyrite requires 2 moles of $CaCO_3$, or 200 g of $CaCO_3$, or 31.25 tons of $CaCO_3$ per 1000 tons containing 1% pyritic sulfur.

Most natural situations probably fall between these two extremes. Air within most strip mine spoil can contain significant amounts of CO_2 (Lusardi and Erickson, 1985; Cravotta et al., 1994a), so that some CO_2 is clearly exsolving. If O_2 can get into the spoil to drive the pyrite oxidation reaction, then some CO_2 can escape into the open air. On the other hand, in order to provide detectable alkalinity in the effluent, some HCO_3^- must be present. Thus, the theoretical amount of carbonate required to neutralize AMD generally falls intermediate between the two endmember cases.

If the neutralizing material is lime composed mainly of CaO or $Ca(OH)_2$, then the neutralization reaction is

$$Ca(OH)_2 + 2\ H^+ = Ca^{2+} + 2\ H_2O \qquad (1.17)$$

If the standard tests for neutralization potential are applied (Sobek et al., 1978) then AMD produced by oxidation of 1000 tons of material with 1% S may be neutralized by interaction with lime at a factor of 31.25 tons of $CaCO_3$ equivalent, equal to 23 tons of $Ca(OH)_2$. However, note that $Ca(OH)_2$ tends to react with CO_2 from the air to form $CaCO_3$, so that aged "lime" can contain substantial $CaCO_3$ (Rose et al., 1995).

Siderite ($FeCO_3$) is common in many coal-bearing sequences in Pennsylvania (Morrison et al., 1990). Dissolution of pure siderite followed by precipitation of $Fe(OH)_3$ generates no net alkalinity, even if CO_2 is exsolved:

$$FeCO_3 + 0.25\ O_2 + 2.5\ H_2O = Fe(OH)_3 + CO_2(g) + H_2O \qquad (1.18)$$

However, if siderite is exposed to H^+ and the reaction proceeds in stages, with some CO_2 exsolution to the gas phase, then some neutralization may temporarily take place:

$$FeCO_3 + 2\ H^+ = Fe^{2+} + CO_2(g) + H_2O \qquad (1.19)$$

Although some H^+ has been consumed and the pH will increase, note that the dissolved Fe^{2+} represents acidity equivalent to the H^+ consumed, so no change in acidity has occurred. When the Fe^{2+} oxidizes and precipitates, then H^+ is regenerated. If the CO_2 does not exsolve, then the dissolved H_2CO_3 requires additional alkalinity to convert it to HCO_3^- and produce a neutral solution. Thus, although it is possible that siderite constitutes a temporary neutralizing agent, it is not effective overall. Unfortunately, the conventional Neutralization Potential test (Sobek et al., 1978) measures some NP for siderite, if present, since the test allows evolution of CO_2 and does not promote oxidation of Fe (reaction 1.19). The testing of effervescence ("fizz") of pulverized rock samples with dilute HCl can indicate whether samples with measurable NP contain siderite, since siderite does not effervesce with normal acid strengths (see Chapter 6).

Most natural siderite is actually a solid solution containing some Ca, Mg and Mn in addition to Fe (Mozley, 1989; Morrison et al., 1990). Dissolution of siderite can produce elevated concentrations of Mn in groundwater at mines (Table 1.1, mine 1; Cravotta et al., 1994a). To the extent that siderite contains Ca and Mg in solid solution, its dissolution will contribute some net alkalinity, analogous to reaction of the $CaCO_3$ or $MgCO_3$ component in the siderite. This alkalinity is validly measured by the NP test.

The dissolution of silicate minerals consumes acidity by reactions like:

$$2\ KAlSi_3O_8\ (K\ feldspar) + 2\ H^+ + H_2O = 2\ K^+ + Al_2Si_2O_5(OH)_4 + 4\ SiO_2 \qquad (1.20)$$

$$Al_2Si_2O_5(OH)_4\ (kaolinite) + 6\ H^+ = 3\ Al^{3+} + 2\ SiO_2 + 5\ H_2O \qquad (1.21)$$

$$Mg_2A_2SiO_5(OH)_4(\text{chlorite}) + 4\ H^+ + SiO_2 = 2\ Mg^{2+} + Al_2Si_2O_5(OH)_4 + 2\ H_2O \qquad (1.22)$$

Reactions of these types are responsible for most or all of the dissolved K, Na, Al, Mg, some of the Ca, and locally some of the Fe in AMD solutions. Although H^+ is consumed by these reactions, Al and Fe released by dissolution will generate acidity upon hydrolysis. However, the dissolution of alkali and alkaline earth cations in such reactions reduces acidity. Nevertheless, reactions with silicate minerals are relatively slow, so they typically consume only a small part of the acidity present in the solution. Crouse and Rose (1976) demonstrate changes in the clay mineralogy of sediments in acid streams because of this type of reaction.

In some situations, ion exchange can affect the chemistry of AMD, by reactions of the type

$$Na_{0.66}Al_4Si_{7.3}Si_{7.34}Al_{0.66}O_{20}(OH)_4(\text{smectite}) + 0.33\ Fe^{2+} = Fe_{0.33}Al_4Si_{7.34}Al_{0.66}O_{20}(OH)_4 + 0.66\ Na^+ \qquad (1.23)$$

The Na^+ and Fe^{2+} in the smectite are in exchangeable form and can be replaced by other species in any way that compensates the charge. This reaction removes some Fe and acidity from the solution, and stores it in the solid phase. Cravotta et al. (1994b) report analogous Ca-Na exchange in AMD systems. In the latter case, by removing Ca^{2+} from solution, calcite dissolution was more extensive, and alkalinity more extreme than otherwise possible. Because smectites are not generally stable in acid solutions, such reactions probably are of minor importance until alkaline conditions are reached.

In most situations, the SO_4 generated by pyrite dissolution remains in solution and is a good measure of the amount of pyrite oxidized. However, in the presence of calcite and other Ca-bearing materials, gypsum ($CaSO_4 \cdot 2H_2O$) can precipitate and remove SO_4 from solution. For example, Table 1.1 shows that water at mine 1 is generally saturated with gypsum, and Evans and Rose (1995) observed formation of gypsum in spoil to which lime had been added. Precipitation of Fe, Al and Mg sulfate compounds also can decrease the concentration of SO_4 in AMD.

Models For AMD Formation

The rate of AMD generation and the chemical character of the AMD vary widely depending on the mine hydrology, the relative abundance of acid-forming and alkaline materials, and the physical characteristics of the spoil. The intent of this section is to discuss how the key variables interact to define several idealized models.

Oxygen is a key reactant in forming AMD. Because of the low solubility of O_2 in water, only minor amounts of O_2 can be carried into spoil dissolved in infiltrating precipitation. Two main processes operate in strip mine spoil to supply O_2 for pyrite or Fe^{2+} oxidation. One process is the diffusion of O_2 molecules from zones of higher O_2 concentration to zones of lower O_2 concentration through air-filled pore space in the spoil (Figure 1.12a). If diffusion is the dominant process supplying O_2, then most oxidation tends to occur at shallow depths in the spoil, typically in the upper 1 to 8 meters (Figure 1.13). Below this depth, little O_2 is present, and downward percolating solutions are relatively reduced, containing mainly Fe^{2+} and little Fe^{3+}. Erickson (1985) and Lusardi and Erickson (1985) report O_2 concentrations that decrease from 21% to a few percent between the surface and 8 m depth in coal refuse and reclaimed spoil at several sites. Cravotta et al. (1994b) report O_2 concentrations in spoil air that decrease from 21% at the surface to

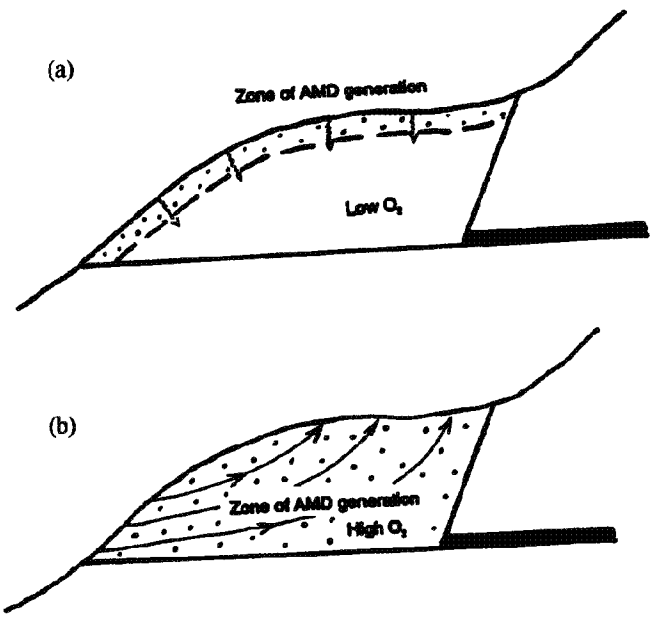


Figure 1.12 Conceptual models of O_2 transport in mine spoil profiles: a) Diffusive transport of O_2, dominant where air permeability of spoil is low, such as compacted, shaley spoil; b) advective transport of O_2, dominant where air permeability of spoil is high, such as blocky, sandstone spoil. Modified from Guo (1993).

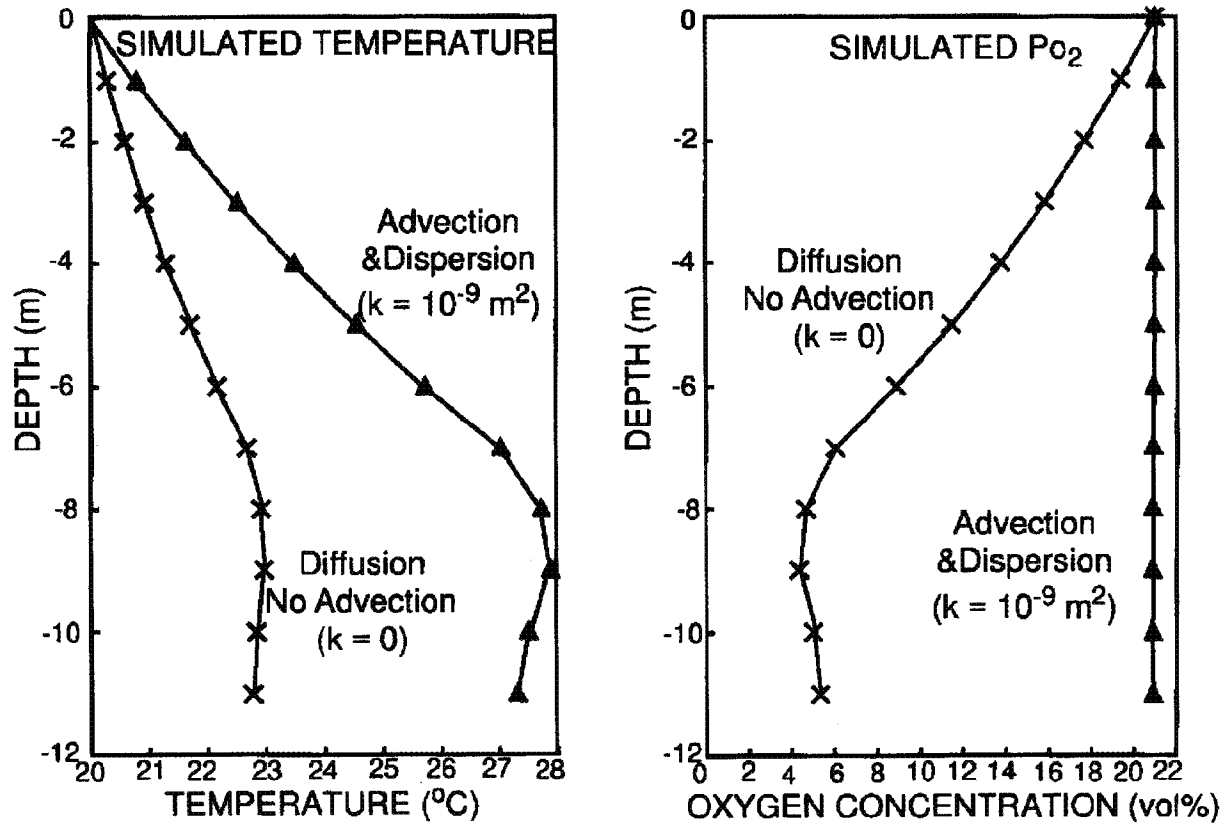


Figure 1.13 Simulated profiles of temperature and O_2 in spoil with different air permeabilities (k), which result in advective ($k>10^{-9}$ m^2) or diffusive ($k<10^{-10}$ m^2) dominated transport. Modified from Guo (1993).

about 4% at 10 m depth in spoil at Mine 1 (Table 1.1) in Clarion Co (Figure 1.14). High CO_2 concentrations also build up at depth in spoil air at this site. The distribution of O_2 and CO_2 at these sites is consistent with diffusional transport of the gases in spoil. Jaynes et al. (1984a, b) discuss a computer model for this type of O_2 transport. The pyrite oxidation rates at these sites are probably controlled more by diffusion of O_2 than by pyrite abundance and reactivity (Cravotta et al., 1994b).

The second main process of O_2 transport is by advection or flow of air within spoil (Figure 1.12b). The flow is driven mainly by the upward flow of air warmed by the heat generated during pyrite oxidation. Where advection is dominant, high concentrations of O_2 can occur in deep spoil. Guo (1993) and Guo et al. (1994a, b) describe spoil in Clearfield County (Mine 4 in Table 1.1) that has O_2 concentrations exceeding 18% at depths of 10 to 35 m (Figure 1.14), and showed with computer simulations that thermally driven convection is expected and can produce the observed effects (Figure 1.13).

Jaynes et al. (1983) recorded similar high values of O_2 at depth in spoil. Models and experiments by Cathles and Apps (1975) showed that the advection process also operates in pyrite-bearing waste dumps at copper mines.

The advective mode of O_2 transport appears to predominate in spoil that contains a significant proportion of sandstone or other strong rock that leaves appreciable open space between fragments. In contrast, the diffusive mode of transport predominates in less permeable spoil composed of small fragments of weak shale or similar rocks.

AMD generation may also be strongly influenced by the position of alkaline materials relative to pyritic materials. For example, in northwestern Pennsylvania, glacial till containing small to moderate amounts of limestone fragments overlies coal-bearing rocks. Sur-

face mines in this region, even those with considerable pyrite in the overburden, generally do not produce AMD (Hornberger, 1985; Williams et al., 1982; Chapter 8). This lack of AMD generation appears to result from the alkaline quality of water percolating into the spoil after first passing through the carbonate-bearing till.

The reaction of ferric oxides, hydroxides or sulfates with pyrite is a possible means of producing AMD in mine spoil (Figure 1.6). The ferric ions released by dissolution of these phases could act as oxidant of pyrite. The stoichiometry of the reaction with ferric hydroxide would be as follows:

$$FeS_2 + 14\ Fe(OH)_3 + 26\ H^+ = 15\ Fe^{2+} + 2\ SO_4^{2-} + 34\ H_2O \qquad (1.24)$$

Note that this and similar reactions involving ferric minerals consume considerable H^+ in order to occur, but do produce additional acidity as Fe^{2+} in solution and are therefore only significant in acidic environments. Temple and Koehler (1954) proposed that ferric sulfate minerals could be significant sources of acidity, sulfate and ferric ions. The subsequent oxidation of pyrite by Fe^{3+} and/or hydrolysis of Fe^{3+} can produce acidic water, even under water-saturated conditions (Cravotta, 1994).

At a few surface mines, it appears that burial of brush or other organic matter in spoil may generate discharges with the characteristics of AMD. Although the mechanism requires further study, organic matter could, with microbial catalysis, reduce $Fe(OH)_3$ or other ferric compounds to produce ferrous iron in solution:

$$CH_2O(\text{organic matter}) + 4\ Fe(OH)_3 + 8\ H^+ = 4\ Fe^{2+} + CO_2 + 11\ H_2O \qquad (1.25)$$

The acidity increases by the formation of CO_2; however, if the CO_2 exsolves, this reaction produces no net additional acidity. Although the reaction produces Fe^{2+}, it consumes considerable H^+ and it does not pro-

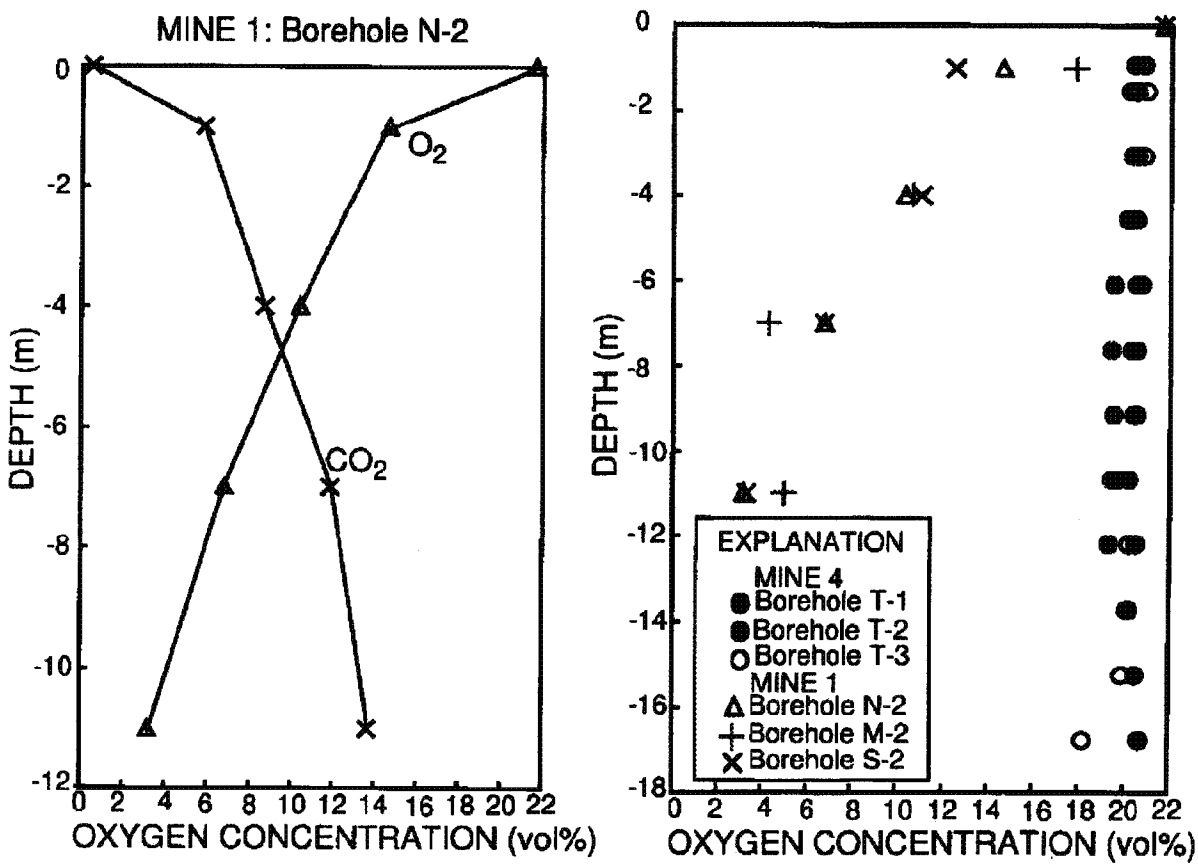


Figure 1.14 Measured profiles of oxygen and CO_2 in unsaturated spoil, after Guo et al (1994) and Guo and Cravotta (1996). At Mine 1, gas transport is by diffusion, and at Mine 4 it is by convection.

duce SO_4^{2-}. Some AMD containing low SO_4 but high Fe may have formed by this mechanism.

Mine drainage containing relatively low SO_4 concentrations could be caused by dilution or by SO_4-reduction, which involves the reaction of AMD with organic matter (Rose et al., 1996):

$$2\ CH_2O + SO_4^{2-} = H_2S + 2\ HCO_3^- \qquad (1.26)$$

Evidence for sulfate reduction is the fact that H_2S or similar reduced sulfur gases can be smelled at some localities. In addition, this reaction is known to proceed in wetlands and other natural environments where SO_4-bearing water encounters organic matter. For example, Herlihy et al. (1987) report that about half the SO_4 in an AMD-affected stream is removed by SO_4-reduction in the sediments of a shallow lake in Virginia. Reduction of ferric iron by Fe^{3+}-reducing bacteria would be required before SO_4-reducing bacteria would be able to prevail over Fe-reducers (Chappelle and Lovley, 1992). In most AMD, the H_2S will react immediately with Fe to precipitate FeS. Because most AMD originates from oxidation of pyrite (FeS_2) and has more S than Fe, it is unlikely that SO_4-reduction will form an effluent with low SO_4 and high Fe. However, any unreacted H_2S can be oxidized to form H_2SO_4 where oxygen is available. Oxidation of organic S in coal could also form an acid SO_4-bearing solution (Harvey and Dollkopf, 1986).

Conclusions

Although in principle the formation of AMD by pyrite oxidation is simple, the preceding discussion indicates that the possible processes are many and complex. An understanding of the geochemistry is aided by writing balanced chemical reactions using reactants and products appropriate for the conditions. The water quality is clearly dependent on geologic and hydrologic conditions at a given site. Careful field observation and laboratory analysis combined with an understanding of possible processes is necessary to draw conclusions for a particular location.

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Chapter 2

GROUNDWATER FLOW ON THE APPALACHIAN PLATEAU OF PENNSYLVANIA

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Introduction

Acid mine drainage (AMD) results from the oxidation of sulfide minerals in the strata disturbed by mining. The products of this reaction. acidity, sulfate, and iron, (see Chapter 1) are dissolved in and transported by groundwater. Consequently, in addition to understanding the geochemical nature of the enveloping strata, prediction and prevention of AMD requires an understanding of how groundwater flows through the mine and adjacent area. Groundwater flow in the coal fields of the Appalachian Plateau of Pennsylvania can be viewed from the scale of the entire groundwater flow system down to the detailed level of flow through aquifers and aquitards on a mine site. This flow system can be influenced by many factors including stratigraphy and lithology, structural geology, tectonic stresses and their cumulative effects on rock-mass integrity, geomorphology, topography, and any substantial man-made influences such as mine subsidence related fracturing.

An understanding of the groundwater flow regime is essential to the design of site-specific monitoring plans to determine the impact of mining on groundwater quality and the hydrologic balance. The more thorough the understanding of this system, the more efficient this plan can be, maximizing the information which can be obtained and minimizing the costs of monitoring. This knowledge also gives the groundwater chemistry of the site meaning by providing a frame of reference regarding a given monitoring point's location and relative importance within the groundwater flow system. Absent this understanding, considerable time and money can be wasted by the poor placement of groundwater monitoring wells and the subsequent collection of meaningless water quality data. Although groundwater chemistry can be used to help characterize the flow system, it must be integrated within a broader effort intended to define groundwater potential and hydraulic gradient. The importance of understanding groundwater flow at a site is emphasized by Earl (1986) who suggested that for groundwater investigations, 90% of the budget should be used to define the flow system, and the remainder for water chemistry analysis.

Many of the principal concerns in the review of mine permit applications - prevention of adverse impacts to water resources, prevention of postmining AMD, and the prediction of impacts to water supplies, require knowledge of premining groundwater conditions and an understanding of how mining will change these conditions. An environmentally prudent mine-site design relies on accurate characterization of the premining groundwater flow regime. See Chapters 15 and 16 for discussions on the management of mine-site water.

Climate

AMD problems in the northern and central Appalachian coal mining region far outstrip problems in other coal producing regions of the United States (see Chapter 8). Some of the regional differences are related to climate. The process of rock weathering is strongly influenced by temperature and by amount and distribution of precipitation (Hem, 1992). AMD formation is most severe in humid areas with moderate rainfall where rapid oxidation and dissolution of exposed minerals can occur. Therefore, any discussion of AMD prediction and prevention in Pennsylvania must be considered within the context of Pennsylvania's climate. Observations and conclusions made in Pennsylvania may not be relevant to other areas of the country due to climatic differences. For example, the interplay between pyritic oxidation and the dissolution of carbonate minerals may be very different in semi-arid or arid climates.

Pennsylvania has a humid climate with precipitation distributed relatively evenly throughout the year. The amount of rainfall and snowfall vary over Pennsylvania. The most recent precipitation normals from the

National Climatic Data Center for Pennsylvania for the time period of 1961 to 1990 show the lowest annual average amount to be 32 inches near Covington, Tioga County, and the highest amount of precipitation to be 49.5 inches is near Tamaqua, Schuylkill County. Figure 2.1 shows precipitation isolines which range from 36 inches to 50 inches in Pennsylvania. Snowfall isolines (Figure 2.2) illustrate average snowfalls of 20 to 100 inches throughout the state.

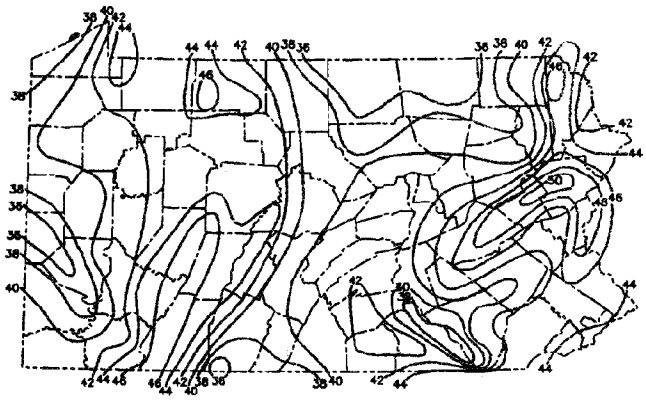


Figure 2.1 Mean annual precipitation, inches. (Based on the period 1931-1960)

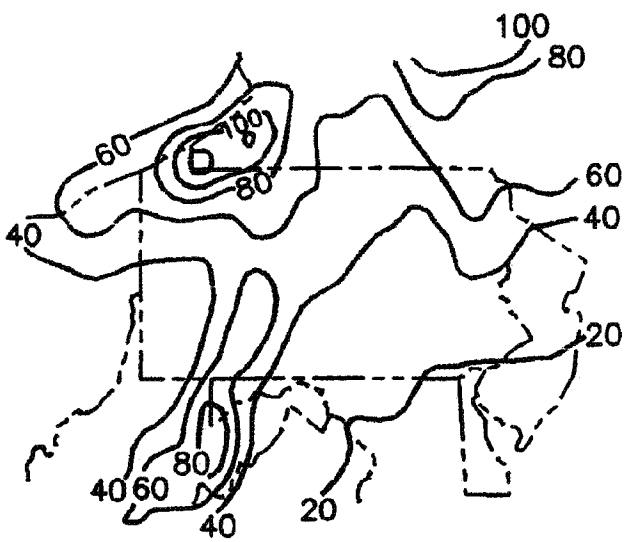


Figure 2.2 Total snowfall (inches), 50th percentile, seasonal.

Pennsylvania's temperatures vary greatly across the state during the year. The average temperature for the most recent time period (1961-1990) is about 48° F. The temperature fluctuations are revealed by examining the temperatures during the normally coldest month (January) and the normally hottest month (July). Figures 2.3 and 2.4 show the mean minimum and the mean maximum temperatures for January, while Figures 2.5 and 2.6 show the mean minimum and the mean maximum temperatures for July. This information is from data published by the National Climatic Data Center and covers the time period of 1931-1960. During a more recent time period (1961-1990) a similar pattern appears to hold.

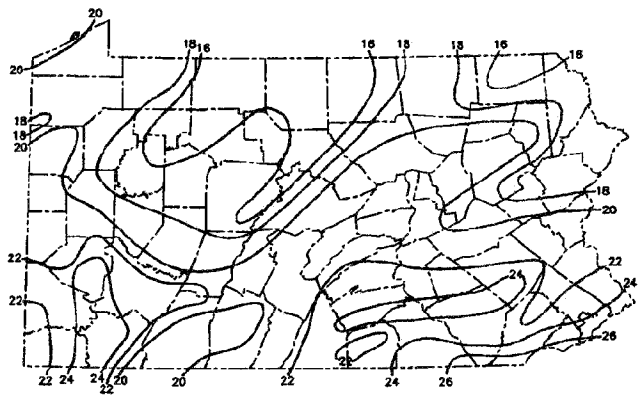


Figure 2.3 Mean minimum temperature (°F), January. (Based on period 1931-1960)

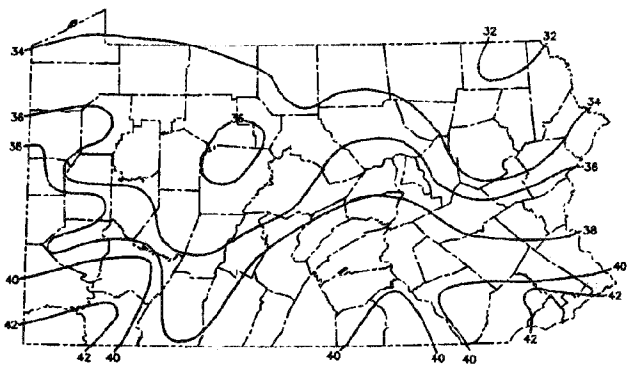


Figure 2.4 Mean maximum temperature (°F), January (Based on period 1931-1960)

In Pennsylvania approximately 12 to 15 inches annually, or about one third of the average precipitation, infiltrates to the groundwater system. Evaporation and transpiration account for about 20 inches returning to the atmosphere annually (Becher, 1978). The remaining precipitation directly runs off to surface waterways. Of course, these are averages. The actual amounts vary from place-to-place depending on geology, soils, vegetation, topography, and from year-to-year. Areas with readily permeable soils, porous bedrock, or closed surface depressions generally have higher infiltration rates (Smith, 1986).

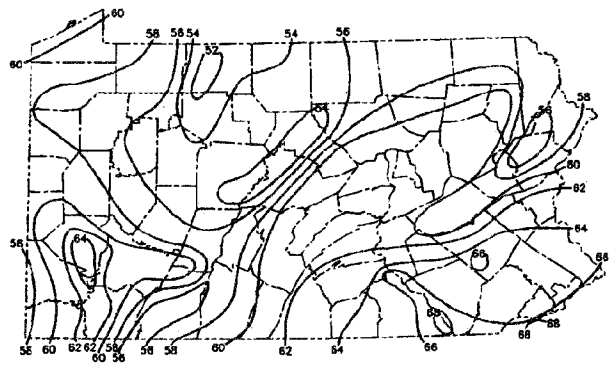


Figure 2.5 Mean minimum temperature (°F), July. (Based on period 1931-1960)

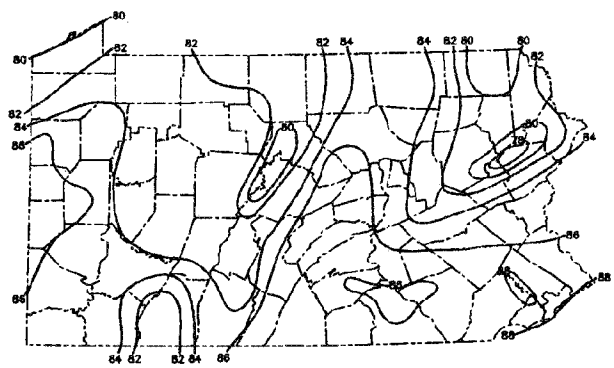


Figure 2.6 Mean maximum temperature (°F), July. (Based on period 1931-1960)

There are several aspects of this "hydrologic budget" which are important to consider. First, because precipitation exceeds evapotranspiration in all of Pennsylvania, virtually all areas, unless capped with some impervious material, are subject to infiltration and produce groundwater. In this respect, there is no such thing as a completely dry mine site - one that does not produce groundwater drainage. If 12 to 15 inches of annual groundwater discharge were expressed as an average flow rate, every acre of land would produce a flow of 0.62 to 0.77 gallons per minute (alternately, one hectare would produce 5.8 to 7.2 L/sec). Also, groundwater recharge does not occur uniformly throughout the year. Recharge is greatest during the non-growing season when there is minimal uptake of water by plants and evapotranspiration is minimal (Smith, 1986).

Groundwater Flow

Groundwater flow is largely controlled by three factors - the distribution and quantity of recharge to the flow system, surface topography, and the hydraulic conductivity of the material through which the groundwater flows. These factors may in turn be affected by a host of other elements - soils, climate, lithology, and geologic structure. But, at a fundamental level, the groundwater flow system can be reduced to these principal elements. Mining, both surface and underground, can drastically alter each of these factors. Groundwater recharge rates can be altered depending on how the surface material is handled and how the site is revegetated. Surface topography can be altered depending on the final reclamation contours (see Chapter 12). Hydraulic conductivity of the overburden, which must be removed and replaced at surface mines and which can be collapsed and fractured above underground mines, is dramatically and permanently altered by the mining process. Additionally, mine spoil may be more conductive than parent material by several orders of magnitude. (The hydraulic properties of mine spoil are discussed in detail in Chapter 3.)

Hydraulic Head

Groundwater flow is driven by differences in hydraulic head. Groundwater flows from areas with higher hydraulic head to areas with lower hydraulic head. In an unconfined aquifer, the elevation of the water table surface can be used to determine distribution of hydraulic head and to infer the direction of groundwater flow. The hydraulic head at any point can be determined by the water level in a piezometer. Determination of the hydraulic head at a sufficient number of locations can be used to create a potentiometric map showing lines of equal potential (head). This map can be used to determine the direction of groundwater flow - from high potential to low potential.

Determination of the hydraulic head in an unconfined system or in multiple aquifers at the same location indicates whether the vertical component of groundwater flow is down or up (recharge or discharge area). Determination of the hydraulic head at a sufficient number of locations areally and vertically can be used to obtain a three-dimensional determination of groundwater flow. The flow directions within a local flow system are frequently estimated by assuming they approximate the topography, coupled with spring (discharge area) and, possibly, well (water level) mapping. Static water levels in wells can be used as estimates of hydraulic head in single aquifer wells. These approximations are reasonably accurate for fairly homogeneous bedrock flow systems but may be in error for areas with large permeability contrasts.

The hydraulic gradient and anisotropy of the transmitting medium control the specific flow paths between recharge and discharge areas. In homogeneous, isotropic media groundwater flows perpendicular to equipotential lines. Anisotropy can result in flow which is oblique with respect to equipotential lines (Fetter, 1981).

Static Water Level

When a borehole is drilled, the water level will stabilize at the static water level which represents the composite hydraulic head of the open interval of the well. Figure 2.7 illustrates the relationship between a producing aquifer (aquifer 1), a thieving aquifer (aquifer 2), their piezometric surfaces, and the resulting static water level in a recharge area well in Mercer County. Each of the aquifers has a different hydraulic head, represented by the potentiometric surface. The static water level is the composite of the hydraulic heads of the two aquifers.

In recharge areas groundwater movement has a downward component. Therefore, as a borehole is deepened and additional aquifers are penetrated, the composite head decreases resulting in a drop in the static water level. In discharge areas the reverse is true, as deeper aquifers are penetrated the composite head increases and the static water level rises (Bennett and Patten, 1960; Carswell and Bennett, 1963; Poth, 1963).

An erroneous interpretation of the significance of the static water level is that it indicates the water table. The water table is the boundary between saturated and unsaturated media under atmospheric pressure. The depth of the water table cannot be determined by the static water level unless the borehole is shallow and is just deep enough to encounter standing water at the bottom, generally no more than 6 feet (1.83 m) into the zone of saturation (Saines, 1981). Because the static water level indicates the composite head of the open interval in the borehole, immediately upon further deepening of a borehole, the static water level no longer reflects the water table. Interpreting the static water level to be the water table infers that the water table at the locale of a flowing well is above the land surface. The often used terms "local" and "regional" water table should not be confused with local and regional flow systems or aquifers. The "local" water table, or perched water table, is one with unsaturated media beneath it. It is usually associated with a perched aquifer.

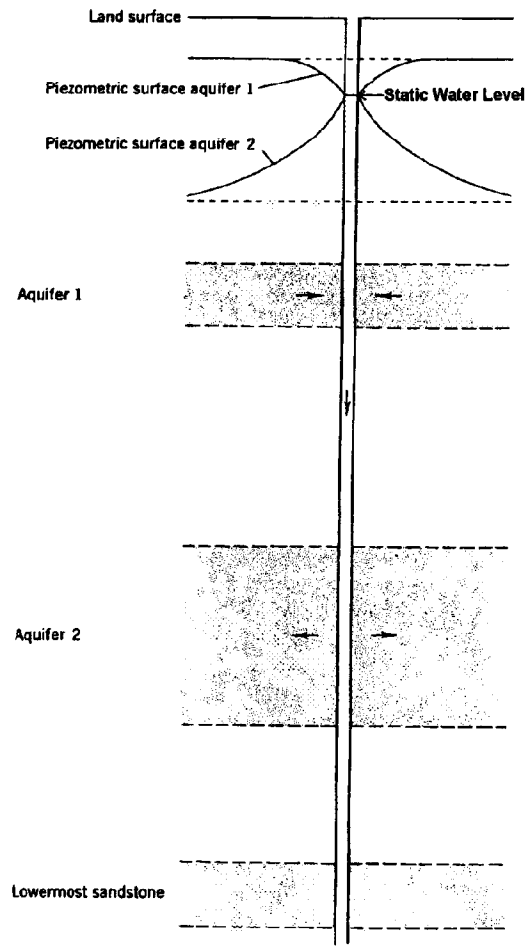


Figure 2.7 Diagram of well through two aquifers in Mercer County, PA (modified from Bennett and Patten, 1960).

Another common misconception is that the static water level indicates the level at which water is entering the borehole. That infers that the pressure head in the aquifer is atmospheric, which is true only at the water table. It also infers that the level that water is entering a flowing well is above the land surface. In Figure 2.7, neither the static water level of the well, nor the potentiometric surface, is at the level of either aquifer.

Hydraulic Conductivity

Porous media may be characterized by their hydraulic conductivity (permeability), described in general terms as either primary or secondary. Primary permeability refers to the intergranular spaces of the transmitting medium. It may be dominant in unconsolidated sediments, but is less important in consolidated bedrock of the Appalachian Plateau of Pennsylvania (Figure 2.8). A significant amount of

permeability (and porosity) in this system is secondary (Schubert, 1980). Bedding-plane partings, stress-relief fractures, zones of fracture concentration, tectonic joints, and faults serve as secondary pathways for fluid migration. Fracture zones (high concentrations of near vertical joints) are especially permeable (Lattman and Parizek, 1964). Where a coal serves as an aquifer, permeability is usually secondary along the cleat (Wunsch, 1993). High yielding aquifers in Pennsylvania's Appalachian Plateau tend to be mainly sandstones (Carswell and Bennett, 1963; Peffer, 1991), suggesting that primary permeability is a factor. However, it may be that secondary permeability tends to be better developed in the more brittle sandstones, than in shales (Carswell and Bennett, 1963; Peffer, 1991). Brown and Parizek (1971) and Wyrick and Borchers (1981) found secondary fracture permeability to be considerably greater than primary permeability. As a general rule, secondary permeability decreases with depth because fractures close due to overburden pressures and routinely decrease in frequency and distribution. Because the secondary permeability features are less pronounced in deeper regional flow systems, their overall transmissivity is significantly lower than in shallow aquifers in the local flow systems.

A general decrease in hydraulic conductivity and storativity with depth has been documented many times. Bruhn (1985) found that the average hydraulic conductivity within 150 feet (46 m) of the surface at a West Virginia mine site was 10^{-5} m/sec, decreasing to 10^{-9} m/sec for depths greater than 300 feet (90 m). Specific storativities for sandstone aquifers also decreased from 10^{-5} to 10^{-12}/ft. Stoner (1983), working in Greene County, PA, found the hydraulic conductivity reduced by one order of magnitude per 100 feet (30.48 m) of depth to a depth of 500 feet (152.4 m).

Brown and Parizek (1971) documented considerable differences between values of permeability determined from core analysis and those determined from pumping test data in Clearfield County, Pennsylvania. Values of permeability obtained from cores were markedly lower than those obtained from the pumping tests. This was attributed to the fact that the core analyses measured only the primary or intergranular permeability, whereas the field pumping test data combined the effects of both intergranular and fracture permeability.

Abandoned underground coal mine voids and caves, mainly in the Vanport Limestone, also serve as secondary permeability pathways. The flow is different from intergranular and fracture flow, especially if the conduits are not full. Shuster and White (1971) have described this flow in caves of carbonate terrain as

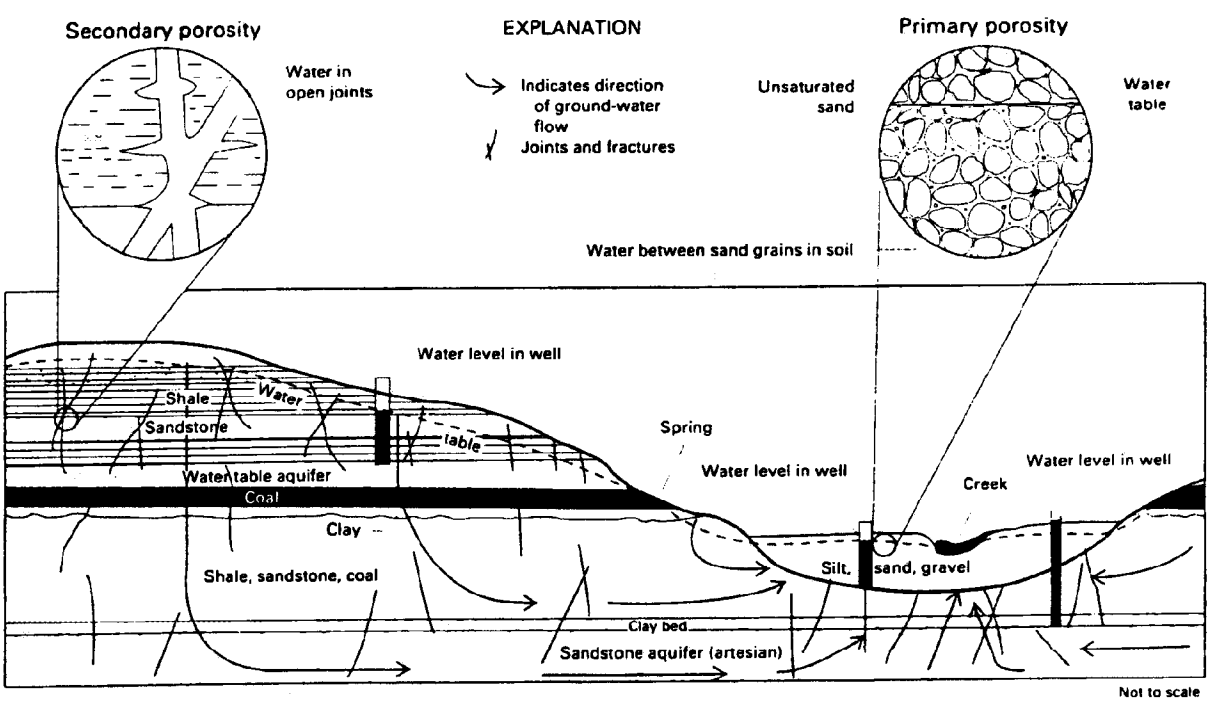


Figure 2.8 Water table aquifer (upper), confined aquifer (lower), and groundwater flow lines (modified from Hobbs, 1987).

conduit flow. This term is also appropriate on the Appalachian Plateau. It is an extreme form of anisotropy in the transmitting medium. Conduit flow effectively reduces recharge to deeper aquifers and flow systems. Dispersion of groundwater via intergranular, and to a lesser extent, fracture flow, is virtually eliminated in conduit flow. As a result, contaminants are more likely to move as a slug for long distances through discrete conduits rather than being dispersed over a larger area (Freeze and Cherry, 1987).

Over large areas of the Appalachian Plateau extensive underground mining has taken place leaving, as a remnant, substantial man-made aquifers (mine-void and subsidence-fracture zones) which can have a profound influence on groundwater flow. Research by government agencies, coal producers, and major universities in the eastern coal fields has resulted in a good understanding of subsidence-fracture profiles which develop above underground mine excavations. The result is that mining associated zones of collapse, fracturing, fracture dilation, and surface disturbance can be anticipated. Various conceptual models linking strata deformation, hydraulic property changes, and impacts to groundwater uses have been put forward (Kendorski, 1994; Booth, 1986; Peng and Chiang, 1984; Hill et al.,1984; Owili-Eger, 1983; Tieman and Rauch, 1986, to name a few). Impacts to local groundwater resources vary depending on factors such as proximity to mining, mining sequence, geology, coal extraction percentage, thickness and strength of overburden, height of target coal, topography, and presence of preexisting fracture sets which may extend mining induced hydrologic impacts.

Underground mines, because of the scale of the operations, may impact the hydrology of a given locale much more profoundly than a surface mine. Underground mines have the potential to impact surface and groundwater systems on a relatively large scale. Interbasin transfer of groundwater is a common occurrence associated with underground mines. During mining the underground excavation acts as a large sink which draws in groundwater. Upon closure and flooding, it becomes a highly permeable aquifer which can permanently alter the premining flow regime both physically and chemically. Due to the open nature of the mine-void aquifer, there is a postmining transfer of the resulting mine-pool potential throughout the interconnected mine workings. This is an important factor regarding the potential for mine pool breakout since areas within and adjacent to the downdip portions of the mine workings can often realize abnormally high postmining heads comparative to premining values.

Effect of Dip on Groundwater Flow

A common misconception is that groundwater always flows downdip. Groundwater flows from recharge to discharge areas. If the discharge area is in the updip direction (from B to C on Figure 2.9), groundwater will move counter to the control of dip. Flow is governed by the relative distribution of head and not necessarily attitude of the beds.

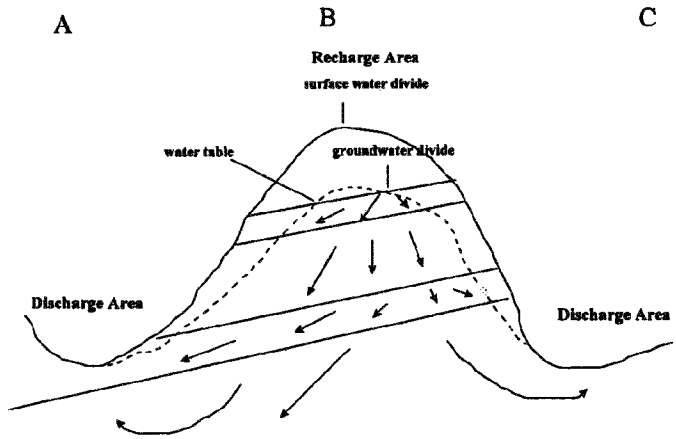


Figure 2.9 Hypothetical groundwater flow in area of dipping bedrock

The effect that dip has on groundwater flow is that it can shift the groundwater divide updip from the surface water divide (Figure 2.9) (Earl, 1986; Shuster, 1979). Excavations, such as surface and underground mines, can serve to magnify the shifting of the groundwater divide due to their abilities to disturb hydraulic gradients and convey groundwater.

Also, bedding can have an important effect on postmining groundwater flow at surface mines. Due to the large permeability contrast between the poorly-permeable pit floor and the readily-permeable mine spoil, groundwater will flow laterally through the spoil, parallel to the pit floor, to a point of discharge at the spoil toe. Where the pit floor is inclined away from the spoil outslope, groundwater commonly impounds in the spoil to the elevation necessary to discharge either laterally or at the up-dip spoil outslope.

Pit Floor Leakage

On many surface mines, downward leakage of groundwater thorough the pit floor exceeds the rate of recharge. Where this occurs, there may be no observable discharges from the surface mine spoil, or dis-

charges may only occur during wet seasons when recharge is greater. Instead, water migrates vertically through the pit floor material at a rate sufficient to drain the overlying spoil This water ultimately reports to lower groundwater discharge zones, commonly associated with underlying coal seams.

Surface mine spoils with no apparent groundwater discharge are often erroneously thought to represent "dry sites" which do not produce drainage. But in Pennsylvania and other humid states with precipitation exceeding evapotranspiration, short of capping the site with an impermeable barrier, it is virtually impossible to prevent infiltration into the groundwater system. Instead, an apparently dry site is indicative of a leaking pit floor which transmits groundwater to underlying horizons. Leakage through the pit floor may result from the intrinsic permeability of the pit floor material, jointing or faults in the pet floor material, mine subsident fracturing, or drill hole penetration.

Fractures

Fractures and bedding-plane partings are commonly the main groundwater flow paths on the Appalachian Plateau. Near-vertical fractures (joints and faults) may cause flow to be oblique, instead of perpendicular, to the hydraulic gradient (Fetter, 1981). However, hydraulic head must decrease along the flow path. The hydraulic gradient, not the fractures, exerts the dominant control on the direction of groundwater flow. Fractures can have a direct influence on groundwater flow rate due to the generally lower frictional resistance to groundwater flow within fractures versus intergranular pores and to the fractures' role in lessening flow system tortuosity.

The following is a list of secondary permeability features which can impart significant local and/or regional controls on the flow system of the northern Appalachian coal measures:

Joints - A joint is a rock fracture along which displacement has not occurred. The joint pattern is cumulative and represents a record of all stress events sufficient to induce fractures. On the Appalachian Plateau there are two ubiquitous, orthogonal joint sets which form the *fundamental joint system.* The joint sets are the systematic joints (planar joints in shales and sandstones, face cleats in coal) and the nonsystematic joints (curved joints in shales and sandstones, butt cleats in coal). Systematic joints are the dominate set and continue across other joints; are generally perpendicular to upper and lower rock unit boundaries; are commonly perpendicular to bedding; and are <u>not</u> confined to rock type but can pass downward or upward into adjacent units. Nonsystematic joints are nonplanar; do not generally cross other joints; and commonly terminate against bedding planes (Nickelsen and Hough, 1967).

Joints from different sets and/or different lithologies have different properties. Spacing (distance between joints) and width (distance across a joint) are generally greatest in coarser, more resistant lithologies. Systematic joints may continue into adjacent beds or lithologies, whereas nonsystematic joints generally terminate against systematic joints, bedding planes, and lithologic contacts. Joints (cleats) in coal do not usually pass into adjacent lithologies. Joints in sandstones are parallel and of similar planeness as shale joints but are more widely spaced (sandstones show spacing of many meters; shales show spacing of several centimeters to many meters; coals show spacing of fractions of a millimeter to several centimeters) (Nickelsen and Hough, 1967).

Joint characteristics affect groundwater flow. Spacing suggests the number of joints available for groundwater pathways. The width indicates the ability of the joints to transmit water. Systematic joints are often continuous and can transmit water longer distances, more rapidly, than non-continuous, nonsystematic joints. Joint permeability is particularly significant, if not dominant, in shallow rock strata of western Pennsylvania (50-500 feet) (15-150 m) and may increase permeability values by ten to a thousand times when compared to intergranular permeability values taken alone (Parizek, 1971).

Stress-relief fractures - Stress-relief fractures are a fracture network unrelated in age and orientation to tectonic stresses. They are often the most transmissive part of an aquifer (Wyrick and Borchers, 1981). They were first documented during abutment characterization prior to the construction of dams throughout Pennsylvania, Ohio, Kentucky, New York, West Virginia, and other areas worldwide where similar flat-lying sedimentary rocks were drilled or excavated during foundation work (Burwell and Moneymaker, 1950; Ferguson, 1967, 1974; Ferguson et al., 1981). Stress-relief fractures include vertical fractures parallel to valley walls, caused by the release of stress as lateral rock support is removed during erosional downcutting. Slumping along the fractures on both sides of a valley cause compression in the center of the valley, resulting in thrust faults, bedding-plane partings, arching, and

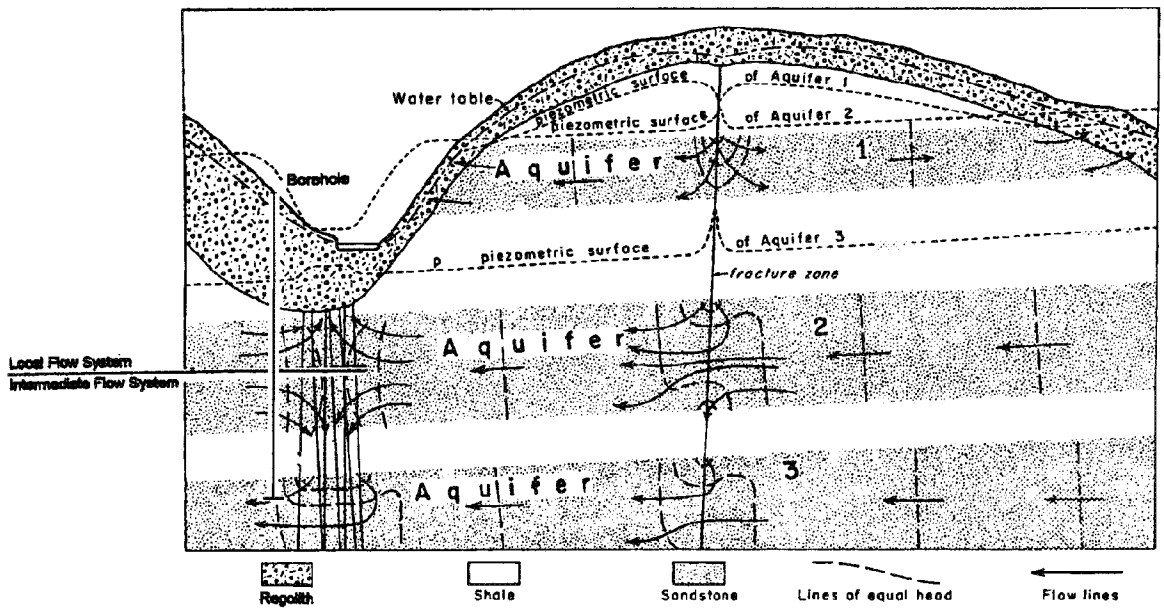


Figure 2.10 Idealized pattern of groundwater flow in and beneath a "hydrologic island" (modified from Poth, 1963).

vertical extension fractures above arches (see Figure 2.16). Studies by Wyrick and Borchers (1981), Kipp and Dinger (1987), and Davis (1987) describe a highly permeable, valley-related, shallow flow system which consists of interconnected valley-wall and valley-floor fracture sets. Sections of the valley-floor portion of the subsystem can become artesian due to the presence of alluvial clay which generally occurs mid-valley and can serve as a confining layer. Sames and Moebs (1991) describe the character and extent of valley-wall, stress-relief fractures as follows:

> "...Stress-relief joints occur in the shallow overburden where surface slopes are steep, with the greatest frequency and degree of weathering in mine roof within 200 feet laterally of coalbed outcrop. They are usually discontinuous along strike, and decrease in frequency and degree of weathering to about 700 feet from the outcrop and under 300 feet or more of overburden, as the effects of stress relief gradually disappear."

Zones of fracture concentration - Fracture zones (see Figure 2.10 and 2.11) are relatively restricted areas where numerous fractures dissect the rock mass. The degree of interconnectedness varies as depicted on Figure 2.12. Fracture zone widths of 7 to 12 meters are common in the central Appalachian region (Gold, 1980). Depths range into the hundreds of meters. The hydrologic impacts of a fracture zone can be profound. An entire discipline has evolved around locating fracture zones by mapping their surface expressions (fracture traces and lineaments) and exploiting their relatively high permeabilities for the development of water supply wells. Fracture zones are often valley related phenomena where they can become integrated with valley stress-relief fracture systems. These features can, and do, serve as major conduits for groundwater. In zones of relatively intense fracturing, hydraulic conductivities are often several orders of magnitude higher than in unfractured rocks, resulting in fracture-dominated flow (Schubert, 1980).

Bedding-plane partings - Inherent weaknesses in rock arising from thin bedding (laminations), fissility and/or lithologic contacts often are zones which will provide avenues for groundwater migration. Schubert (1980) discusses the following observation from a drilling project in West Virginia, ... "The only large quantities of water encountered during drilling originated from fractures or from contacts between formations. Shales often supplied more water than did the coarse but well-cemented sandstones, apparently because of slight fracturing which permitted good lateral movement of water"

Fault zones - A fault is a fracture or fracture set along which there has been displacement. Faults can be important conveyers of groundwater relative to the surrounding unbroken rock mass and are common in some of the more eastern portions of the Plateau, near the Allegheny Front, where stresses were maximized

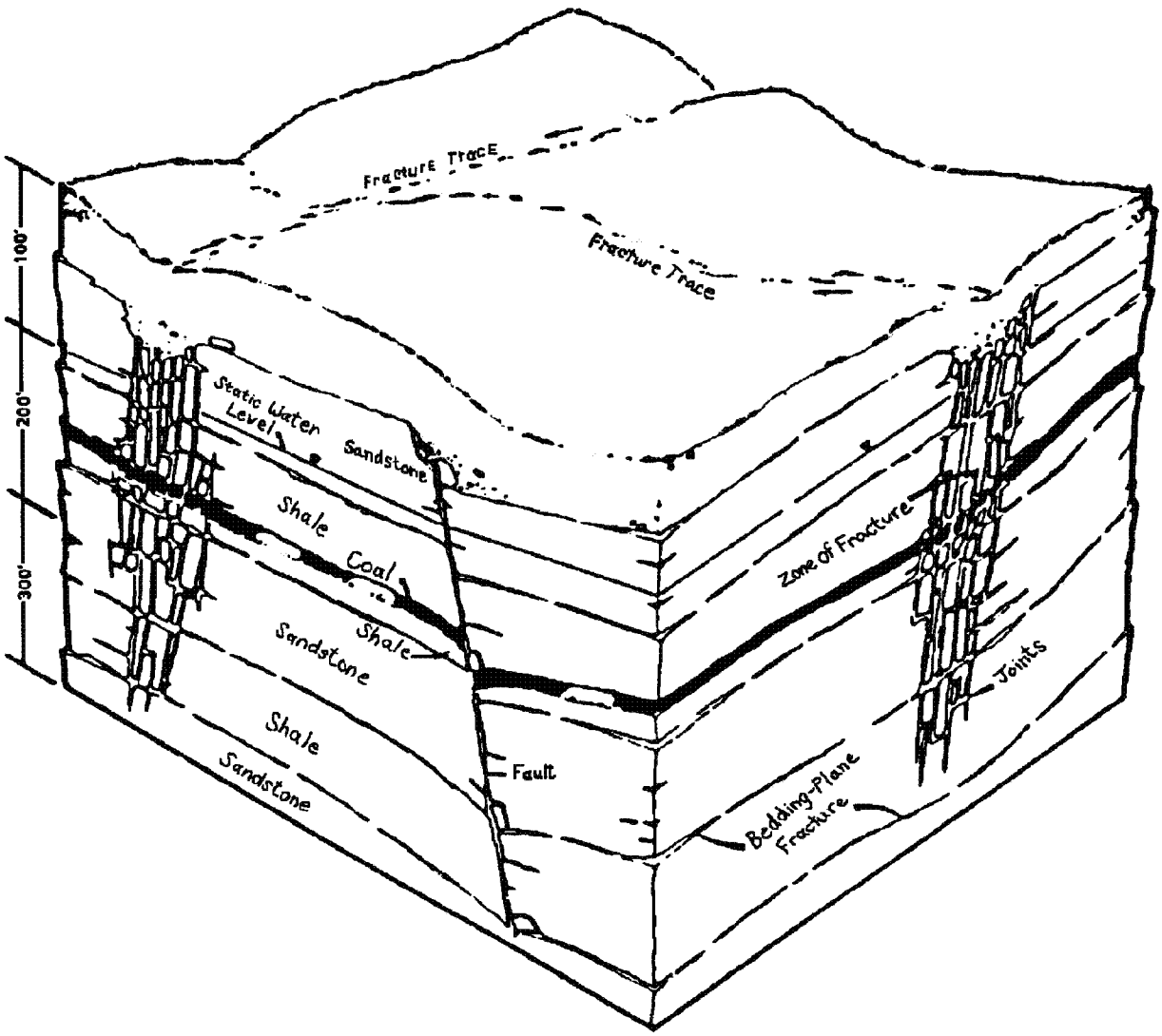


Figure 2.11 Idealized block diagram of fracture zones in the eastern coal region (modified from Ebaugh, 1986)

due to bending of rock units. Studies in Virginia regarding coal bed methane have documented highly permeable zones related to faults. Low-angle, imbricate thrust faults and broken rock were encountered in an Upper Freeport underground mine in western Pennsylvania, also yielding large quantities of gas and water when intersected (Elder et al.,1974; and McCulloch et al., 1975)

Geology

Pennsylvania's Appalachian Plateau physiographic province (Figure 2.13) extends from the western state border to the Allegheny Front. The Front is a prominent southeast-facing escarpment of approximately 1000 feet (305 m) of relief (Fenneman, 1938). The bituminous coal fields of Pennsylvania are almost entirely contained within this province. The effects of glaciers (extent shown on figure 2.13) on the northwest section of the plateau has served to scour and erode preglacial topography, fill topographic lows with glacial deposits thereby reducing relief, and in general produce characteristic glacial landforms such as drumlins and morainal features (Hornberger et al., 1981).

The rocks of the Appalachian Plateau are almost entirely sedimentary. Rock types consist of shale, sandstone, conglomerate, limestone, underclay, claystone, coal, and siltstone. The strata are relatively flat lying with northeast-southwest trending folds. Structural relief decreases north-westward in a step-like fashion from the well-defined folds of the southeastern

side of the Plateau where anticlines rise 800 to 2500 feet (244 to 1067 m) above adjacent synclines (Gwinn, 1964). The prominent structural forms of the coal bearing rocks of the Plateau, especially the anticlines of the Allegheny Mountain Section, may be reflected in the configuration of the present topographic surface except where deposition of the recent sediments, as in the Glaciated Section, has masked the underlying geologic structure (Hornberger et al., 1981).

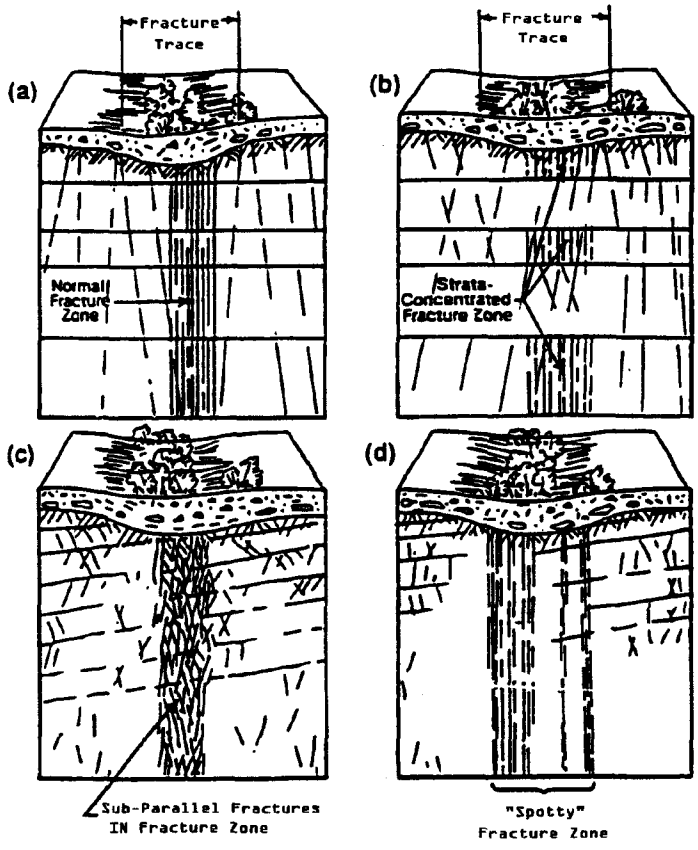


Figure 2.12 Styles of fracture development below fracture traces (Parizek, 1991)

Numerous factors combined to define the nature and extent of the cyclic deposits of sediments (cyclothems) which resulted in the repetitive coal measures of the basin. The result is a complex, somewhat cyclical, relatively flat-lying mix of sedimentary rocks with the prevailing characteristics being numerous lateral facies changes and interfingering lithologies.

Although referred to as cyclical, the sequence is generally not regular especially when considered in three dimensions. Marine zones, coals, and underclays are the most persistent units, with interfingering, pinching out, and local replacement by sandstone channels occurring commonly (Bieniawski and Mack, 1986). These thin, flat-lying, layered strata of contrasting permeability impart a layered heterogeneity, with a preferred horizontal flow component, upon the groundwater flow system. (See Chapter 8 for additional details regarding the region's geology.)

Aquifer "Types" of the Plateau

Since the rock matrix serves as a flow medium for groundwater, its origin and physical properties are controlling factors regarding the character of the flow system. Physical properties such as grain size, grain shape, degree of sorting, type and extent of cementation, degree of induration, and amount of compaction can affect the hydrologic properties of the rock mass. Sedimentary processes, which include weathering, transportation, deposition, and lithification, ultimately affect the resultant groundwater flow system by controlling certain of these physical properties. Shale, coal, siltstone, underclay, massive limestone, and tightly cemented sandstone generally display poor primary permeabilities (intergranular permeabilities) (Williams et al., 1982). Post-depositional processes can profoundly alter a unit's hydraulic conductivity through the development of secondary permeability features. On the Plateau, these secondary features govern the flow system's character.

Topographic relief affects head differences between areas of groundwater recharge and discharge, thereby influencing the depth of local groundwater circulation. In hilly terrain, such as is found in the northern Appalachian coal measures, the incised topography produces numerous subsystems within the major flow system. Water will often discharge to the nearest topographic low in this type of setting or it may continue to a more regional discharge area in the bottom of a major valley. Natural discharge occurs mainly as cropline springs and seeps, and base flow into streams and lakes. The water table located within the ridges between surface drainageways tends to become depressed to the level of the surface streams. However, semi-perched zones occur routinely within the ridges due to the numerous low permeability units.

Most porosity and permeability in the Appalachian Plateau is secondary. For example, bedrock aquifers usually include bedding-plane partings and near-vertical fractures, both secondary permeability features. Without such secondary features, the bedrock would likely not be a significant aquifer (Heath, 1984). However, the characteristics of the fractures (width, spacing, frequency, etc.) differ between, but may be consistent within, various stratigraphic units. Therefore, it is convenient to consider the stratigraphic units

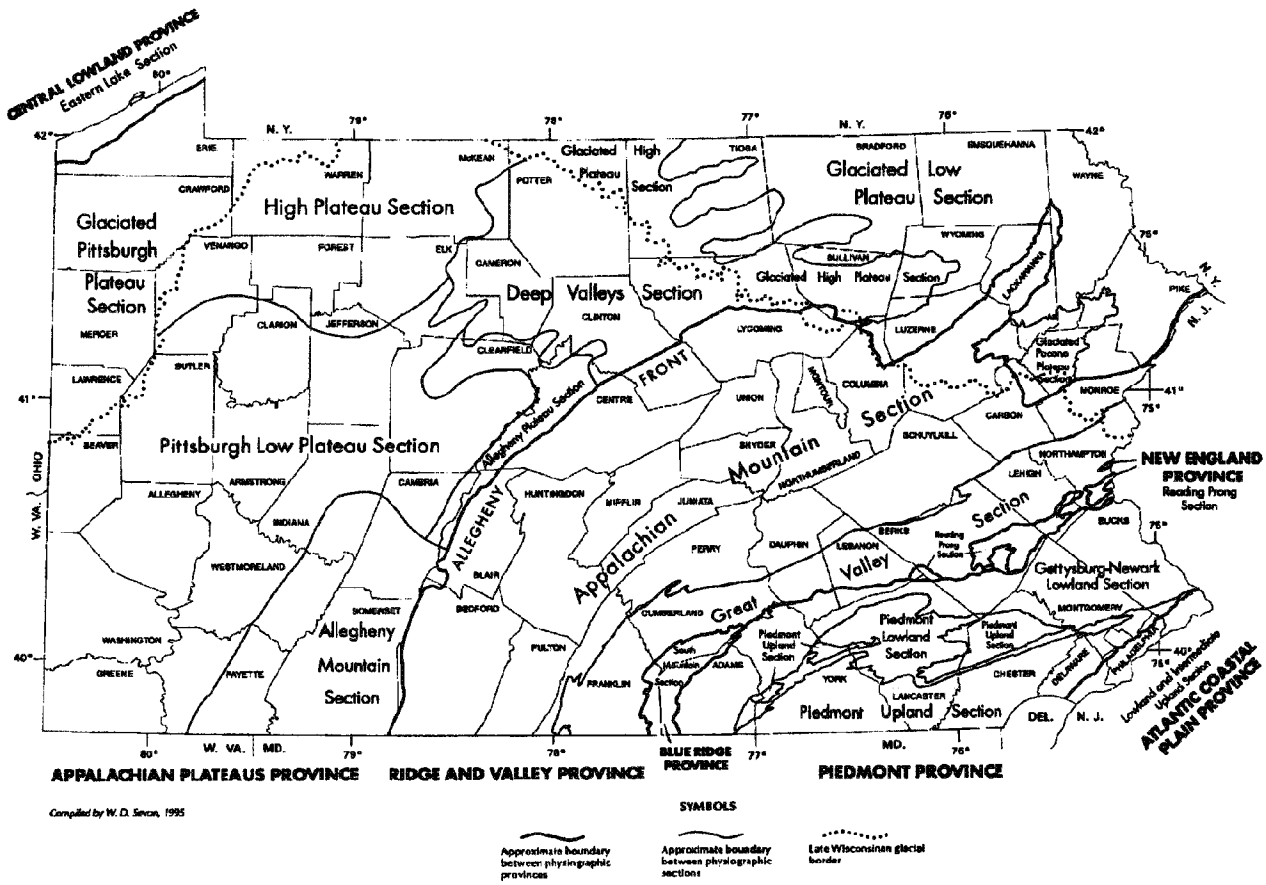


Figure 2.13 Physiographic Provinces of Pennsylvania (PA-DCNR MAP 13)

as the aquifers. The "typical" vertical profile on the Plateau consists of a shallow, unconfined (possibly including seasonally perched or semi-perched zones) system grading to a semi-confined system at intermediate depth.

Secondary openings such as joints, fractures, bedding-plane partings, zones of fracture concentration, fault zones, and slaty cleavage may greatly increase the water movement and storage within the coal measures (Parizek, 1979). Joint development within coals and associated strata add significantly to the vertical permeability of both aquifers and confining beds (Parizek, Sgambat, and Clar, 1979). Solution enlargement of secondary openings within marine and fresh-water limestones can transform these units of poor permeability into major aquifers (Parizek, White, and Langmuir, 1971). These features commonly counteract the previously outlined layered heterogeneity of the coal measures by augmenting vertical hydraulic conductivities allowing for significant vertical communication within the system. Additionally, rock types with relatively low primary permeabilities can become significant water producers due to interconnected fractures. Because of the importance of secondary permeability features to groundwater flow in this setting, the classic use of terms such as aquifer, aquitard, and confining layer can become obscured even on a local scale. A single lithologic unit, such as a shale, can be characterized as either an aquifer or an aquitard over a relatively short lateral distance depending on conditions such as proximity to the shallow weathered zone, proximity to stream valleys, and magnitude of open joints (generally decreasing with depth).

Equipotential lines are roughly parallel to bedding in low permeability zones and nearly perpendicular to bedding in high permeability zones. As a result, water flows laterally through high permeability units and vertically through low permeability units (Carswell and Bennett, 1963). Shales and other units with low permeability, still may transmit large amounts of water,

but transmit it vertically. A study in eastern Ohio estimated that 85% of the discharge from the local flow system was due to leakage through aquitards to deeper levels (Weiss and Razem, 1984). This contrasts with the findings that most groundwater in the stress-relief/weathered regolith subsystem never reaches the deeper flow systems. Weiss and Razem's study was in a low relief area, probably dominated by intermediate and/or regional flow systems. Nevertheless, their study suggests that low permeability units can transmit large amounts of water vertically. Most of the vertical change in head occurs across low permeability units (Carswell and Bennett, 1963; Peffer, 1991). The Appalachian Plateau contains substantial ranges of permeability. Permeability in sandstones may be hundreds of times greater than in shales (Brown and Parizek, 1971). Hawkins et al. (1996) also found permeability differences of over 100 times between the stress-relief/weathered regolith subsystem and the ridge-core subsystem. Schubert (1980), using laboratory-determined air permeabilities, showed the average ratio of horizontal to vertical hydraulic conductivities varied with lithology, ranging from 2.6 in sandstone to 14.9 in siltstone in rock samples from the coal fields of Pennsylvania.

Semi-perched aquifers occur when a relatively impermeable layer impedes the downward vertical flow of groundwater, but not to the extent that an unsaturated zone occurs uniformly beneath this flow-restricting zone. This type of aquifer is common on the Appalachian Plateau. They result where enhanced vertical hydraulic conductivity along the rind of a hill leads to step-like offsets in the water table near croplines. Under semi-perched conditions, the hill core remains saturated with perching occurring along the margins of the hill where the increased vertical permeability eliminates the "confining" properties of aquitard units resulting in free draining. The groundwater then migrates downward to a point where a sufficient permeability contrast exists to direct flow to a hillside spring (Figure 2.14).

Perched aquifers, where an unsaturated zone consistently exists beneath a poorly permeable zone, appear to be the exception rather than the rule on the Plateau. Their existence depends on consistent vertical permeability contrasts within the layered coal measures which is rare due to numerous and often abrupt lateral facies changes and extensive fracturing. By definition, a perched aquifer has unsaturated conditions both above and below (Figure 2.14). As a general rule on the Plateau, aquitard units within hills allow considerable leakage, thereby precluding the development of classic perched aquifers. Where they do exist, perched conditions are often temporary, dissipating with time due to downward leakage, sporadic recharge, and evaporation from the surface. Water chemistry data from the cores of hills versus cropline springs routinely indicate that the springs are fed by shallow dilute groundwater as opposed to water moving laterally from the middle of the hill. The chemistry data generally supports the semi-perched model where significant downward leakage occurs through aquitards in the cores of hills with only minor amounts of water moving laterally from hill cores to emanate as cropline springs.

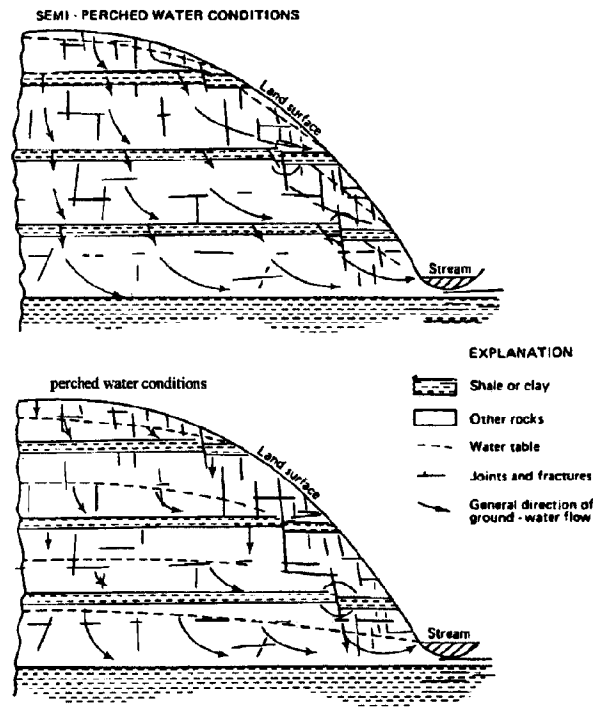


Figure 2.14 Idealized semi-perched and perched water conditions (modified from Ward and Wilmoth, 1968).

Confined aquifers are common at depth on the Appalachian Plateau. The majority of what are often termed confined aquifers, particularly those at intermediate depths, are better designated as semi-confined or "leaky" aquifers in that the associated aquitards have only marginal confining capabilities, i.e., are capable of transmitting significant quantities of water. Confining layers bounding aquifers need to be properly characterized particularly in cases where mine inflow may depend on the hydrologic properties of a nearby confining layer.

Many flowing wells in Pennsylvania are from confined aquifers that are recharged at their outcrops along the crests or flanks of anticlines (T. McElroy, personal communication, 1995). Of course flowing wells need not be from confined aquifers. In groundwater discharge areas, hydraulic head increases with depth and may eventually exceed the elevation of the land surface. A well in that type of setting, if cased to the appropriate depth, would flow. In Figure 2.10, a well drilled within the valley would flow at the surface, even though it is not tapping a confined aquifer.

Unconsolidated aquifers occur on the Appalachian Plateau in major alluvial valleys and terraces, and in glacial sands and gravels. Tills are usually capable of storing significant quantities of groundwater, but cannot transmit large amounts. In contrast to consolidated bedrock, primary porosity dominates in unconsolidated sediments. In certain areas such as the Allegheny-Ohio River valley of western Pennsylvania, alluvial deposits can be the most productive water-bearing formations. Alluvial valley aquifers receive most of their recharge from discharge from the underlying bedrock, and discharge into the rivers.

Groundwater Flow Systems

Recharge and Discharge Areas

Groundwater flow systems are commonly defined by their recharge and discharge areas. Groundwater routinely moves from recharge areas, generally topographic highs, to topographic lows. Recharge and discharge zones have unique "potential" signatures regardless of the flow system. In a recharge area hydraulic head decreases with depth causing downward flow; in a discharge area hydraulic head increases with depth causing upward flow (Saines, 1981). Flow systems can be classified as local, intermediate, or regional to characterize the areal extent of the flow system, the time required for groundwater to travel from the recharge to discharge areas, and the proximity of the discharge area to the most distant recharge area.

The relative size of the recharge versus discharge zones varies. However, for most topographic settings the hinge line is much closer to valley bottoms than to topographic highs. The "hinge line" is an imaginary line separating recharge areas from the discharge area. Discharge areas commonly constitute only 5-30% of the surface area of a watershed (Freeze and Cherry, 1987). Experience gained through locating and mislocating discharge zone piezometer clusters on the Plateau has indicated that upward gradients associated with stream valleys will be detected routinely only where the piezometers are in proximity to the stream, i.e. - the discharge area is very small compared to the recharge and lateral flow zones. Harlow and LeCain (1991), working in a similar setting in Virginia, confirm that upward gradients were detected only in proximity to streams.

Regions such as the Appalachian coal measures with their small basins, marked relief, and humid climate generally develop a groundwater flow system which can be readily broken into distinct parts - local, intermediate, and regional (Toth, 1963) (Figure 2.15). Superimposed on these systems (particularly on the shallow system) are additional distinct flow zones (subsystems) defined by the density, interconnectedness, and aperture of rock fractures. Although the ideal is to characterize the flow systems by defining the density, orientation, and transmissivity of fractures for each rock type and each distinct flow zone, Brown and Parizek, (1971) have demonstrated that useful groundwater flow models can be constructed with limited data by assuming uniform fracture distribution.

Local (Shallow) Groundwater Flow System

The shallow flow system underlies hills, discharges to local streams, and, to some extent, leaks downward into the deeper, intermediate system, which discharge to higher order streams at lower elevations (Duigon, 1987). In some areas, local systems include water which is "perched" above beds of lower permeability. This groundwater may then flow laterally due to permeability contrasts and discharge as springs above stream level.

Poth (1963) describes shallow groundwater in the Mercer, PA 15-minute quadrangle as circulating in a series of "hydrologic islands" (Figure 2.9). The dissected nature of the bedrock surface has resulted in hills, largely surrounded by valleys containing perennial streams. These hills constitute the hydrologic islands. This description can be extended over most of the Appalachian Plateau. A shallow, local groundwater flow system operates within each hydrologic island and is hydrologically segregated from the local groundwater flow systems in adjacent islands. The base of the local flow system (particularly for islands adjacent to first and second order streams) is a distance below the level of the stream valleys bordering the island, defined by the maximum depth at which groundwater originating within the hydrologic island will flow upward to discharge in the adjacent stream valley (see Figure 2.9).

Recharge to the local system is completely from within the hydrologic island. Discharge from the local system is into the adjacent stream valleys and via leakage into deeper intermediate and regional groundwater flow systems. In areas adjacent to larger streams and rivers, local groundwater which leaks downward may commingle with intermediate or even regional flow which is rising to discharge within the valley.

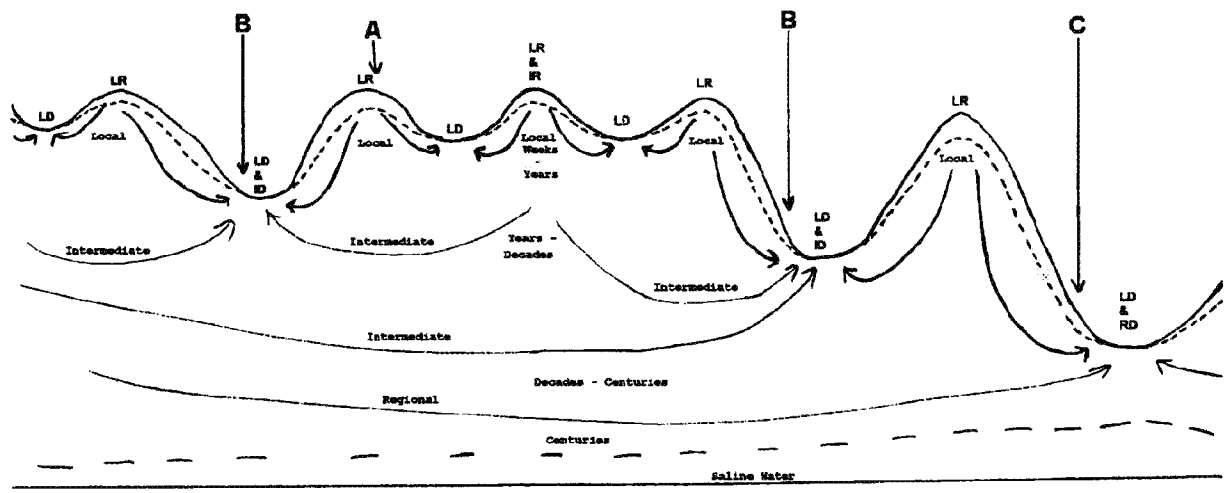
This shallow flow system is the area of the most active groundwater circulation. It is the zone which contributes water to the vast majority of domestic wells. Because hydraulic conductivity routinely decreases with increasing depth (studies have indicated an order of magnitude decline for every 100 feet (30 meters)), it is estimated that as much as 99.5% of total groundwater circulation occurs within the shallow (within 175 feet (53 m) of the surface) zone (Stoner et al., 1987).

The local flow system can often be divided into subsystems (Kipp and Dinger, 1987). Subsystems include the stress-relief fracture (Ferguson, 1967, 1974) and weathered regolith zone and the ridge-core subsystem which is controlled by lithology and tectonic fractures (joints and faults).

Stress-relief/weathered regolith subsystem - The stress-relief/weathered regolith subsystem exhibits distinctive groundwater flow and chemical characteristics, relative to the ridge-core subsystem and deeper flow systems. This is due to the non-reactive (weathered) nature of the transmitting medium and the short residence time of groundwater in this system.

The weathered regolith is a highly transmissive zone consisting of soil, unconsolidated sediment (colluvial, glacial, alluvial, etc.), and weathered, highly fractured rock. It has been documented to a depth of approximately 10-20 meters (Hawkins et al., 1996; Gburek and Urban, 1990; Merin, 1992). Weathering has removed most soluble minerals, and groundwater flowing through this material picks up little mineral matter. Because of the open nature of the fractures within this zone, the groundwater "flow-through" time is short and this subsystem allows a significant portion of the recharge to short-cut to local discharge points. Various hydrologic tests have shown hydraulic conductivities within this zone to be one to two orders of magnitude greater than in zones which are only marginally deeper (Schubert, 1980).

Water chemistry within the stress-relief/weathered regolith subsystem should not be used to characterize groundwater under deeper cover which flows through unweathered rock. For example, rock units closer to the ridge center may contain groundwater with significant alkalinity due to circulation through unweathered calcareous strata. In comparison, an outcrop spring at the same stratigraphic interval shows little or no alkalinity because it is largely fed by groundwater which traveled an abbreviated path through leached and



LR = Local Flow System Recharge Area
LD = Local Flow System Discharge Area
IR = Intermediate Flow System Recharge Area
ID = Intermediate Flow System Discharge Area
RD = Regional Flow System Discharge Area

Figure 2.15 Sketch illustrating various characteristics of the composite fresh-water groundwater flow system.

weathered rock along the "rind" of the hill. (Refer to Chapter 9 for information regarding premining water chemistry.)

Recharge to the stress-relief/weathered regolith subsystem is through ridge-top and valley-wall fractures. Groundwater flows through the interconnected bedding-plane partings and fractures to springs flanking the hill sides (frequently located on coal outcrops) and into stream channels where the fractures are exposed. Much of the water that enters this shallow subsystem never penetrates to the nearby ridge-core subsystem, nor to deeper flow systems. Residence time is as short as days to a week (Hawkins et al., 1996). Water levels in wells in the stress-relief zone respond quickly to precipitation events (Kipp and Dinger, 1987; Hawkins, et al., 1996). Wyrick and Borchers (1981) determined that stress-relief fractures significantly affect the surface water hydrology in Appalachian Plateau valleys. Their study in the Black Fork valley in West Virginia showed that stream flow per square mile of drainage area increased 6 to 11 times downstream from the outcrop of stress-relief and bedding-plane fractures in the stream bed.

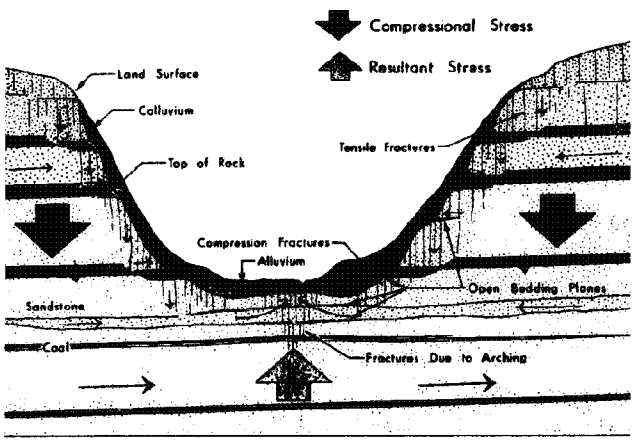


Figure 2.16 Generalized geologic section showing features of stress-relief fracturing and associated groundwater flow (modified from Ferguson, 1974).

Ridge-core subsystem - Flow within the ridge-core subsystem is controlled by lithology and regional joint sets. The ridge-core subsystem receives recharge through the stress-relief/weathered regolith subsystem. Groundwater flow is through tectonic fractures, bedding-plane partings, and to a much lesser degree, through intergranular porosity. Low permeability units (such as claystones and shales) exert more control within the ridge cores due to the lack of stress-relief joints and weathering which controls groundwater movement along the margins of the hills. Because the integrity of these low permeability layers has not been compromised fully in the ridge cores, as may be the case along the hillsides, groundwater can mound on these layers and either flow laterally to mix with groundwater within the stress-relief/weathered regolith subsystem and discharge to the local stream valley; or can leak downward to an intermediate or even regional flow system.

Residence times and response times to precipitation events within the ridge cores are intermediate between those for the stress-relief/weathered regolith subsystem and deeper systems. The ridge-core subsystem is part of the local flow system because it is part of the hydrologic island which discharges into the valley adjacent to the local recharge area.

Intermediate Flow Systems

Intermediate groundwater flow systems are those below the local shallow flow system but above the regional system (Richards, 1985). The intermediate system has some distinctive features which allow it to be separated out as a distinct zone. Although this zone may very well contain some components of the local and/or regional systems, the primary controls on groundwater flow are regional joint sets, bedding-plane partings, lithology, and zones of fracture concentration. At least one local flow system occurs between its surface recharge area and its discharge area. Recharge to intermediate systems is from leakage from overlying local systems, shallower intermediate systems, and at the basin divide of the defining recharge area. The flow passes beneath two or more hydrologic islands, similar to regional systems, but discharges in valleys above the lowest level of the drainage basin. Flow rates and residence times are generally between those of local and regional groundwater flow systems, probably varying from years to decades, depending on the level of the intermediate system and the length of the flow path. Vertically, at any given point, there is a single local flow system and a single regional flow system. However, there may be multiple intermediate flow systems at different levels, defined by multiple discharge areas, between the local and the regional flow systems (A in Figure 2.15).

Also, in intermediate flow systems regional structure tends to play a more important role in groundwater movement than with local flow systems. The important controls on the shallow system, such as incised topography with its associated undulating water table,

weathering, and fracture enhanced permeability, are less important at these depths.

Regional Flow Systems

A deep, regional groundwater flow system, which lies beneath the level of the low order stream valleys bordering the hydrologic islands and intermediate flow systems, operates independently of the shallower systems. The base of the regional system is the fresh water/saline water contact. The vast majority of groundwater circulation is primarily at shallow to moderate depths (< 300 feet (90 m)). Recharge to the regional system is from major drainage basin divides and leakage from multiple shallower (local and intermediate) systems. Regional groundwater does not flow to the surface to discharge in the stream valleys bordering the hydrologic islands (unless they are master streams), but continues beneath adjacent hydrologic islands and intermediate flow system discharge points to larger, deeper, regional discharge areas. These discharge areas are usually in larger, master stream valleys. These master stream valleys are commonly a major stream valley at the lowest level of the drainage basin (Richards, 1985). Within these regional groundwater systems flow rates are very slow and residence time is probably measured in decades or centuries.

Discussion

Local flow systems dominate in areas of high relief, while regional flow systems dominate in areas of low relief (Toth, 1963; Freeze and Cherry, 1987). Most surface mines are confined to a single hydrologic island. The majority of groundwater flow is probably in the local system, and most of that is probably within the stress-relief/weathered regolith subsystem (Harlow and LeCain, 1991). However, because substantial recharge to regional and intermediate flow systems consists of leakage from shallow (local) flow systems within the hydrologic islands, surface mines can potentially affect the deeper groundwater flow systems. Consideration of groundwater flow at a mine site requires recognition of at least the local and the first underlying groundwater flow systems because they are the most directly impacted by mining. Generally, little information exists for deeper intermediate and regional flow systems. Because a single hydrologic island comprises such a small part of the total recharge area for deeper flow systems, the effects of a single local flow system are probably insignificant to most of these deep systems.

There is little age dating of water on the Plateau. Wunsch (1993) used tritium (^3H) concentrations in nested piezometers on an unmined hill in the Eastern Kentucky coal field to obtain relative dates on the groundwater. Tritium dating is possible because high levels of tritium were introduced into the hydrologic cycle by large-scale atmospheric testing of nuclear weapons from 1953 through the 1960's. Pre-bomb tritium in precipitation was 5 to 20 tritium units (1 tritium unit = 1 tritium atom in 10^{18} H atoms). Post-bomb tritium levels were as high as thousands of tritium units. Tritium has a half-life of 12.3 years, so water with less than 2-4 tritium units is generally older than 1953 (Freeze and Cherry, 1979). The deepest piezometer installed by Wunsch was at the top of a hill and was open at a depth of 416 feet (126.8 m); approximately the same elevation as the adjacent second-order stream valley. The water at this depth, measured in 1991, had < 1 tritium unit. This suggests that this water is minimally decades, and possibly centuries, old. Water in the same nest at a depth of 195 feet (64 m) had a value of 2 tritium units, thus probably at least four decades old. Shallower water (168 feet (51.2 m) or less) in the hill core had values of 13 tritium units or higher, thus was conceivably younger than 1953. This tritium data provides some insight into groundwater ages for at least this area of the Plateau in Kentucky. The 416-foot (126.8-m) piezometer is probably in the intermediate flow system (possibly the deep ridge-core subsystem) and is decades or centuries old. Water in the shallow flow system (down to a depth of 168 feet (51.2 m) in the hill core) is probably several decades old or younger. The US Geological Survey has just begun to date Plateau water using chlorofluorocarbons, however this work has not yet been fully analyzed and has not been published.

Identification of Flow Systems

It is crucial to identify the various flow systems at a mine site. Several types of data will provide clues to delineating groundwater flow systems at a given location. These include physical, hydrochemical, and thermal data, discussed below, and the previously discussed age dating.

Physical data - Some physical data useful in obtaining a first estimate of the flow systems can be obtained from topographic maps. Hydrologic islands can be discerned on topographic maps to determine the approximate extent of the local flow system(s). Deeper flow systems can by estimated based on the location of probable discharge areas (large streams and rivers).

Boundaries between vertically adjacent flow systems (e.g., between the local and the first underlying system) may be determined from piezometer data, if available. The piezometric surfaces for aquifers 2 (in the local flow system) and 3 (in the first underlying flow system) on Figure 2.10 show how there can be abrupt head changes when passing from one flow system into another. Sufficient piezometer data to show flow direction might indicate flow in different directions in adjacent flow systems. Flow directions may diverge by 180° at flow system boundaries.

Discharge and water level fluctuation provides clues to the flow system contributing water to springs and wells. Shallow groundwater flow responds more quickly to precipitation. As a result, spring discharge and well water levels from the stress-relief/weathered regolith subsystem of the local flow system are often quite variable relative to springs and wells from the ridge-core subsystem or from deeper flow systems (Hawkins et al., 1996).

Hydrochemical data - Because of differences in rock mineralogy, residence time, and influence of the brine underlying the composite flow system, the chemistry of groundwater in different flow systems and subsystems varies.

Poth (1963) and Rose and Dresel (1990) identify three stages of "flushing" that roughly correspond with the three levels of the previously outlined flow systems. The deepest zone, directly affected by concentrated brines which exist at depth throughout all areas west of the Allegheny Front, is a NaCl-rich diluted brine zone. This zone is diluted with surface water, that has leaked from shallower flow systems, but retains appreciable amounts of both Na and Cl. This chemical signature is indicative of the more regional flow systems described above.

A shallower system (intermediate zone) exists in which Cl has been removed by flushing with surface waters, but considerable Na remains adsorbed to clays and similar materials, leading to the Na-HCO_3 waters that are commonly found at intermediate depths. The elevated Na is a result of cation exchange, with Na released from the exchange sites in response to replacement by Ca, Mg, and possibly Fe (especially with mine waters). Piper (1933) outlined this process as follows, "...Many of the water-bearing beds - whether they are sandstone, shale, or limestone - contain soft sodium bicarbonate water where they lie at intermediate depths. This soft water is believed by the writer to represent calcium bicarbonate water that has exchanged its calcium and magnesium for sodium by reaction with base-exchange silicates in the rock as it has percolated downward along the dip of the water-bearing bed. The hardness due to the bicarbonate of calcium and magnesium is removed in proportion to the completeness of the exchange reaction, and the water finally passes into the sodium bicarbonate type..."

In the upper-most zone Na is completely flushed leaving a Ca-HCO_3 water typical of shallow groundwater. The shallow flow system is further divided (Brady et al., 1996) into a low dissolved-solids zone associated with the stress-relief/weathered regolith subsystem, and a zone with higher dissolved solids associated with unweathered rock (ridge cores). (This is discussed in greater detail in Chapter 9).

Because stream valleys function as sumps for the discharge of both fresh and saline groundwater, the contact between the fresh and saline groundwater probably "cones up" beneath the streams and lies at successively greater depths away from the streams. Mining activity and practices for controlling water quality or quantity may alter the depth to saline water and the amount of discharge of saline water to the streams (Hobba, 1987).

Wunsch (1993) developed a conceptual "hydrochemical-facies" model (Figure 2.17) for an unmined ridge based on site-specific data from eastern Kentucky. According to Wunsch (1993, p. 72), ..."The model shows four zones where the major cations and anions comprising the water type for a particular water sample could be predicted with a high degree of probability. The model shows a depressed salt-water interface below the ridge due to downward movement and accumulation of fresh water. The hydrostatic pressure imparted on the salt water is transmitted in the salt-water zone, causing it to rise at locations where fractures breech confining layers (valley bottoms)..."

Data collected at numerous mining sites in southwestern Pennsylvania (including the 580 Pocket site which is incorporated as Case Study No. 1 at the end of this chapter) support Wunsch's hydrochemical model for shallow groundwater flow on the dissected Appalachian Plateau of Pennsylvania.

Thermal Data - Groundwater temperature, relative to annual mean air temperature, and annual fluctuations of groundwater temperature can provide clues to help delineate the flow systems. Groundwater flow

serves to redistribute terrestrial heat. "In the upper 10 m or so, diurnal and seasonal variations in air temperature create a zone that is thermally transient."(Freeze and Cherry, 1987). Within the local flow system and especially within the stress-relief/weathered regolith subsystem, there is usually an annual groundwater temperature fluctuation of up to 10° C. The mean annual groundwater temperature within shallow groundwater (at the base of the zone of groundwater temperature fluctuation) is generally 1° to 2° C higher than the mean annual air temperature at that site (Heath, 1989). Beneath the zone of groundwater temperature fluctuation, the temperature increases with depth at a rate dependent on the geothermal gradient. Van Orstrand (1918), working in Washington County, PA, measured groundwater temperatures at a gas well site to a depth of 7000 feet (2296.6 m). Between depths of 100 to 2000 feet (32.8 to 656.2 m) he found temperature increasing at a rate of 1°F for each 110 feet (36 m) of depth). According to Piper (1933), the average groundwater temperatures observed in wells in southwestern Pennsylvania were; for wells less than 100 feet (32.8 m), 51.8°F: for wells between 100-200 feet (32.8-65.6 m), 52.1°F; and for wells between 200-450 feet (65.6-147.6 m), 52.5°F.

Discussion - The above data types will often be helpful in determining whether a particular groundwater sample is from the stress-relief/weathered regolith subsystem, the ridge-core subsystem, or from a deeper flow system. Generally, the shallowest flow will be low in dissolved solids, variable in flow and temperature, and discharge along the flank of a hydrologic island. Springs in intermediate and regional discharge areas may show characteristics of local groundwater flow (B and C on Figure 2.16), such as the example in Table 2.1 for a proposed mine in the Yellow Creek valley in Indiana County. Springs SG-10 and SG-15 are higher in pH, specific conductance, and alkalinity than other springs, and are similar in those parameters to water from nearby wells. These springs probably produce water from an intermediate flow system discharging into the Yellow Creek valley. Other springs produce water that originated as recharge on the adjacent uplands, and are discharges of the local flow system. (Another example of springs representing both local and intermediate flow systems is discussed in Chapter 9.)

Table 2.1

sample pt.	Median pH	Mean Specific Conduct.	Mean alk.(mg/l)
springs 10 and 15	7.59	428	105
wells	7.56	595	170
other springs	6.5	144	9

Case Studies

Case Study No. 1 - 580 Pocket Mine

This underground coal mine complex is located in Greene and Susquehanna Townships, Indiana County, PA. The mine is located on the Appalachian Plateau in an area of broad, rolling uplands that is drained by incised, dendritic stream valleys typically 200 to 500 feet

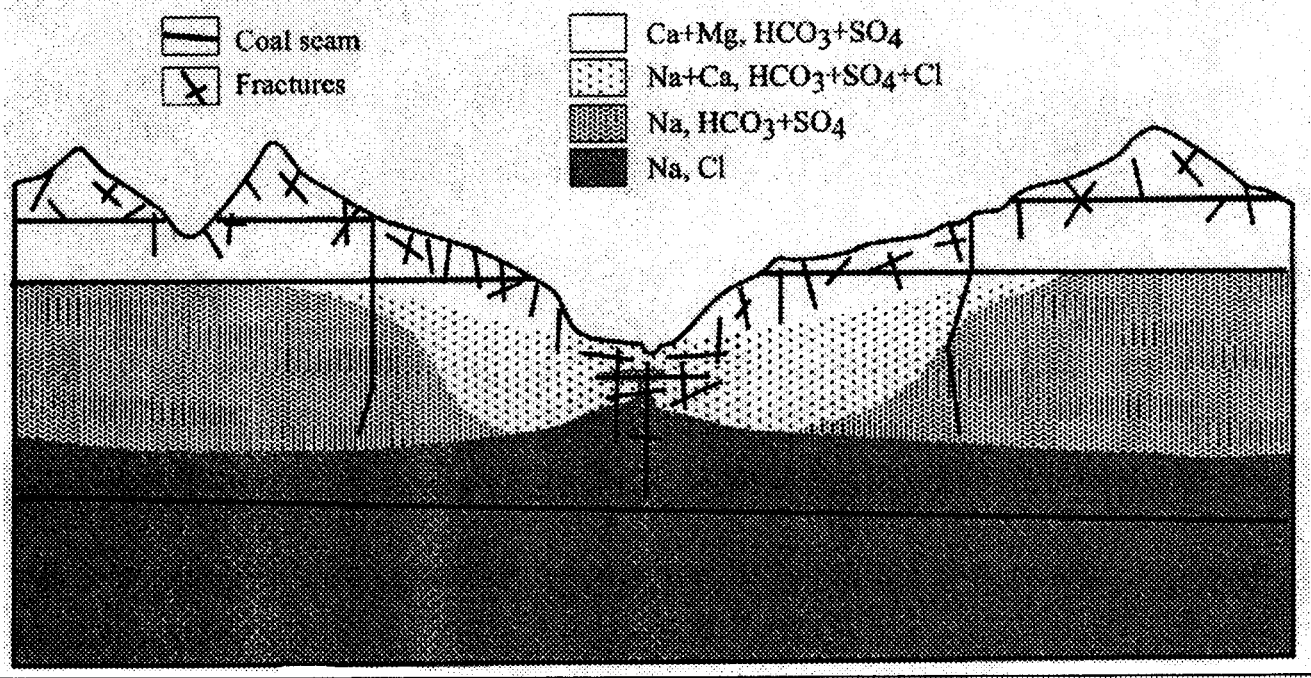


Figure 2.17 Conceptural model of hydrochemical facies (Wunsch, 1995).

(60 to 150 m) deep. The geologic structure is essentially flat-lying sedimentary rocks which have been folded such that the folds generally dip at two to six percent to the west toward the Brush Valley syncline. Rock types consist of shale, sandstone, siltstone, claystone, limestone, coal, and underclay. The overburden sequence includes the upper portion of the Freeport Formation (Allegheny Group) and the lower two-thirds of the Glenshaw Formation (Conemaugh Group) (see Figure 2.18).

The 580 Pocket is part of a large underground mine complex consisting of the approximately 3500-acre (1420-hectare) North Mine and the approximately 4550-acre (1840-hectare) South Mine which includes the 580 Pocket (see Figure 2.19). The North and South Mines are physically separated by a 250-foot (76-meter) wide unmined zone. The mine complex, particularly the South Mine and 580 Pocket, has been studied and evaluated over the past decade due to mining-induced dewatering episodes at domestic wells and superjacent streams. Additional mining related problems developed after the cessation of mining in 1992 when the pumps were turned off and the mine began to flood.

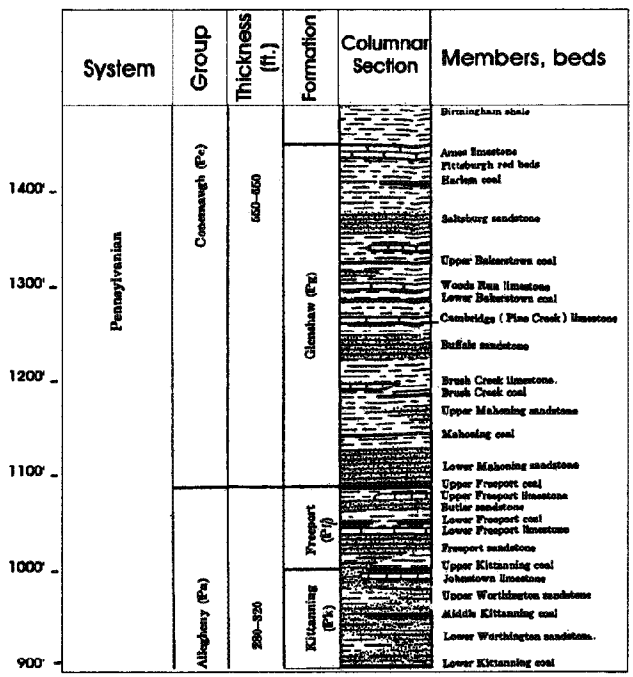


Figure 2.18 Generalized geologic column, 580 Pocket area.

The mine pool eventually emerged as seeps in the valleys above and adjacent to the 580 Pocket section of the South Mine.

Mining of the complex began in the Lower Freeport seam in 1969 and progressed down dip toward the Brush Valley synclinal axis (see Figure 2.19). Longwall, room and pillar, and room and pillar with retreat mining were all conducted within the complex. Typical cover ranged between 250 and 450 feet (76 to 137 m). Mining height was typically four to six feet (1.22 to 1.83 m).

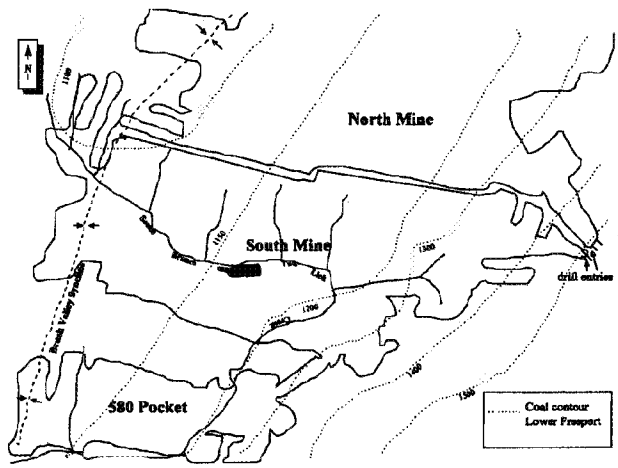


Figure 2.19 Map showing relative positions of sections of Greenwich mine complex.

Mining in the South Mine started at a drift opening (see Figure 2.19). Inconsistent seam thickness caused the mining company to leave a section south of the South Mine unmined. However, mineable coal was present farther to the south and a series of entries was driven through the low coal zone to access the 580 Pocket.

Due to the stream dewatering problems which accompanied the mining (1985 through 1994) and the subsequent postmining pool breakout in 1994, the South Mine has been and remains one of the most scrutinized and best instrumented underground mine sites in Pennsylvania. More than 50 piezometer points (many including continuous recorders) have been developed over the past decade at the site. Extensive surface and groundwater quality sampling has been conducted by various consultants and by Pennsylvania DEP staff. Additional site work has included: geophysical logging, bedrock coring, aquatic surveys, slug tests, pumping tests, whole-rock geochemical testing, and petrographic analysis.

Site Characteristics - Beginning in 1985, reports of stream diminution were being received by the Pennsylvania Fish Commission for sections of the South Branch of Two Lick Creek above the South Mine workings. High extraction mining, including a series of longwall panels, was conducted throughout the South Branch of Two Lick Creek basin during the 1980's and early 1990's. Dewatering episodes in the upper portions of the stream precipitated a number of hydrologic studies which were conducted within the basin beginning in 1988. Weirs and piezometer nests were installed in 1988 within the 580 Pocket area to characterize stream and groundwater flow and assess mining impacts. Impacts from mining in terms of groundwater level declines and stream base flow reductions were documented. Subsequent approvals for additional mining within the 580 Pocket section of the South Mine were conditioned to limit mining below and adjacent to the South Branch of Two Lick Creek and Repine Run watersheds. Mining was restricted to "first mining only", an extraction rate of approximately 55%, beneath stream valleys. This was an attempt to protect the perennial nature of the South Branch's lower sections and reduce impacts to Repine Run by minimizing the likelihood of subsidence fractures which may capture stream flow. This limited mining continued within the 580 Pocket until March of 1992 when mining ceased in the South Mine and the workings began to flood.

During 1992 and 1993, as the mine flooded and groundwater levels recovered, an ongoing hydrogeologic evaluation was conducted to document conditions during mine closure. The evaluation included stream gauging, mine pool level monitoring, and water quality sampling. Due to the dewatering which accompanied the mining there were concerns regarding development of postmining seeps along the impacted stream valleys below the final pool elevation. In February of 1994, contemporaneous with the mine pool potential reaching the stream bottom elevation, mine pool breakouts occurred to the South Branch of Two Lick Creek and Repine Run at several locations near their confluence. The seeps bore the standard high sulfate, high specific conductance signature of mine water. Additionally the seeps exhibited a high sodium signature which is often indicative of the intermediate flow system on the Plateau where considerable sodium remains adsorbed to clays due to cation exchange as outlined earlier in this chapter. This sodium signature is therefore an indicator of water from a deeper part of the flow regime as opposed to the usual Ca-HCO_3 signature water which is common for the shallow flow system. The mine pool also exhibited this sodium marker.

Immediately following the discovery of the seeps a more comprehensive hydrogeologic site characterization was conducted. Eight additional piezometer nests were installed, rock coring from the surface to the Lower Freeport seam was conducted, and geophysical logging was performed at all drill sites. Chemical sampling of the mine pool and the surface seeps was initiated and included major anions and cations. Adjacent mine discharges were inventoried and sampled. Weirs were constructed at seeps with measurable flows. Additional aquatic surveys were conducted to evaluate the impacts of the discharges on the aquatic community and related stream uses. Additional testing included slug tests, pumping tests, and petrographic analysis.

Figure 2.20 (located in the pocket at the rear of this book) is a flow net depicting conditions at the down-structure end of the mine. The flow net is based on measured piezometric head values (after mine pool stabilization) at the site. This flow net is a semi-qualitative, conceptual model of groundwater flow at the site. The ridges between the valleys act as groundwater recharge areas. Water entering the ridge tops discharges locally to nearby streams, exits at contact springs, or continues downward to recharge deeper portions of the flow system. As can be seen, the arrangement of equipotential and flow lines has been predictably altered at depth due to the presence of the mine-void aquifer. The mine-void aquifer is highly transmissive and has essentially uniform head across the mined area. This is an important factor since areas within and adjacent to the down-structure portions of the mine workings will realize abnormally high post-mining heads relative to their premining head potentials. Where the mine void meets virgin coal, the head will reestablish the necessary gradient to drive water down structure through the intact coal aquifer. However, in stream valleys at the margins of the mine workings a large reservoir of mine water exists with head potential exceeding the surface elevation.

As pointed out previously in this chapter, stream valleys are typically locations containing a disproportionate number of secondary permeability features. This combination of conditions (head potential at depth exceeding the surface elevation; a large reservoir of highly ionized mine water; and fractured, transmissive overburden within the valley settings along the margins

of the mine workings) resulted in the postmining mine pool discharges to the South Branch of Two Lick Creek and Repine Run.

When considered against the backdrop of the previously outlined conceptual groundwater flow model for the northern Appalachian Plateau, the mine water emerged at the most logical location. The following is a listing of site-specific data and findings and their relationship to significant, ubiquitous features of the conceptual groundwater flow model outlined previously in this chapter. Information gathered during the hydrogeologic studies conducted at the 580 Pocket mine site is in accord with, and reinforces, the established groundwater flow model for the Appalachian Plateau of Pennsylvania.

Shallow flow system

Weathered surface zone - Data collected during the 580 Pocket site characterization confirmed the presence of a shallow, weathered, highly tranmissive zone devoid of significant, readily leachable or oxidizable minerals. Representative water quality data from shallow piezometers (in zones not affected by upwelling mine water) and from hillside springs are compiled in Table 2.2.

Water data (Table 2.2) are consistent with what would be expected within the shallow flow zone along the rind of the hill.

Site drill logs typically show weathered, fractured, and broken material down to a depth of about 15 meters (40-50 feet). This shallow zone routinely bottoms out at about 18-20 meters (55-65 feet) as documented by extensive on-site drilling.

Stress-relief fractures - At the 580 Pocket site the postmining seepage was valley associated. The valleys above and adjacent to the mine workings served as natural pressure release zones where the mine pool could migrate to the surface along valley-related fracture sets (valley stress-relief fractures and zones of fracture concentration). In addition to valleys being proximal to the discharges, other evidence indicates the presence of valley stress-relief fractures and valley-related fracture sets at this site, including: (1) valley corings showing a consistent fracture profile; (2) piezometer pumping tests demonstrating vertical communication; (3) mining-associated dewatering events indicating direct hydrologic communication between the shallow flow system and the mine; (4) the similar groundwater chemical signature throughout the vertical section between the mine level and the stream valley floor; (5) fracture trace analyses indicating that certain straight stream segments are fracture related; and (6) on-site research which found that fracture densities and orientations were statistically relevant factors to consider when evaluating conditions contributory to unstable mine roof. Each piece of evidence is addressed below:

(1) rock corings from valleys:

Broken and fractured rock is indicated in core logs to a depth of 150-200 feet (46-61 m) in valley settings at the 580 Pocket site. Core 95-08 included a rock quality designation (RQD) run contemporaneous with drilling. The RQD data indicate a steady progression from poor to excellent quality rock at a depth of approximately 140 feet (42 m). The RQD data for Core 95-06 shows a similar pattern - i.e., rock quality improving with depth to approximately 190 feet (52 m). RQD is based on the ratio of recovered core length to the total length of the core run, or to a defined section of the core. Only recovered core pieces four inches or longer are counted. In consolidated rock, it can be a good indicator of the degree of fracturing within the rock mass. A high RQD points to infrequent fracturing and a low RQD points to more frequent fracturing of the rock mass.

(2) pumping exercises at piezometer clusters:

A five-day pumping test was conducted at piezometer cluster 95-04 in late September-early October, 1995 as part of the site evaluation. The 95-04 piezometer cluster is open to six different horizons. These monitoring zones are spaced over the 266-foot (81.08-meter) distance between the mine level and the surface (see Figure 2.21). The 198-foot (60.35-meter) piezometer was pumped while monitoring was conducted (with pressure transducers) at the other five intervals. All monitored intervals showed water level declines and recoveries concurrent with the pumping event.

A similar pumping test was conducted on piezometer 95-07. Figure 2.22 shows reactions within the vertically segregated monitoring zones of piezometer cluster 95-07.

(3) dewatering events during mining:

As pointed out earlier in this chapter, dewatering of surface streams above the Greenwich mine workings was occurring for approximately seven years (1985 to 1992) prior to mine closure. A study conducted in 1988 and 1989 by a Greenwich Collieries consulting hydrogeologist documented mining-induced dewatering

Table 2.2 Typical shallow (weathered) zone groundwater chemistry (mg/L)

sam. pt	depth	date	alk.	SO_4	Ca	Mg	Na	sp.cond. (umhos/cm)
piez. 9506	35 ft.	10/5/95	38	36	38	7	13	88
"	"	10/24/95	12	21	4	1	6	62
"	"	12/13/95	12	19	5	2	4	62
"	"	2/27/96	6	45	6	2	4	72
DM-3	spring	3/6/96	12	11	----	----	3	136
TS-8	spring	3/6/96	7	17	----	----	2	62
TS-7	spring	3/6/96	2	20	----	----	2	56
TS-6	spring	3/6/96	2	19	----	----	2	58
TS-5	spring	3/6/96	5	17	----	----	2	61
TS-4	spring	3/6/96	4	19	----	----	2	60
ST-101	spring	3/6/96	2	17	----	----	2	54
ST-102	spring	3/6/96	2	15	----	----	2	50
RPD3/6-1	spring	3/6/96	5	14	----	----	3	52
ST-123	spring	3/13/96	9	24	----	----	2	74
RPD3/6-2	spring	3/6/96	12	15	----	----	2	75
RPD3/6-3	spring	3/6/96	11	16	----	----	2	86
RPD3/6-4	spring	3/6/96	7	14	----	----	3	84
RPD3/6-5	spring	3/6/96	2	14	----	----	2	58
RPD3/6-6	spring	3/6/96	2	18	----	----	2	62
RPD3/6-7	spring	3/6/96	2	19	----	----	2	65
RPD3/6-8	spring	3/6/96	2	19	----	----	3	63
RPD3/6-9	spring	3/6/96	2	17	----	----	2	64

in the form of reduced base flow to Repine Run. The study relied on stream flow measurements upstream and downstream of mining, groundwater level monitoring, and groundwater and surface water "control" points outside the influence of the mining to define baseline conditions.

(4) groundwater chemical signatures:

95-07 is the only piezometer cluster located along the center line of a valley. The piezometers within the 95-07 cluster are spaced at depths of 37 feet (11.28 m), 59 feet (17.98 m), 104 feet (31.7 m), 153 feet (46.63 m), 190 feet (57.91 m), and 235 feet (71.63 m)(coal seam). Chemical data are listed in Table 2.3. The piezometers are located in a groundwater discharge zone. The water chemistry has a similar signature along the entire vertical extent of the cluster.

(5) fracture trace analysis:

A consultant for the mine operator performed a fracture trace analysis based on air photograph interpretation. Several stream valley segments line up with the mapped fracture traces. They include: (1) portions of the South Branch of Two Lick Creek above the confluence with Repine Run; (2) Rock Run; and (3) several unnamed tributaries to South Branch of Two Lick Creek. A significant shortcoming of this mapping exercise is the lack of any ensuing field verification.

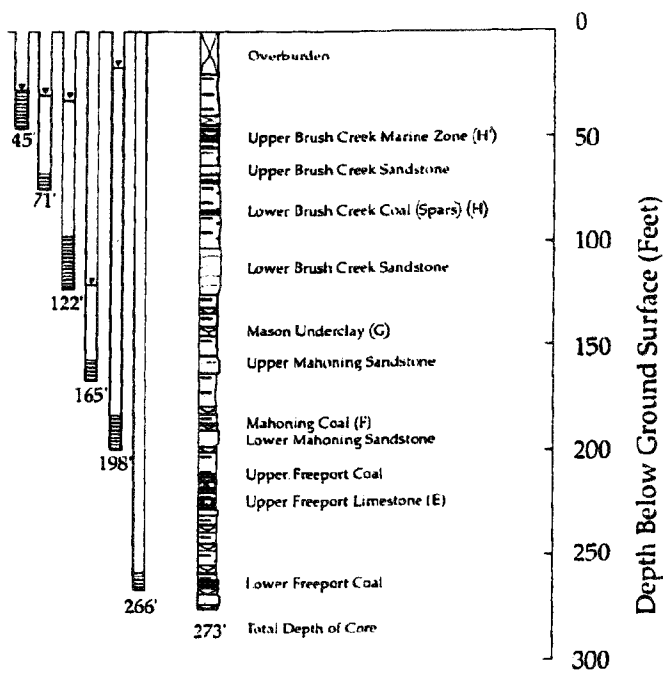


Figure 2.21 Piezometer 95-04 schematic

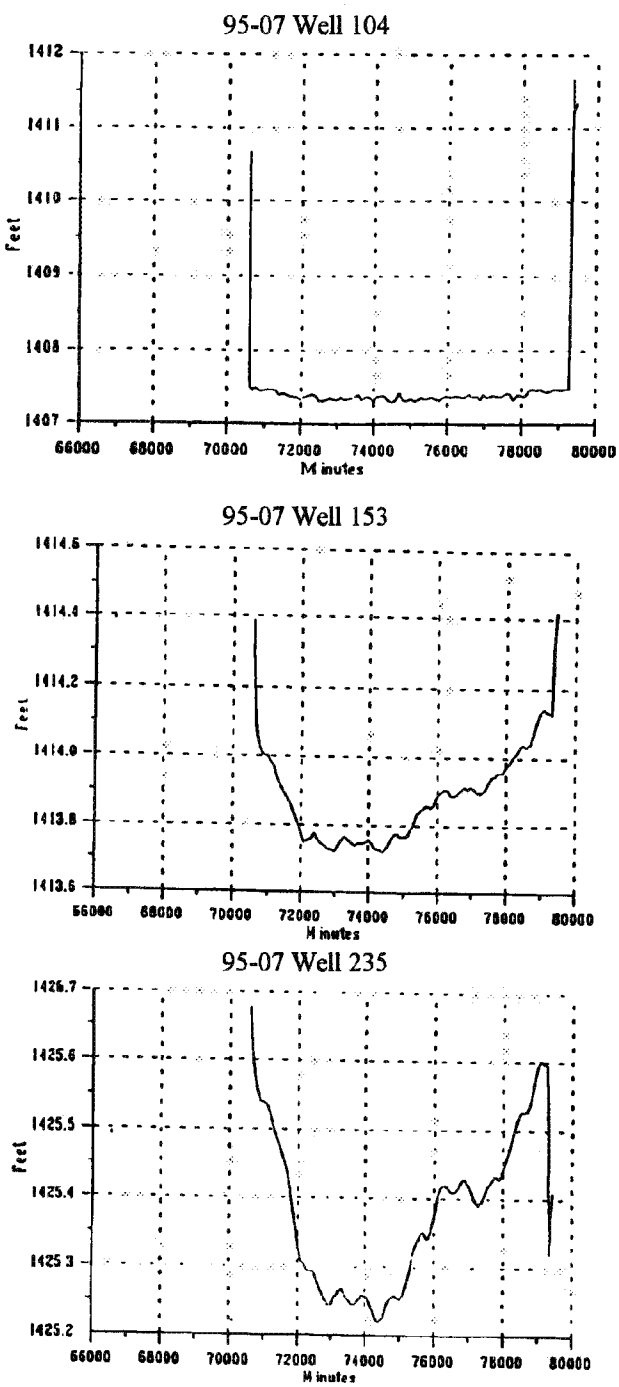


Figure 2.22 Groundwater responses at 95-07 piezometer cluster during pumping interval (pumping rate, 11 gpm)

(6) mine roof stability research:

Research conducted at the Greenwich mine in 1987 (Blackmer, 1987), with the goal of developing valid parameters for a Roof Stability Index (used to predict general mine roof stability), focused on "controls" which are significant when assessing mine roof stability. The four statistically relevant controls were geologic structure, fracture trace orientation, fracture trace density, and density of clay veins. This work points out the significance of naturally occurring fracture sets at mine depth.

Table 2.3 Water chemistry for piezometer cluster 95-07 (mg/L)

piez.	date	alk	spec. con. (umhos/cm)	Na	Ca	Mg	SO_4
37 ft.	2/22/96	504	1550	252	137	18	471
59 ft.	10/25/95	601	2050	570	63	13	561
59 ft.	2/22/96	560	1700	370	95	14	459
104 ft.	2/22/96	607	2000	420	76	15	564
153 ft.	10/10/95	616	2100	625	56	14	646
153 ft.	10/25/95	610	2050	660	35	8	550
153 ft.	2/22/96	611	2050	470	51	10	575
190 ft.	2/22/96	560	1800	420	46	11	453
235 ft.	10/25/95	23	1220	370	3	0.3	440
235 ft.	2/22/96	142	1240	250	2	0.1	450

Ridge cores - Groundwater samples pulled from piezometers located in ridge cores between stream valleys show a markedly different chemical signature than nearby spring data and data from shallow, weathered-zone piezometers. Table 2.4 lists the typical chemistry for the ridge cores at the Greenwich Mine. These points are located above the final mine pool level or in recharge areas with a strong downward flow component precluding the upward migration of mine water. The water is a Ca-HCO_3 type with low sulfate concentrations and low sodium concentrations.

Intermediate Flow System - Some difficulty in delineating the intermediate flow system at the 580 Pocket site occurs because of chemical and hydrologic influences from the deep mine complex. Even the sodium signature, which is an indicator of intermediate zone chemistry, can be influenced indirectly by the mining. For example, iron in the mine water may bump sodium ions from their exchange sites thus further elevating sodium levels. Additionally, the characteristic flow patterns of an intermediate flow regime, e.g., bypassing of local discharge points, can be mimicked by the insertion of a highly transmissive mine-void aquifer at depth. No piezometers were developed below the Lower Freeport coal horizon. Therefore comparisons cannot be made between the mine pool chemistry and deeper groundwater. Another limiting factor is the that chemical data prior to mining and flooding did not include analyses for major anions and cations (e.g., Na).

Table 2.4 Ridge core groundwater chemistry (mg/L)

piez.	depth	date	Alk.	spec. cond. (umhos/cm)	SO_4	Ca	Mg	Na
95-03	88 ft.	8/21/95	146	435	55	70	12	----
95-03	88 ft.	9/13/95	160	470	46	69	11	17
95-03	88 ft.	10/13/95	150	470	46	70		14
95-03	88 ft.	10/23/95	155	450	88	69	10	13
95-03	88 ft.	12/13/95	80	350	60	41	10	7
95-03	88 ft.	2/28/96	90	300	39	40	9	2
95-01*	181 ft.		134-199		41-75		-----	-----

* Data for piezometer 95-01 is presented as a range of values

Regardless of mine influences, the presence of sodium at mine depth indicates this zone is in the intermediate system. Table 2.5 lists representative mine pool and piezometer samples of this deeper, intermediate system. In addition to high concentrations of Na, SO_4 is also elevated. The SO_4 results from pyrite oxidation which occurred as a consequence of mining.

580 Pocket Site Versus Conceptual Model - The 580 Pocket site-characterization studies are consistent with the outlined conceptual flow model of the Appalachian Plateau. One important aspect of fracture flow is that the significance of any given fracture is scale dependent (major fractures on one scale can become minor fractures on another scale). Therefore, even for areas where fracture flow is dominant, sites can be modeled based on continuum assumptions if the fractures are relatively consistently spaced, are routinely interconnected, and the scale of the study area is large enough to treat as porous media. The fracture controlled nature of the groundwater flow system at the 580 Pocket site appears to manifest itself in the direct connection between the mine and the stream bottom and in the discrete, point source character of the seeps. Regardless of the controls on the flow system (secondary permeability features or intergranular flow), the seeps would have in all probability manifested themselves in the same location. The overriding controls on the occurrence and location of the seeps are: (1) the introduction of an highly transmissive, man-made aquifer at a relatively shallow depth; and (2) the related permeability contrast between the man-made aquifer and the adjacent rock mass which controls the mine pool elevation.

Table 2.5 Intermediate zone groundwater chemistry (mg/L)

samp. pt.	Depth	date	spec. conductance (umhos/cm)	alkalinity	sulfate	sodium	calcium
T-8 BH	mine pool	9/12/95	2200	639	670	530	58
T-8 BH	mine pool	10/2/95	2300	614	646	535	82
T-8 BH	mine pool	10/23/95	2250	640	713	635	39
T-8 BH	mine pool	12/12/95	2100	640	574	490	46
580 shaft	mine pool	2/21/96	2300	550	833	360	202
580 shaft	mine pool	2/22/96	2200	540	1000	430	176
95-08	212 ft.	11/21/95	2000	609	583	-----	49
95-08	212 ft.	12/13/95	2100	625	574	485	64
95-08	212 ft.	2/15/96	2050	610	559	520	72
95-06	272 ft.	10/5/95	3500	861	286	191	207
95-06	272 ft.	10/25/95	2950	685	130	288	4
95-06	272 ft.	12/13/95	1300	435	119	265	2
95-06	272 ft.	2/27/96	1260	450	108	280	3
95-07	235 ft.	10/25/95	1220	23	440	370	2.5
95-07	235 ft.	2/22/96	1240	142	449	250	2.1
95-04	266 ft.	9/12/95	4500	8	2850	945	246
95-04	266 ft.	10/13/95	4000	78	2215	840	234
95-04	266 ft.	10/24/95	3400	90	2040	840	191
95-04	266 ft.	12/13/95	3000	75	1630	520	158
95-04	266 ft.	2/27/96	3100	180	1705	690	183
95-03	374 ft.	8/21/95	1380	640	645	-------	28
95-03	374 ft.	9/13/95	2350	652	615	665	27
95-03	374 ft.	10/12/95	2300	619	590	600	31
95-03	374 ft.	10/23/95	2300	617	648	745	32
95-03	374 ft.	12/13/95	2300	625	583	550	26
95-03	374 ft.	2/28/96	2000	690	538	500	24

Case Study No. 2 - Kauffman Mine

The Kauffman mine is a bituminous surface mine located in Boggs Township, Clearfield County, Pennsylvania. The topographic setting is fairly typical of the bituminous coal mining region of Pennsylvania's Appalachian Plateau - i.e., broad uplands dissected by deeply incised tributaries. The permit is bounded by a major state highway to the east (SR0153), Clearfield Creek to the west, and two northwest-flowing tributaries to Clearfield Creek, Camp Hope Run to the north and Sanbourn Run to the south. The topographic relief ranges from about 200 feet (60 m) near the headwaters of these tributaries to more than 525 feet (160 m) where the western hillside drops off to the level of Clearfield Creek. The soils of the hilltops are thin and sandy, reflecting the abundance of sandstone within the coal overburden. A cover of colluvial material blankets the relatively steep hillsides and clay-rich alluvium fills the valley bottoms adjacent to the streams (see Figure 2.23).

At the time this volume was written the Kauffman mine was being mined as a "demonstration" surface

mining permit. That is, the operator plans to demonstrate, by special handling high sulfur spoil and importing alkaline material, that they can mine this site without creating AMD. It should be noted that past mining at an adjacent mine (Thompson mine) on the same coal seam, just east of State Route 0153, resulted in severe AMD pollution to the surface water and groundwater. The Thompson mine has impacted both Sanbourn Run and Camp Hope Run to the extent that aquatic life is no longer present. Additionally, a pollutive groundwater plume of considerable lateral and vertical extent has migrated westward from the Thompson mine to beneath the eastern portion of the Kauffman permit. The complexities of this demonstration mining project, with respect to the site's geology, hydrogeology, and influences of past mining, necessitated the collection and study of a large volume of data. Many researchers, consultants, students, and other investigators have examined the site. Some of the published literature related to the Kauffman site includes Abate (1993), Evans (1994), Rose et al. (1995), Hawkins et al. (1996), and Brady et al. (1996).

The Kauffman permit stands apart from most surface mining permits in Pennsylvania by the abundance of geologic and hydrogeologic data that have been collected. During the application review period for this project, Hamilton and their consultants constructed 44 individual piezometers, drilled and analyzed the rock samples from 13 air rotary drill holes and six continuous core holes, and collected hundreds of samples from springs, ponds, streams, mine discharges, and others monitoring points. From this data researchers have arrived at a fairly good understanding of the local and intermediate flow systems that underlie the Kauffman permit (the regional flow system was not encountered). Nevertheless, there are still some anomalous data that have not been explained, so there is more to be learned from this site.

Geology

Stratigraphy - The geologic strata encountered during data collection for the Kauffman surface mine permit range from the middle of the Kittanning formation (hilltops) to the Mercer coal group (bottom of the deepest piezometers). Figure 2.24 is a generalized stratigraphic section of the Lower Kittanning coal to the Lower Mercer coal. The coal seam targeted for mining is the Lower Kittanning no. 3 seam, which serves as our reference horizon. The underlying Lower Kittanning no. 2 seam, separated from the Lower Kittanning no. 3 coal by a carbonaceous shale binder, is not of mineable quality (although it had been extracted over most of Phase I of the Kauffman permit). Above the Lower Kittanning no. 3 seam, the strata are commonly dark shales or siltstones which coarsen upward to the base of the Worthington sandstone. The Lower Kittanning no. 4 seam is not present on this site. However, at or near its stratigraphic horizon, approximately 10 feet (3 m) above the Lower Kittanning no. 3 seam, is a *Lingula*-bearing, dark gray to black shale of relatively high sulfur content. The Lower Kittanning no. 5 coal is referred to as the Lower Kittanning rider in the Kauffman permit file. Where present, it is a thin seam about 15 to 25 feet (4.5-7.5 m) above the Lower Kittanning no. 3 coal, near the base of the Worthington channel sandstone. The Worthington sandstone caps most of the high ground on the Kauffman permit. In places, this channel sandstone has encroached upon the Lower Kittanning no. 3 coal seam and replaced the coal in some areas. In the central and western portion of the Kauffman mine, the base of the Worthington sandstone may contain carbonate cements, calcite coatings on open fractures, and calcite fillings in "healed" fractures. The presence of this calcite has imparted some natural alkalinity to the deeper groundwater within the core of the hill.

Below the Lower Kittanning no. 2 coal are the Clarion no. 3, no. 2, and no. 1 coals in descending stratigraphic order. The Lower Kittanning no. 1 coal seam is sometimes present about 10 feet (3 m) beneath the Lower Kittanning no. 2, but that seam does not commonly occur on the Kauffman property. Between the Lower Kittanning no. 2 seam and the Clarion no. 3 seam, there lies a fairly persistent sandstone body of 5 feet (1.5 m) to more than 30 feet (9 m) in thickness. This stratum is designated the Kittanning sandstone and serves as a target aquifer for some of the piezometers. It appears that much of the strata among the Clarion coal seams are made up of shales, but much of the drilling below the Clarion no. 2 encountered so much water that identification of air rotary rock chips proved very difficult. Below the Clarion no. 1 seam and just above the Upper Mercer coal is the Homewood sandstone. The top of the Homewood sandstone served as the deepest aquifer encountered during piezometer construction.

Structure - Strata at the Kauffman site have an average dip of one to two degrees to the west-northwest. Stratigraphic and structural variations have imparted

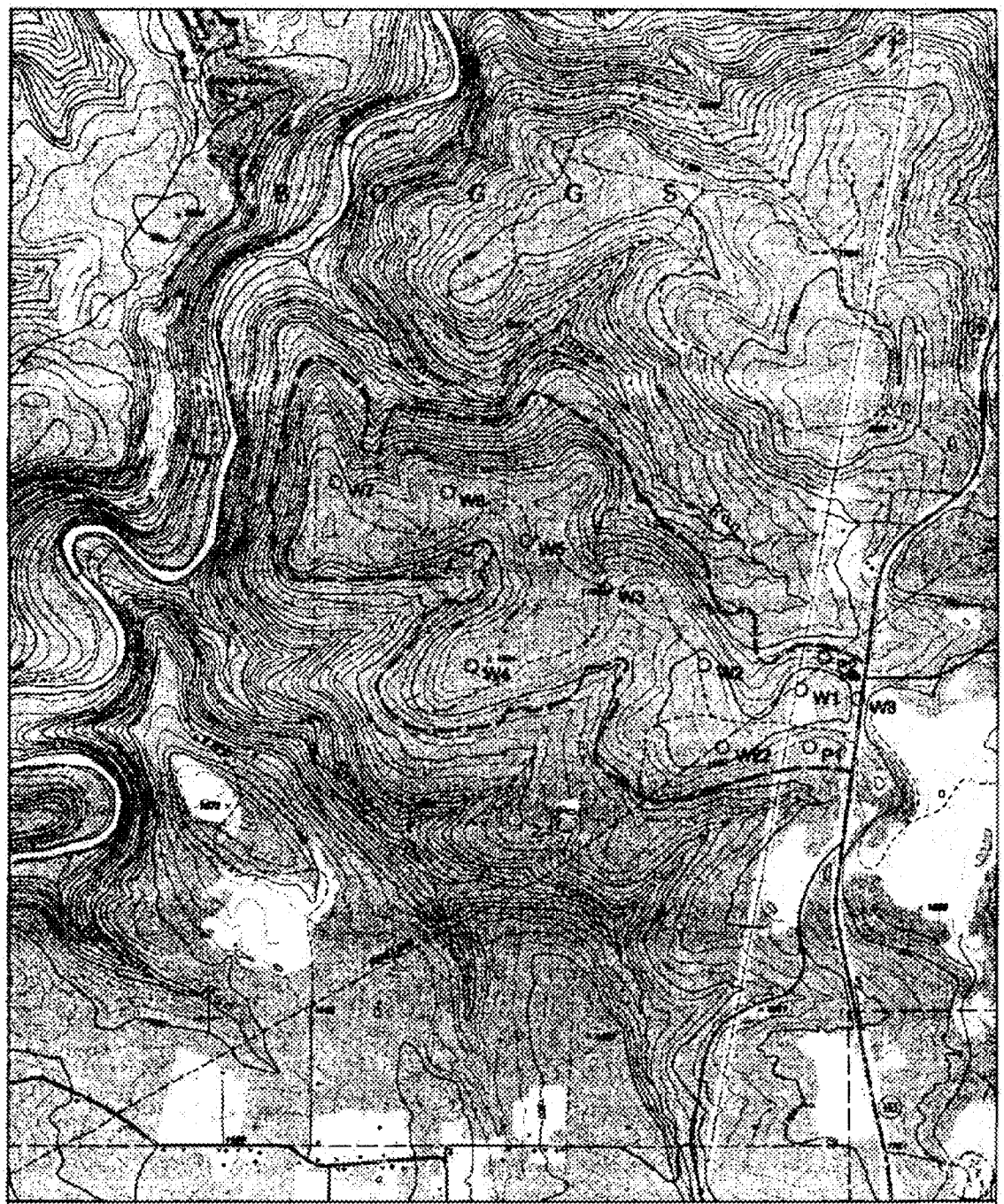


Figure 2.23 Kauffman site map.

some minor rolls to the coal surface, so dip directions and inclinations deviate slightly. In places the dip is very slight, less than one degree. In other areas, the dip exceeds eight degrees. According to Edmunds (1968), a major tear fault exists on the Thompson permit area just east of State Route 0153. However, its existence is only inferred on the Kauffman site. This fault strikes northwest-southeast and accounts for a stratigraphic offset of more than 295 feet (90 m) near the headwaters of Coal Run (about four and one half kilometers southeast of the Kauffman permit). In the eastern portion of the Kauffman permit, Edmunds (1968) infers that the fault could offset the strata by about 40 feet (12 m). However, pit-floor surveys on

Phase I of the Kauffman permit did not reveal displacement of the Lower Kittanning coal seam. Bedding-plane faults, however, do occur on the Kauffman site. These are evidenced by deformed bedding. The faulting east of the site may have dissipated at the Kauffman site as bedding-plane faults.

Jointing - Nickelsen and Williams (1955) indicate that the systematic joints in rock above the coal seams strike between N30°W and N45°W in the Houtzdale-Philipsburg area and that nonsystematic joints strike between N45°E and N60°E. These directions correspond to the general trend of drainage in the area of the Kauffman mine. Site specific studies at the Kauffman permit have not been done to confirm these joint orientations.

Hawkins et al. (1996) refers to the importance of stress-relief fractures. His discussion of Appalachian Plateau shallow groundwater flow is based to a large extent on observations at the Kauffman site. Bedding-plane or horizontal fractures are supposedly more common to the valley bottoms where rocks are under horizontal compressional stresses. However, Hawkins observed that horizontal fractures on the uplands of the Kauffman site were very common as well. Unlike tectonic joints, stress-relief fractures are associated with the surface and decrease in frequency with depth. Beyond the realm of the stress-relief fractures, the fracture frequency drops off considerably and groundwater movement is much more impeded.

Hydrogeology

Groundwater monitoring - Over 40 piezometers were constructed on the proposed Kauffman mine site as part of the mining company's application for a surface mining permit. Additionally, the operator drilled open boreholes to determine hydrogeologic properties of individual strata overlying the coal to be mined. Many piezometers were developed in clusters in which the individual wells were drilled about 6.5 to 13 feet (2 to 4 m) apart. There were nine main piezometer clusters of three, four, and five piezometers each. These piezometer clusters were identified as W1 through W8, and W22. Other piezometer locations included P1 and P2 for examining the pollutive groundwater plume on the flanks of the hill in the eastern Kauffman permit area, and SW1, SW2, and SW3 for monitoring shallow groundwater at certain permit locations.

Piezometers were constructed using four-inch (11.4-cm), thread-flush, Schedule 40 PVC pipe. Only the "AS" wells (this letter identification of piezometers is explained in the following paragraph) were constructed from one-inch (2.8-cm) pipe. All piezometers were installed with a 5.5-foot (1.7-m) section of slotted pipe (screen) at the base, except for the "C" wells which had an 11-foot (3.4-m) section of screen. The construction method was to backfill the annular region around the screen with sand to the top of the screen. The height of the sand pack for the "E" wells varied and sometimes extended above the screen by as much as 10.5 feet (3.3 m). Above the sand pack, rounded bentonite pellets were poured into the annular spacing to a pre-swell height of about 5.5 feet (1.7 m). The depth to the top of these construction layers was constantly checked with a weight and steel tape. The rounded bentonite pellets were used because they were less likely to bridge between the side of the borehole and piezometer pipe when the hole was wet or flooded. After the rounded pellets were poured in, the rest of the hole was completely filled with bentonite chips (Volplug®). No drill cuttings or dirt was pushed in. This further reduced the chance of an artificial connection developing between aquifers via the annular space. A steel cover, set in concrete, was then placed at the surface to protect the plastic casing. This cover is kept locked until the sampler needs to access the piezometer.

Each piezometer within a well cluster was identified by a letter indicating the target horizon being tested. Figure 2.24 shows the generalized stratigraphic section and the corresponding piezometer target zones. Piezometers designated as "A" wells were constructed so as to monitor the Lower Kittanning no. 2 and no. 3 coal seam aquifer. At this sampling horizon, a 5-foot (1.5-m) screen was installed to monitor the groundwater pressures. Inside the boreholes used to construct the A wells, the operator installed an "AS" level piezometer of smaller diameter down to the base of the Worthington sandstone. The level of the AS screen with respect to the "A" piezometer screen varied as the depth of the Worthington sandstone varied. Next, the "B" wells were installed and were usually open (5-foot (1.5-m) screen) to the Clarion no. 2 coal horizon. One exception was piezometer W1B, which was finished to the shallower Clarion no. 3 horizon. The "C" wells were open (10-foot (3-m) screen) between 9 and 15 meters below the B level screens, either at the Clarion no. 1 coal horizon or the top of the Homewood sandstone just beneath that seam. Generally speaking, piezometers W1C, W2C, W3C, and W4C were screened at about the Clarion no. 1 coal horizon, and the C-level piezometers at well pods W5C, W6C, W7C, W8C,

and W22C were screened just below the Clarion no. 1 within the Homewood sandstone. In most locations, the drilling became so wet below the Clarion no. 2 horizon that logging of the strata was very difficult. Evidently, a significant aquifer(s) exists beneath the Clarion no. 2 underclay. Finally, the wells designated as "D" wells were intended as open boreholes, not true piezometers, and were developed to conduct packer pumping tests on various strata at and above the main coal.

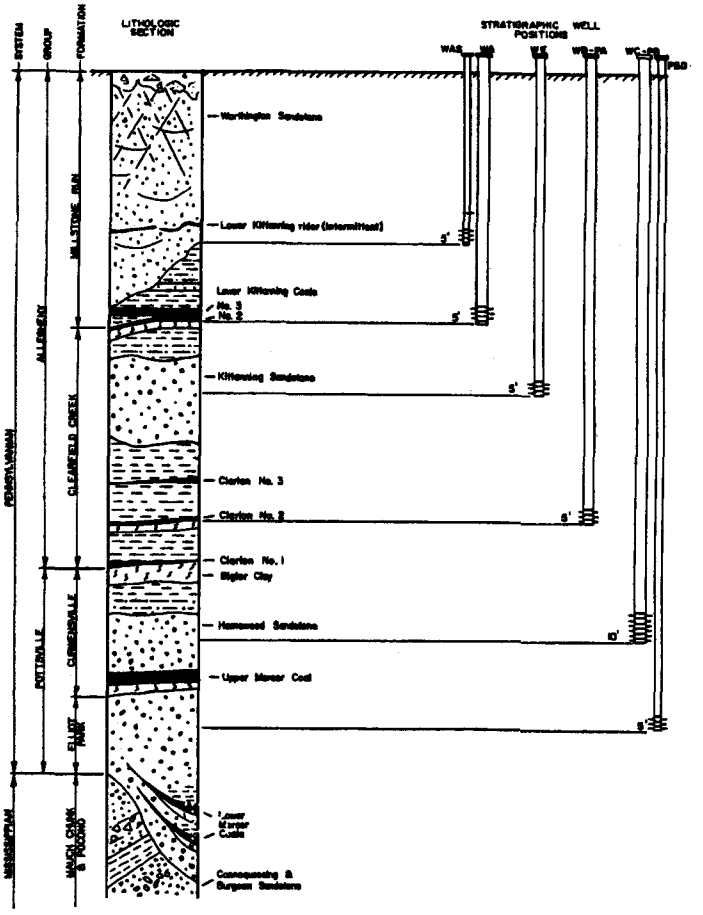


Figure 2.24 Generalized geologic section with piezometer cluster schematic.

After the initial piezometers were installed, a fifth piezometer was drilled at well pods W1, W2, W6, W7, and W22. These "E" piezometers were completed into the Kittanning sandstone between the Lower Kittanning no. 2 and Clarion no. 3 coal seams. These wells were developed to monitor the Thompson pollution plume. They monitored an unaffected groundwater horizon between the Lower Kittanning coal that was to be mined under the Kauffman permit and the underlying pollution plume. The "E" piezometers monitored for possible downward migration of AMD through the new Lower Kittanning pit floor. Other piezometers were installed to monitor the Thompson pollution plume on the flanks of the ridge within the eastern portion of the Kauffman site. They were designated as "PA", "PB", and "PBD" wells, and were screened at the Clarion no. 2, the Homewood sandstone, and the Upper/Lower Mercer coal interburden, respectively.

Groundwater flow within the weathered zone - Groundwater flow on the Kauffman site is controlled by numerous natural factors including topography, relief, stratigraphy, dip, joint sets, bedding-plane separations, zones of fracture concentration, and stress-relief fractures. Additionally, man-induced influences such as road excavations, surface mining, underground mining, and numerous exploratory drill holes have also influenced the groundwater flow.

Hawkins et al. (1996) described the relatively shallow groundwater system at the Kauffman site as fracture flow. Two distinct hydrogeologic settings through which most groundwaters flow were described: 1) a highly fractured weathered zone near the surface, and 2) a less fractured, non-weathered zone at depth. The weathered zone is characterized by numerous stress-relief fractures and bedding-plane separations that become less abundant with increasing depth. This abundance of stress-relief fractures provides a highly transmissive environment for groundwater flow. Underlying the weathered zone, the rock is less densely fractured due largely to the paucity of stress-relief fractures. Data and observations by Hawkins et al. (1996) do not show a sharp transition from the weathered zone to the unweathered zone. Rather, the frequency of stress-relief fractures diminishes somewhat gradually as the depth increases. The "effective" depth of the densely fractured weathered zone varies with different topographic settings (hilltop, valley wall, and valley bottom) and from location to location within similar topographic settings. Hawkins et al. (1996) estimates a general depth for the weathered zone of about 65 feet (20 m) based upon his observations at Kauffman and actual measurements within highwalls of other mine sites. Kipp and Dinger (1987) noted that the depth of the weathered zone was usually 50 feet (15 m) on the hilltops and near 80 feet (24 m) along the valley walls.

Beneath the weathered zone, the main fractures conveying groundwater are the near-vertical systematic joints and concentrated fracture zones developed from tectonic stresses. Unlike stress-relief fractures, these tectonic fractures are not depth related. They can extend from the surface to depths of several hundred feet.

However, at considerable depth their ability to transmit groundwater is usually much reduced. Due to the conductivity contrast, the unweathered rock underlying the surface and near-surface, weathered zone behaves as an aquitard and maintains a perched water table within the weathered fracture zone. Groundwater movement within this near-surface "aquifer" generally follows the topography and migrates toward the surrounding hillslopes and adjacent valley floor. Where a confining layer such as a coal underclay is present, groundwater may be diverted to the surface as contact springs along the hillside.

Not all groundwater within the stress-relief fracture zone is directed laterally toward the stream valleys. The aquitard zone, which serves to perch water, only represents a relative contrast in hydraulic conductivity and is not an impermeable barrier. Therefore, a significant amount of groundwater will leak vertically into the underlying strata. Vertical fracture zones of tectonic origin enhance this downward leakage in areas adjacent to such features. Also, abandoned boreholes that have remained open will present a means of quickly conveying shallow groundwater into the deeper systems.

Groundwater that emanates from a particular stratigraphic horizon along the hillside is not necessarily associated with groundwater at that same horizon within the core of the hill. Water chemistry data of contact springs sampled along the unmined hillslopes of the Kauffman property were compared to water chemistry data collected from deeper hilltop piezometers. The more dilute chemistry of the hillside springs is thought to represent groundwater of the weathered-rock zone. In contrast, groundwater deep within the hill comes in contact with less weathered rock and moves much more slowly, thereby increasing the contact time with the adjacent rock. Consequently, the deeper groundwater is higher in dissolved constituents.

At the Kauffman mine, a good example of this concept involves contact springs GR438 and GR439. Both apparently emanate from the Clarion formation just 175 meters (570 ft.) northwest and downdip of well pod W1. At well pod W1, piezometers W1B and W1C are open at the Clarion no. 3 and Clarion no. 1 coals. Both reveal the effects of AMD from the Thompson pollution plume. Initially it was thought this plume would spread north and west and reach springs GR438 and GR439. However, the springs do not exhibit characteristics of AMD. Apparently, the polluted water within the Clarion horizon at W1 "steps down" into deeper strata as the plume approaches the stream valley. The springs represent shallow groundwater from the weathered zone and are not necessarily representative of the "Clarion waters" within the hill core.

Groundwater flow within the unweathered zone - As discussed above, groundwater within the weathered zone flows laterally in accordance with the surface contours. This is due to the gradational contact between the weathered and non-weathered strata. This contact mirrors the topography. However, there also is a significant component of vertical leakage into deeper aquifer systems. As downward-flowing groundwater reaches stratigraphic layers of low vertical hydraulic conductivity relative to the adjacent strata, lateral flow occurs. Of course there will always be vertical leakage through each aquitard encountered, but the volume of vertical groundwater recharge is gradually reduced with increasing depth.

Initial monitoring of the Kauffman piezometers during the permit application review period confirmed that the general movement of groundwater is downward on the Kauffman site. The shallowest piezometers had the highest pressure head, the deepest piezometers had the lowest pressure head, and the intermediate piezometers fell somewhere in between. This is the textbook pattern for an upland setting that serves as a groundwater recharge area. However, certain well pods indicated that the groundwater flow patterns may be more complicated. Specifically, at well pods W3 and W6, the pressure heads for the deepest piezometers were equal to, or higher than, the pressure heads within the shallowest piezometers, maintaining very high water levels in the piezometer tubes. In fact, the water levels within the W3 and W6 piezometers were about 120 feet (37 m) and 111 feet (34 m), respectively, above the top of the screen.

Hydrographs for the W3 and W6 piezometer pods are provided as Figures 2.25 and 2.26, respectively. The hydrograph for the W3 pod includes several years of weekly water level measurements at piezometers W3AS, W3A, W3B, and W3C. For the first couple of years, the water levels within the W3C piezometer were elevated above the level of the W3A piezometer. During the permit application review period, the permittee's consultants interpreted this as localized confining conditions. However, subsequent data revealed that pressures fluctuate greatly at the W3C horizon, and for much of the time since 1994, the groundwater flow pattern has been more typical of the "normal" well pods. Also, the water level plots for the W3AS,

W3A, and W3B piezometers exhibit similar seasonal and climatic patterns. The mimicry of the lows and highs suggests that these aquifers are hydrologically connected. On the other hand, there appears to be no such relationship between W3C and the other three piezometers.

Thus far, there has been no complete aquifer testing of the W3 piezometers. We do not yet know how each screened zone responds to pumping and/or slug testing, or even how rapidly the wells recharge after being pumped dry. Nonetheless, recharge data from the well sampler's records provide indications of the relative transmissivity among the water-bearing zones adjacent to each piezometer screen. For instance at W3C, the deepest piezometer of the W3 pod, recharge is very slow after pumping - probably less than 0.05 liters per minute (L/m) (0.013 gpm). On the other hand, recharge is relatively rapid, probably more than 3.5 L/m (0.92 gpm), within the intermediate-level W3B piezometer. The shallow W3A piezometer recharges at a relatively moderate rate of about 1.5 L/m (0.39 gpm).

The hydrograph for the W6 well pod reveals a much different response in the deepest piezometer, W6C, as compared to W3C. Soon after W6C was developed, the water level climbed to just below that of W6A, and it has mimicked very closely the hydrograph of that piezometer ever since. In fact, piezometers W6A, W6C, and W6E are all closely associated with respect to water elevation and hydrographs. Furthermore, the W6B hydrograph also mimics the other three piezometers, but does not maintain such a high water level. This elevation difference between the water levels within the W6B piezometer and the other three piezometers was initially over 46 feet (14 m), but it has been reduced recently to about 33 feet (10 m).

Interestingly, as noted on the W6 hydrograph, the water levels in all four piezometers had dropped following the excavation of an open cut on the Lower Kittanning coal seam about 900 feet (275 m) to the west-northwest of the well pod. The floor of this mining cut, in addition to being relatively far from the W6 piezometers, was about 100 feet (30 m) higher in elevation than the stratigraphic horizon open to the W6C piezometer screen, and about 62 feet (19 m) above the horizon open to the W6B screen. Nevertheless, these deeper aquifers still responded to the excavation of the open mining pit.

The mimicry among the four aquifers tested at the W6 well pod (and among three of the four piezometers at the W3 well pod) suggests there is a vertical hydrologic connection, either natural or artificial. As for an artificial connection, the most likely explanation would be poor piezometer construction. For example, if the piezometer was not backfilled properly, groundwater from the upper aquifers may drain to the screen through the annulus. Another possibility could be a defect in the piezometer casing, such as a crack or separation at the joints, allowing shallower groundwater to seep into the piezometer above the screen. In either case, bentonite seals would have been compromised. This seems unlikely since bentonite pellets and chips were used from the top of the screen to the surface. Furthermore, because more than one piezometer exhibits a mimicry, each piezometer would have to be faulty to explain an artificial connection in this manner.

Artificial connection of aquifers can also occur through open and abandoned exploratory boreholes. Although the Kauffman property is riddled with exploratory boreholes down to the Lower Kittanning coal seam, there are probably few, if any, old boreholes as deep as the Homewood sandstone. Therefore, it seems to be more likely that the connection among the various aquifers is natural rather than artificial.

As for a natural connection, the aquifers could be connected through tectonic fractures, zones of fracture concentration, or fault zones. If discrete fractures or fracture zones are present at or very near well pod W6, vertical communication between the aquifers at that location could be established. Such fractures or fracture zones could serve as avenues for groundwater recharge to deeper aquifers.

As with the W3 well pod, the sampler's records during pumping and sampling at the W6 pod reveal some qualitative aquifer characteristics. The deep W6C piezometer recharged the quickest, approximately 2.8 L/m (0.74 gpm). In comparison, intermediate piezometer W6B recharges the slowest, approximately 0.4 L/m (0.1 gpm) while piezometer W6E recharged at a moderate rate of approximately 0.9 L/m (0.24 gpm). Although the sampler's records provide some qualitative information regarding the relative transmissivities among the aquifers, quantitative pumping tests, slug tests, and recovery tests should be conducted in the future if further study is desired.

Although the majority of Kauffman piezometers reveal a fairly straightforward groundwater regime, well pods W3 and W6 reveal certain aberrations that may

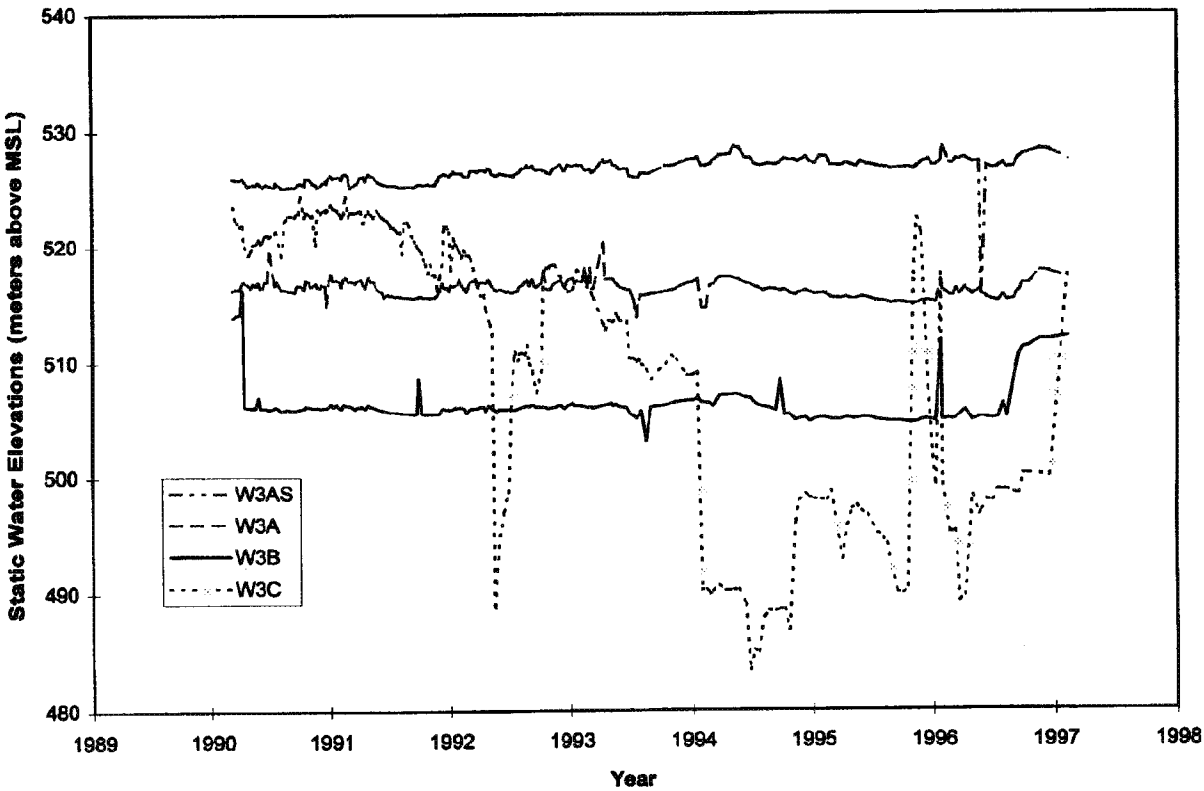


Figure 2.25 Hydrograph of W3 piezometer pod representing weekly water level measurements from March 1990 through February 1997.

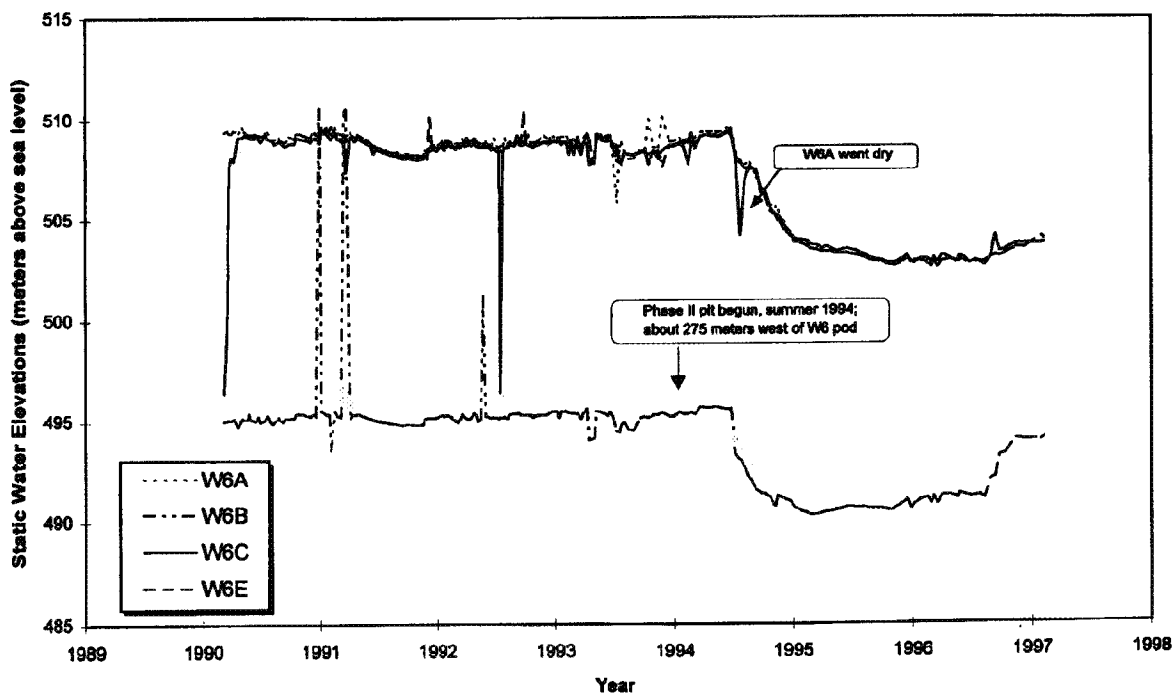


Figure 2.26 Hydrograph of W6 piezometer pod representing weekly water level measurements from March 1990 through February 1997.

be common where significant fracturing of the rock mass is a factor. Such fractures may provide the vertical avenues for interconnecting perched aquifers that would otherwise be hydrologically isolated. The mimicry in hydrograph traces among separate piezometers at various levels can hardly be ignored. The piezometers at well pod W6 present an especially striking example.

Summary - Although tectonic fracturing complicates groundwater flow patterns, the general movement of groundwater on the Kauffman site is fairly typical of an upland setting within the Allegheny Plateau. Stress-relief fracturing near the surface establishes a relatively shallow water table aquifer that responds quickly to precipitation events and directs groundwater flow laterally toward the adjacent stream valleys. Groundwater within this weathered zone has short residence time from infiltration to discharge and therefore contains less concentrations of dissolved minerals than does groundwater deep within the core of the hill. Along the hillsides, this shallow groundwater generally does not emerge from beneath the colluvium but provides baseflow to wetlands and streams on the valley floor. Nevertheless, a confining layer such as a thick clay stratum may divert flow to the surface as a contact spring or seepage face along the clay seam outcrop. Such contact springs that originate from the weathered zone are not representative of groundwater at the same horizon within the core of the hill.

Although groundwater within the weathered zone generally flows in accordance with topography, there is significant vertical leakage to the underlying strata, primarily through joints. This vertical leakage is further enhanced by the presence of faults and major fracture zones. Where these percolating waters reach strata of contrasting vertical conductivities, additional flow zones are established at depth. Flow within these deeper aquifers is again directed laterally but is more controlled by structural features such as dip, joints, fracture zones, and faults. Of course, stratigraphic variations in the aquifer or underlying aquitard will also influence the flow. Each of these aquifers that are established at depth will leak to the underlying strata, but the volume of such leakage will gradually diminish as well the occurrence of joints through which the groundwater flows.

Most piezometers at the Kauffman site confirm this downward movement of groundwater that is typical of a recharge area. However, a couple of piezometer clusters or pods suggest a vertical connection among the various aquifers that are monitored. These piezometers do not show the normal pattern of decreasing pressure head with each lower aquifer, and some reveal a close mimicry among hydrograph plots. Assuming that the piezometers are constructed properly, this interconnection may be caused by the presence of a significant tectonic fracture zone or a fault, but confined groundwater conditions cannot be ruled out either.

Additional study is needed on the Kauffman site to further examine the apparent anomalies in groundwater flow patterns. Thus far, no pumping tests or slug testing has been conducted on the two piezometer pods where unusual water levels were recorded. Further research may provide some additional insight into the behavior of groundwater flow within this type of setting on the Appalachian Plateau.

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Chapter 3

HYDROGEOLOGIC CHARACTERISTICS OF SURFACE-MINE SPOIL

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Introduction

An understanding of the hydrology of surface mine spoil is important in predicting mine drainage quality. However, it is poorly understood and one of the least analyzed aspects of mine drainage prediction. Groundwater is a integral chemical component in acid mine drainage (AMD) formation and it serves as the contaminant transport medium. Therefore, prediction of postmining drainage quality requires the inclusion of a surface mine spoil groundwater hydrology component in the process.

The nature, degree, and duration of groundwater and spoil interactions need to be factored into any comprehensive mine drainage predictive method or model. Recharging waters, moving through the unsaturated portion of backfill, will have intermittent episodes where discrete areas of the spoil are briefly contacted, whereas groundwater within the saturated zone will have a considerably more consistent and longer contact time with that portion of the spoil. Groundwater within the zone of water table fluctuation will contact nearly all of that spoil zone periodically during brief episodes when water levels rise. Groundwater will, in both the unsaturated and saturated zones, chemically and physically react with the spoil material that it contacts. However, mine drainage quality prediction is often based on the assumption of uniform contact with 100 percent of the spoil material and does not take into consideration that groundwater only contacts a limited fraction of the spoil. Also, under differing hydrologic conditions, the sections of the spoil contacted by groundwater can change. It is important to determine what portions of the spoil are contacted by the groundwater and what is the nature of this contact. Spoil excavations and aquifer testing indicate that there are areas within backfills that, because of very low permeability, allow very little groundwater flow through them. These relatively "dead" areas contribute little to the groundwater system and to the associated mine drainage quality.

Characteristics of Mine Spoil Groundwater Flow Systems

In the past, the groundwater flow regime in surface mine spoil of the Appalachian coalfields has generally received little attention and study. Most individuals have made the assumption that ground-water flow in mine spoil is a porous media system, similar to flow through unconsolidated alluvium. Recent field work and testing of surface mine spoil indicate that this assumption is not completely valid.

Caruccio et al. (1984) noted that groundwater flow in the backfill of a surface mine in central West Virginia was highly channelized and that it was not observed until one of these randomly located channels was intercepted. Based on their physical observations during excavations in mine spoil, they referred to the groundwater flow regime as pseudokarst, where groundwater flows mainly through large voids and conduits. Pseudokarst hydraulic characteristics are similar to the characteristics observed in some karst (carbonate underlain) terrains, however, the mechanism of channel and void formation differs. These types of systems are more discriptively defined by the term double-porosity.

Hawkins and Aljoe (1990) noted that mine spoil exhibits characteristics of both porous medium and double-porosity aquifers. Under steady-state conditions spoil behaves mainly as a porous medium aquifer. For example, the presence of a relatively continuous water table in the backfill and perennial consistent-flowing mine discharges are indicative of an overall porous media system. Hydraulic conductivity values measured in mine spoil are substantially below values expected for open conduit flow.

Conversely, when a spoil aquifer is stressed (for example, during an aquifer test) or subjected to transient conditions, double-porosity characteristics become more pronounced and can briefly dominate the hydrologic regime. For example, multiple water tables and temporary flowing artesian conditions have been observed during substantial recharge events (Hawkins and Aljoe, 1990). Monitoring and testing indicate that

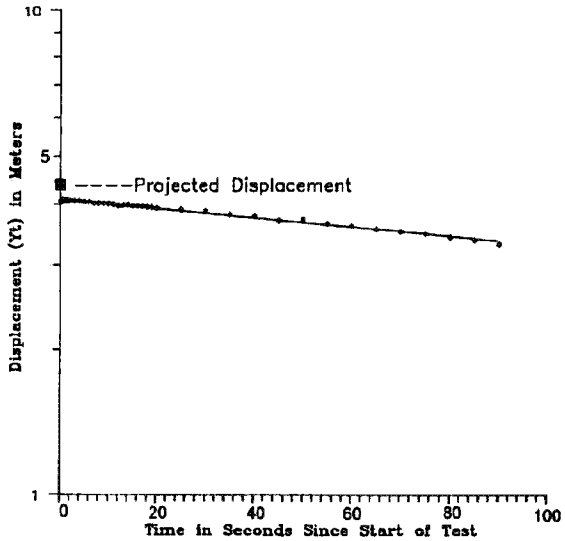

Figure 3.1(a) Slug test exhibiting a "typical" porous media type response. The actual displacement and the projected are nearly the same, because the flow from the well into the aquifer is gradual and diffuse.

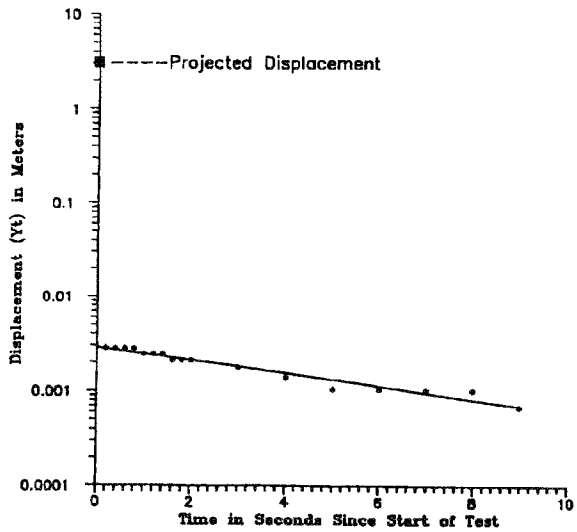

Figure 3.1(b) Slug test exhibiting an "atypical" double-porosity type response. The actual displacement is much lower than the projected displacement, because large voids very quickly accept some of the displaced water. Once the voids are full, a gradual and diffuse flow from the well into the aquifer occurs.

groundwater is stored in and flows through large voids or conduits in spoil; however, these voids are not always well interconnected across a mine site. Therefore, diffuse groundwater flow through the interstices of the fine-grained material between the voids exerts significant control on the overall site hydrology. Slug tests performed in wells penetrating surface mine spoil empirically illustrate the bimodal nature of the groundwater flow regime. These tests yield two distinctly different types of responses in mine spoil (Fig. 3.1(a) and (b)). One type (Fig. 3.1(a)) of response is indicative of a porous media system. The actual displacement and the projected displacement are similar, indicating gradual and diffuse flow from the well into the aquifer as expected in a porous medium. The second type indicates the presence of large voids and conduits of a double-porosity system. The actual displacement is substantially less than the projected displacement, indicating large voids adjacent to the well rapidly fill with water flowing from the well. Once the voids are filled, there is a gradual and diffuse flow from the well into the spoil (Hawkins, 1993). The projected displacement in Figures 3.1(a) and 3.1(b) is determined from the known slug volume.

These dual aquifer flow characteristics exist because mine spoil is an extremely heterogeneous and anisotropic material. The heterogeneities are created by the processes of mining and reclamation. During mining and subsequent reclamation, spoil becomes sorted to some extent. When dumped by a rock truck or dragline and regraded by bulldozers, the larger spoil particles tend to roll toward the base of the spoil ridges into the valley between the ridges, while the midsized and smaller fragments tend to stay on the sides and top of the spoil piles (Rehm et al., 1980). Figure 3.2, a photograph of spoil at an active surface mine in central Pennsylvania, illustrates the results of this process. Groenewold and Bailey (1979) observed that in western North Dakota, monitoring wells completed in the spoil valleys exhibit more variable hydraulic conductivity than wells completed in the spoil ridges. Aquifer testing (constant-discharge tests) of spoil in northern West Virginia and western Pennsylvania indicates that linear zones of high hydraulic conductivity tend to parallel spoil ridge orientation. Hydraulic conductivity perpendicular to the spoil ridges appears to be significantly lower (commonly by several orders of magnitude) than that parallel to the ridges (Hawkins and Aljoe, 1991).

Factors Influencing Hydraulic Characteristics

Lithologic Controls

Lithology of the spoil can influence the hydraulic conductivity in reclaimed mines. Parent rock (overburden) of surface mine spoil in northern Appala-

chia is comprised primarily of sandstone, siltstone, and shale. In some areas, limestone may occur in significant quantities, as may glacial sediments.

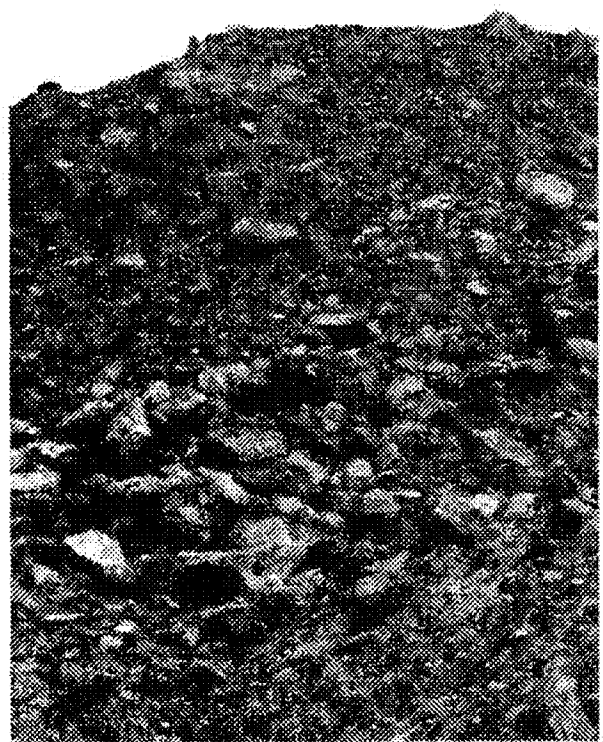

Figure 3.2 Spoil ridge exhibiting fragment size sorting during mining. The sandstone boulders in the foreground are approximately 1 m across and the material in the background is chiefly shale 5 cm or less across.

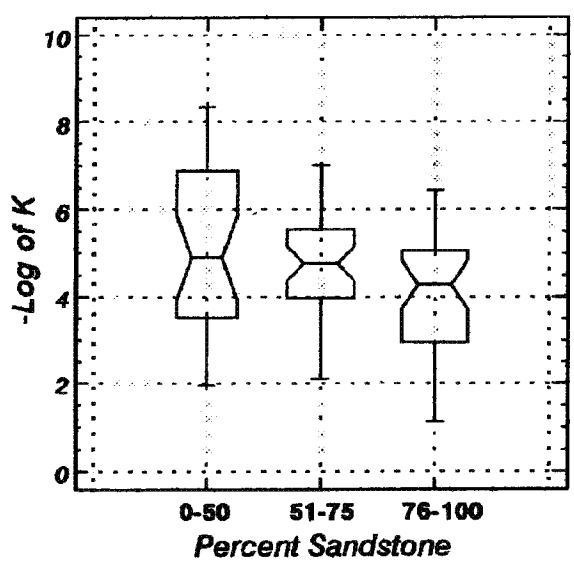

Figure 3.3 Notched box-and-whisker plot illustrating the relationship of spoil lithology to hydraulic conductivity.

Figure 3.3 indicates that increasing percentages of sandstone (and decreasing percentages of shales) in mine spoil appear to yield higher median hydraulic conductivity values and a narrower range of values (Aljoe and Hawkins, 1994). However, the median hydraulic conductivity increases observed were not statistically significant. The apparent trend is explained by the hydraulic properties of the different lithologies and by mechanisms of mining and reclamation. Sandstone-rich spoil zones tend to have larger fragments than shale-rich zones. This is because sandstones of this region tend to be well cemented and are better able to resist breakage and weathering. Shales tend to break into smaller fragments during mining and more readily weather and break down to silt- and clay-sized particles, which decreases the hydraulic conductivity (Aljoe and Hawkins, 1994). An accumulation of clay and silt toward the base of the spoil is often observed in monitoring wells that are purged (pumped or bailed) infrequently, confirming the breakdown.

The processes of mining and reclamation may further facilitate spoil heterogeneity by creating zones comprised predominantly of one lithology. During mining, a dragline or frontend loader often will remove the overburden in layers, spoiling strata composed mainly of one lithology at a time. Monolithic zones are also created by the tendency of large spoil fragments (mainly sandstone) to roll to the base of spoil ridges, while the medium and smaller fragments (shale and some sandstone) tend to remain on the sides and top (Fig. 3.2). This appears to account for the observation of Groenewold and Bailey (1979) that spoil valleys had a higher mean and greater range of hydraulic conductivity than the ridge areas in the northern Great Plains. A test well drilled randomly into spoil with a lithology of 50 percent sandstone and 50 percent shale should have an equal chance of intersecting a shale-rich or a sandstone-rich saturated zone. Therefore, the hydraulic conductivity is expected to range more widely when the sandstone content is 50 percent than when it approaches 100 percent. As the sandstone content of spoil increases, the number of wells that will intersect sandstone-rich zones likewise increases, thus causing the median hydraulic conductivity to increase (Fig. 3.3).

Phelps (1983) observed that spoil bulk density generally decreases with depth. This appears to be caused by the creation of a significant volume of interstitial

voids when the large spoil fragments, commonly sandstone, roll to the bases of spoil piles.

Mining Methods and Topography

Because, surface mine spoil is a highly heterogeneous and anisotropic medium, groundwater flow paths are difficult to determine. However, some general trends have been identified and a few assumptions can be made concerning groundwater flow through mine spoil.

Topography influences groundwater flow in surface mine spoil, because groundwater flows down the hydraulic gradient and topography directly influences the hydraulic gradient. Although, spoil aquifers can exhibit multiple water tables for brief periods under transient conditions (Hawkins and Aljoe, 1990), surface mine spoil generally exhibits a single continuous water table with a moderate hydrologic gradient. Thus, the water table tends to reflect the overlying topography. However, the water table is also influenced by other geologic and hydrologic conditions, such as permeability variations, local structure, and the adjacent unmined areas.

The structural dip of the pit floor is a major influence on the direction of groundwater flow in spoil aquifers. Groundwater tends to flow down dip and perpendicular to the strike of the pit floor. Toe-of-spoil discharges will commonly form at the structural low point of the pit floor outcrop.

Influences from the groundwater system in adjacent unmined areas can cause groundwater in spoil to disregard structural dip and other hydrologic factors. Localized rolls or swales in the pit floor can affect the direction of groundwater flow. When the strata dip toward the final highwall, the groundwater tends to saturate spoil behind the highwall. This is because the hydraulic conductivity of the undisturbed aquifer in the highwall is commonly at least 2 orders of magnitude less than in the spoil and the pit floor material usually has significantly lower permeability than the spoil (Hawkins, 1995). Groundwater impounding at the highwall may flow in any of several directions. Depending on the hydraulic gradient, groundwater may enter the unmined strata and flow down the structural dip, or it may flow laterally, parallel to the highwall, and discharge where the pit floor is exposed at the surface along the structural strike. The spoil may become sufficiently saturated to permit discharges to emanate at the topographic low point of the mine along the original coal cropline, opposite to the dip direction (Fig. 3.4). Depending on the permeability, significant amounts of groundwater may leave the backfill by downward flow through the pit floor. Depending on the configuration and size of adjacent unmined areas, the groundwater gradient may cause flow from the highwall into the spoil, regardless of the structural dip.

Direction of mining and the configuration of the backfill can dramatically impact the direction of groundwater flow. The highly permeable zones that

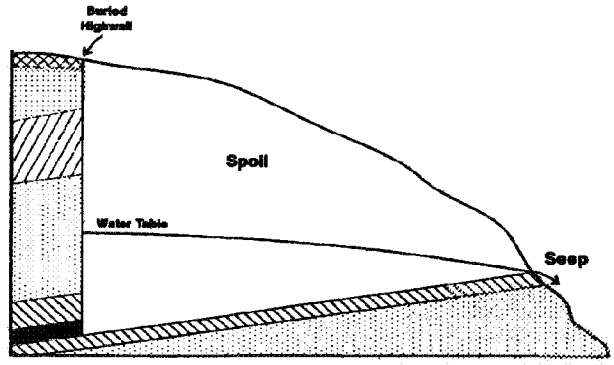

Figure 3.4 A schematic cross section of a reclaimed surface mine with saturated spoil behind the highwall and a seep emanating at the topographic low point opposite the structural dip.

form in the valleys between spoil ridges permit substantial groundwater flow parallel to the ridges. Because groundwater tends to follow the path of least resistance, groundwater flow perpendicular to the spoil ridges is considerably less than flow parallel to them. Constant-discharge testing in a reclaimed surface mine in central West Virginia, conducted by the author, indicates that the hydraulic conductivity difference between buried spoil valleys and ridges can exceed 2 orders of magnitude. Groenewold and Winczewski (1977) observed that the surface over these highly transmissive spoil valleys is more susceptible to subsidence from piping of fine grained spoil materials because of the substantial amount of groundwater movement.

The location of haul roads across the backfill also can influence groundwater flow (Robert S. Evans, personal communication). Spoil underlying haul roads can become highly compacted (less transmissive) from the traffic of vehicles and heavy equipment. The spoil on each side of the haul road will be substantially more transmissive than the spoil under the haul road. The level of spoil compaction is related to the lithology of the spoil material and the amount of equipment traffic.

Groundwater may flow along the road edge until a pathway through exists or impound behind these haul roads which may be buried and hidden in the reclaimed backfill.

Impacts of Spoil Age

Shortly after regrading of the spoil, differential settling and piping of the finer material begin in the backfill (Groenewold and Bailey, 1979). These subsequent processes contribute greatly to the heterogeneity of spoil and are facilitated by infiltrating surface waters and the water table re-establishment. The "uplift" pressure provided by the rebounding groundwater table may aid the shifting and repositioning of spoil fragments (Sweigard, 1987). Sweigard observed significant settling within a year after reclamation on Illinois surface mines and noted that considerable settling may continue at least 2 to 3 years after reclamation. Aquifer testing by the author indicates that settling within spoil continues, apparently at a lesser rate, even 12 years after reclamation.

Hydraulic conductivity has been observed to change as the age of the spoil increases. Aljoe and Hawkins (1994) observed that reclaimed surface mine spoil that was 30 months or less old had a significantly lower (95 percent confidence level) median hydraulic conductivity than reclaimed mine spoil that was over 30 months old (Fig. 3.5). The manner by which hydraulic conductivity increases with time may be caused by the improved interconnectedness of the voids that were created during backfilling. Piping and differential compaction of fine-grained spoil material in response to vertical movement of recharging waters through the unsaturated portion and horizontal movement of groundwater in the saturated portion of the spoil may be the cause of increased void communication. Bulk density also may change as the spoil settles and fine grained materials migrate toward the base of the spoil.

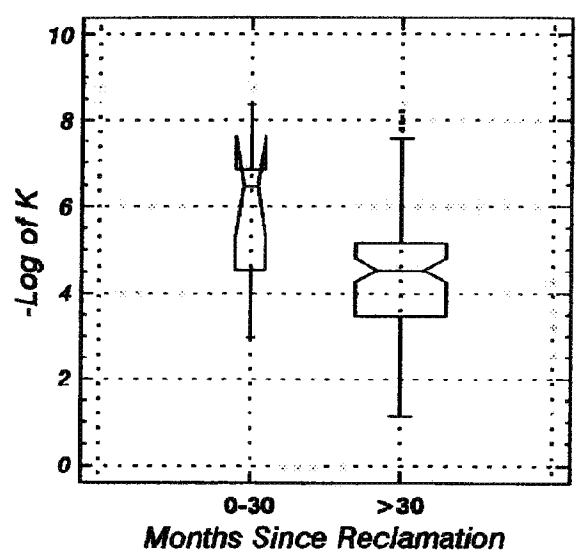

Figure 3.5 Notched box-and-whisker plot illustrating the relationship of spoil age to the hydraulic conductivity.

Changes in hydraulic conductivity in spoil are directly related to the mechanisms and timing of the postmining water table re-establishment. In eastern Ohio, water table re-establishment at three reclaimed surface mines was observed to be nearly complete approximately 22 months after reclamation was completed, (Helgesen and Razem, 1980). Based on the authors experience, recovery of the water table after mining may take 24 months or longer in Pennsylvania. The rate of water table recovery is related to several factors including the precipitation rate, recharge and discharge rates, porosity, topography, and geologic structure.

Rehm et al. (1980) and Moran et al. (1979) stated that spoil permeability decreases with age. This may be caused by differences in physical and chemical properties of the rock units that they encountered in the coalfields of the northern Great Plains compared to the units of the eastern coal fields. Overburden for the western coal fields are mainly comprised of weakly cemented units, which tend to form few large voids. Permeability may be further decreased by swelling clays common to overburden in the northern Great Plains. In the northern Great Plains, postmining hydraulic conductivity values are very similar to premining values (Rehm et al., 1980).

Reported Values of Hydraulic Parameters

Hydraulic conductivity and transmissivity

Performing aquifer tests to determine hydraulic properties (hydraulic conductivity and transmissivity) of spoil can be a difficult procedure. Assumptions must be made as to the homogenity and isotropic nature of the aquifer. However, testing indicates that spoil is highly heterogeneous and anisotopic. Therefore, the values presented below must be viewed in this context. Hawkins (1993) detailed some of the problems incurred while conducting slug tests and during the subsequent data analysis to determine the hydraulic properties of surface mine spoil. Large voids within mine spoil may permit rapid, possibly turbulent groundwater flow during aquifer testing. If turbulence

actually occurs, Darcian methods of data analysis cannot be used. Additional problems are created because the unknown surface area of the adjacent voids is added to the known surface area of test well. This situation can cause the hydraulic conductivity to be overestimated. Conversely, aquifer modeling (MINEFLO AND MODFLOW) of mine spoil indicates that the effective site hydraulic conductivity may be 1 to 2 orders of magnitude higher than the field determined values at individual test wells. This was determined by error reduction during model calibration. The modifications to the hydraulic conductivity may vary substantially under differing hydrologic conditions because of extreme heterogeneity and anisotropy common to reclaimed mine spoil (Hawkins and Aljoe, 1990; Hawkins, 1994). Despite the problems involved in conducting aquifer tests, aquifer testing to determine hydraulic properties is still an integral part of the hydrologic characterization of mine spoil. The hydraulic conductivity and other site-specific hydrologic data can be used to predict the postmining water table elevation within the spoil, which in turn is important for alkaline addition and special handling techniques. Transmissivity, in the strictest sense, refers only to confined aquifers. However, many researchers have reported transmissivity for mine spoil which is mainly unconfined. These values are included below. These hydraulic parameters are important for mine drainage prediction because they are used to determine groundwater velocity, water table fluctuation, groundwater storage turnover rates as well as other factors influencing groundwater contact within different zones in the spoil. Knowledge of these and other hydrologic parameters is especially important to special handling and alkaline addition techniques and other aspects of mine drainage prediction.

Hydraulic conductivity and transmissivity of surface mine spoil exhibit a very broad range of values from location to location and within a mine site. Table 3.1 illustrates the range of hydraulic conductivity and transmissivity values in different regions of North America. Hydraulic conductivity values generated from testing of 103 monitoring wells from 15 surface mines in northern West Virginia and western Pennsylvania ranged from 4.2×10^{-9} to 7.6×10^{-2} m/s (Table 3.1). The data exhibited a geometric mean of 2.5×10^{-5}, a median of 2.8×10^{-5}, and a standard deviation of 9.6×10^{-3} m/s. Hydraulic conductivity within a single mine site ranged over 5 orders of magnitude (6.6×10^{-9} to 9.3×10^{-4} m/s). Hydraulic conductivity ranges exceeding 3 orders of magnitude within a mine site were common when more than 4 wells were tested. Aquifer testing of the 15 mine sites exhibited a range of transmissivity values exceeding 8 orders of magnitude (1.2×10^{-9} to 2.0×10^{-1} m^2/s).

Similar values have been reported by others working with surface mine spoil in the Appalachian coalfields. Weiss and Razem (1984) noted hydraulic conductivity values ranging from 1.13×10^{-6} to 1.89×10^{-5} m/s in a surface mine located in eastern Ohio

Table 3.1 Ranges of Hydraulic Conductivity and Transmissivity in Surface Mine Spoil

Geographic Area	Hydraulic Conductivity in m/s	Transmissivity in m^2/s
Western Pennsylvania (Hawkins, unpublished data)	4.2×10^{-9} to 7.6×10^{-2}	1.2×10^{-9} to 2.0×10^{-1}
Northern West Virginia (Hawkins, unpublished data)	9.5×10^{-8} to 2.7×10^{-4}	1.4×10^{-7} to 2.9×10^{-4}
Eastern Ohio (Weiss and Razem, 1984; Bonta et al., 1992)	5.4×10^{-8} to 1.9×10^{-5}	No Information
Western Kentucky and Southern Illinois (Herring, 1977; Lindorff, 1980)	2.4×10^{-5} to 4.1×10^{-5}	2.2×10^{-4}
Western North Dakota (Groenewold and Bailey, 1979)	2.9×10^{-5} to 4.6×10^{-5}	No Information
Northern Great Plains (Rehm et al., 1980)	8.0×10^{-7}	No Information
Wyoming Moran et al., 1979)	1.9×10^{-6} to 2.1×10^{-4}	No Information
Edmonton, Alberta, Canada (Moran et al., 1979)	1.5×10^{-6}	No Information

(Table 3.1). The hydraulic conductivity of surface mine spoil in three watersheds in eastern Ohio ranged from 5.4×10^{-8} to 6.7×10^{-6} m/s (Bonta and others, 1992).

Published information on spoil aquifer testing in the Midwest is somewhat limited. Herring (1977) measured a hydraulic conductivity of 2.358×10^{-5} m/s and transmissivity 2.2×10^{-4} m^2/s based on a constant-discharge test conducted on a surface mine in western Kentucky (Table 3.1). An average hydraulic conductivity of 4.1×10^{-5} m/s was recorded for three surface mines in Illinois (Lindorff, 1980).

Extensive testing of saturated surface mine spoil for the western coal fields have yielded a wide variability for hydraulic conductivity. Groenewold and Bailey (1979) observed hydraulic conductivity values ranging from 2.9×10^{-9} to 4.6×10^{-5} m/s for surface mine spoils in western North Dakota (Table 3.1). Rehm and others (1980) reported a hydraulic conductivity range of 6 orders of magnitude with a geometric mean of 8×10^{-7} m/s for the northern Great Plains region (North Dakota, Montana, Wyoming, and Alberta, Canada). Similar hydraulic conductivity values were observed by Moran and others (1979) in the northern Great Plains. They recorded hydraulic conductivities of 1.9×10^{-6} and 2.1×10^{-4} m/s from aquifer testing on a Wyoming surface mine. Spoil aquifer testing near Edmonton, Alberta, Canada yielded a mean hydraulic conductivity of 1.5×10^{-6} m/s.

The hydraulic conductivity of mine spoil in the Appalachian coal fields is considerably greater than that of the undisturbed rock. Hawkins (1995) analyzed data from five Northern Appalachian surface mines and observed that the hydraulic conductivity of mine spoil (1.2×10^{-5} to 1.4×10^{-4} m/s) ranged from nearly 1 to over 2.5 orders of magnitude greater than adjacent bedrock (3.8×10^{-8} to 4.1×10^{-6} m/s) with a geometric mean 2 orders of magnitude greater. In other words, mine spoil tends to be approximately 100 times more conductive than undisturbed bedrock. The differences in hydraulic conductivity cause differences in water levels between mined and unmined areas. In some cases, perched aquifers on the unmined rock can also account for these water level differences. Water levels in spoil wells were 50% lower than those measured in wells of similar elevation in adjacent unmined aquifers. This illustrates that premining water level measurements may not be indicative of postmining levels.

Herring (1977) noted that in the Illinois Basin, spoil is more transmissive than aquifers in unmined overburden. This was based on the observation that more water was entering the active pits from adjacent spoils than was coming from adjacent unmined overburden. Weiss and Razem (1984) likewise observed greater conductivities in spoil compared to premining values at a mined watershed in eastern Ohio.

Porosity

As with testing for hydraulic conductivity, porosity determination in mine spoil is difficult. Therefore, the amount of published data concerning porosity is limited and many of the empirically derived values were determined in the laboratory. Spoil porosity is important to mine drainage quality prediction in terms of determining groundwater storage volumes and predicting water level changes stemming from recharge or discharge. These characteristics impact the nature and scope of groundwater contact with different spoil zones.

Wells et al. (1982) reported laboratory porosities of 25 to 36 percent for surface mine spoils from Eastern and Western Kentucky. The spoils tested were composed mainly of shale and sandstone. Laboratory-measured values on eastern Ohio spoil samples ranged from 41 to 48 percent with a mean of 44 percent (Mezga, 1973). Field tests indicate that the laboratory-generated values are significantly greater than actual field conditions.

Cederstrom (1971) estimated that the porosity values of cast spoil ranges between 15 and 25 percent. He stated that this range was 7 to 25 times greater than the porosity of undisturbed strata. The magnitude of increases in porosity depends greatly on the premining aquifer porosity, which is determined mainly by lithology and fracture density. Based on pumping tests, storage coefficients of 17 and 23 percent were determined for spoil in Wyoming (Rahn, 1976, reported in Moran et al., 1979). For unconfined conditions, storage coefficient is roughly equivalent to the effective porosity. Effective porosity calculations for a reclaimed surface mine in Upshur County, West Virginia, determined by the author, ranged from 14 to 16 percent. These values were determined using slug and tracer test results, conducted more than 13 years after the site was reclaimed.

The field-determined porosity values approximate the percentage of backfill volume increase (swell) created when overburden is spoiled during mining. Herring (1977) stated that the swell for the Illinois Basin is about 20 percent. Van Voast (1974) estimated that the

swell is roughly 25 percent. He stated that the backfill volume increase was accompanied by an increase in porosity and vertical permeability.

Given the relatively high porosity values of mine spoil, reclaimed surface mines are capable of storing large volumes of groundwater. For example, a 10 ac (4.05 ha) reclaimed surface mine with a 10 ft (3.05 m) saturated zone and 18% porosity will have nearly 6 million gallons (.023 million m^3) of groundwater in storage. When making this type of calculation, a range of effective porosity values is better than a single value. Effective porosity values for reclaimed surface mine spoil should be based on field testing or measured swell as opposed to laboratory determinations.

The porosity values for Appalachian surface mine spoil tend to be significantly greater than for the undisturbed overburden. Effective porosity values for fractured-rock aquifers have been estimated to range from 0.001 to 0.1% (MacKay and Cherry, 1989). Brown and Parizek (1971) determined porosity for coal-bearing strata in the laboratory. They observed a primary porosity range of 0.8 to 9.4% with a mean of 3.9%. However, secondary porosity can be much higher in the Appalachian Plateau (Chapter 2).

Groundwater Velocity

Aquifer testing indicates that the groundwater velocity in surface mine spoil is substantially greater than that of the undisturbed overburden. Average groundwater velocities are affected by recharge rate, effective porosity, hydraulic conductivity, and head differential, and can vary widely depending on site-specific conditions. Determination of groundwater velocity is important in mine drainage prediction because it relates directly to groundwater contact with the spoil and groundwater storage turnover rates.

Hawkins and Aljoe (1991) measured a groundwater velocity range in the backfill of a reclaimed surface mine in central West Virginia of 1.2×10^{-5} to 4.9×10^{-5} m/s. Caruccio et al. (1984) observed similar velocities, ranging from 1.4×10^{-5} to 1.8×10^{-5} m/s, for another reclaimed mine in central West Virginia. A groundwater velocity of 2.0×10^{-5} m/s was determined for a surface mine in eastern Ohio (Mezga, 1973). Ladwig and Campion (1985) observed a groundwater velocity of 6.1×10^{-4} m/s at a surface mine in Pennsylvania. A groundwater velocity range of 2.7×10^{-3} to 4.3×10^{-3} m/s was measured in surface mine spoil in eastern Kentucky (Wunsch and others, 1992). Most of these velocities are below the groundwater velocities commonly measured for true karst aquifers, underground mines, and accentuated fractured rock aquifers. However, the measured groundwater velocities were similar to velocities in unconsolidated glacial sands and gravels (Hawkins and Aljoe, 1992).

Groundwater velocity measurements from the literature should be considered as a range of values and should be applied as such. Determination of the actual groundwater velocity for a site requires on-site testing, which is not possible for premining prediction.

Groundwater Recharge

Initially, after reclamation, diffuse recharge from the surface is generally well below premining levels because of the destruction of soil structure, soil compaction by mining equipment, and low vegetative growth, which tend to promote surface water runoff rather than infiltration (Razem, 1983; Rogowski and Pionke, 1984). Wunsch and others (1992) noted that, during re-excavation, spoil within a few inches of the surface was dry indicating little infiltration was occurring. Decreases in recharge may also be facilitated by increases in porosity in the unsaturated zone (Razem,

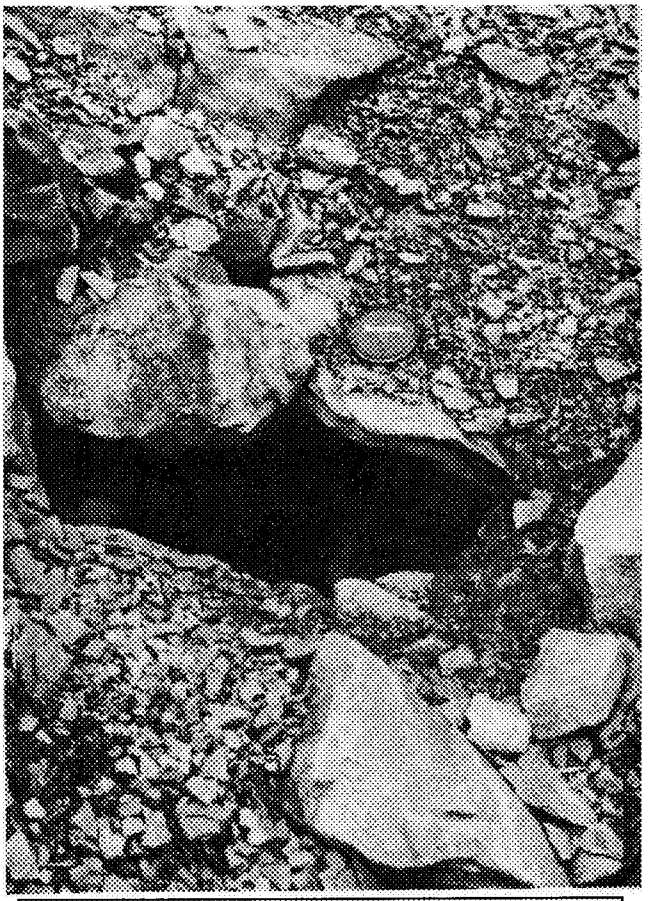

Figure 3.6 Exposed void (swallet) at the surface of a backfilled surface mine.

1984). Flow-duration curves show that receiving streams after mining have reduced base flows, which indicate that recharge is decreased (29% less than pre-mining levels) and surface runoff is increased (Weiss and Razem, 1984). After this initial period, as soil structure and vegetation re-establishes, diffuse recharge from the surface begins to increase. This may coincide with the observed increases in hydraulic conductivity after 30 months, as previously mentioned. The slow recovery of the water table during this period may be linked to the decreased recharge shortly after reclamation and the increased effective porosity and permeability of the spoil.

Some of the recharge from the surface during this early period occurs through discrete openings or voids exposed at the surface (Hawkins and Aljoe, 1991; Wunsch et al., 1992). Figure 3.6 illustrates a surface-exposed void that facilitates groundwater recharge at a surface mine in central Pennsylvania that has been reclaimed for over 15 years. Surface runoff flowing across the mine surface enters the spoil through these exposed voids and flows rapidly downward via conduits to the saturated zone. The recharging water has a limited contact period within the unsaturated spoil zone. In some instances, this infiltrating water will reappear a short distance away (e.g., 100 m) as a high-flowing ephemeral spring, but in most cases the water recharges the spoil aquifer and is more slowly released at perennial discharge points. Experience indicates that these exposed voids continue to receive significant amounts of recharge long after final reclamation, re-establishment of the soil structure, and successful revegetation. Groenewold and Bailey (1979) observed that surface water running into these swallets may enlarge them and cause considerable subsidence from piping of the finer grained materials. However, this has not been observed to be a significant problem in the Appalachian coal fields.

Others contend that mining may improve the recharge potential from undisturbed areas (Cederstrom, 1971). Herring (1977) observed than the overall recharge and surface water runoff to reclaimed surface mines in the Illinois Basin were greatly increased. He attributes the increased recharge to the dramatic increase in permeability of the cast overburden. He observed a four fold increase in recharge from mining one half of a watershed in Indiana. Those two studies did not factor in the impact of mining on the soil horizon as discussed by Razem (1983, 1984). Once the infiltrating water has passed through the soil horizon, it appears that the recharge potential is dramatically increased.

In the Appalachian basin, surface mine spoil aquifers receive a substantial amount of lateral in-flow from adjacent areas (Wunsch and Dinger, 1994). Adjacent unmined areas (low walls and highwalls) as well as previously reclaimed areas will contribute groundwater to the newly reclaimed site. Groundwater modeling by Hawkins and Aljoe (1990) and Hawkins (1994) indicates that groundwater flowing from adjacent areas may be the main source of recharge to the spoil aquifer and that this type of recharge occurs on a more continuous basis at a more consistent but lower rate than the recharge through the exposed surface voids. The surface voids will only recharge the spoil when runoff is occurring. In contrast, lateral recharge is controlled primarily by the hydraulic properties of the adjacent aquifer and the hydraulic gradient.

Under certain conditions, spoil can be recharged from groundwater flow from the underlying strata. If artesian conditions exist beneath the stratum underlying the coal (seat rock), groundwater can flow under pressure via fractures in the intervening strata or through boreholes drilled through the pit floor and recharge the spoil. Artesian-induced recharge has been observed in a reclaimed surface mine in southern Tennessee (Robert S. Evans, personal communication).

Summary

The information and data in this chapter can be used to predict the groundwater hydrologic regime in reclaimed surface mine spoils prior to mining. The data presented here should be viewed as a potential range of values. Given this information, the groundwater velocity, water table elevation, discharge rate, and volume of water that will be stored in the spoil can be predicted. The potential groundwater flow direction and flow paths can also be estimated.

This hydrologic information used in conjunction with the overburden geochemical data can be used to improve mine drainage predictive models and methods. Hydrologic data will give individuals involved with mine drainage prediction a better understanding of the spoil material that is contacted by the groundwater and the physical, spatial, and temporal nature of this contact. This information is directly applicable to the use of special handling of acid-forming materials and placement of alkaline materials to prevent acid mine drainage.

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Chapter 4

IMPACTS OF MINE DRAINAGE ON AQUATIC LIFE, WATER USES, AND MAN-MADE STRUCTURES

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Introduction

"...The influx of untreated acid mine drainage into streams can severely degrade both habitat and water quality often producing an environment devoid of most aquatic life and unfit for desired uses. The severity and extent of damage depends upon a variety of factors including the frequency, volume, and chemistry of the drainage, and the size and buffering capacity of the receiving stream", (Kimmel, 1983).

Drainage from underground coal mines, surface mines, and coal refuse piles is the oldest and most chronic industrial pollution problem in the Appalachian Coal Region. In 1995, 2425 miles (3902 km) of stream in Pennsylvania did not meet EPA-mandated in-stream water quality standards due to over a century of mineral extraction (PA DEP, 1996). The unfavorable repercussions of coal mine drainage in the northern Appalachian Coal Region have been documented in the literature for over a century. It is believed that the first reference to what we now call acid mine drainage in North America was made by Gabriel Thomas, who in 1698 reported: "...And I have reason to believe that there are good coals, also, for I observed the runs of water which have the same colour as that which proceeds from the mines in Wales..."

Pyrite in coal and overlying strata, when exposed to air and water, oxidizes, producing iron and sulfuric acid (Chapter 1). Ferric iron, when discharged to surface water, hydrolizes to produce hydrated iron oxide and more acidity. The acid lowers the pH of the water, making it corrosive and unable to support many forms of aquatic life. Acid formation is most serious in areas of moderate rainfall where rapid oxidation and solution of exposed minerals can occur. Indeed, of the 19,308 km of United States streams reported degraded by acid mine drainage in 1970, 16,920 km or 88 percent were located east of the Mississippi River in the Appalachian coal fields of Pennsylvania, West Virginia, Ohio, eastern Kentucky, Tennessee, Maryland, and Alabama (Warner, 1970). Various impacts range in severity from isolated nuisance type problems to severe water quality impacts affecting large volumes of groundwater and miles of watercourse. Impacted uses include agricultural (irrigation and livestock), industrial, and potability of water supplies along with recreational uses, scenic resource appreciation, and aquatic organism habitat. The aggressive nature of mine drainage may also result in corrosion and incrustation problems with respect to such man-made structures as pipes, well screens, dams, bridges, water intakes, and pumps. The compromising of well casings (water supply or oil and gas wells) can be extremely troublesome because it can then allow the migration and co-mingling of water from one aquifer with another, often leading to inter- and intra- aquifer contamination (Merritt and Emrich, 1970). Acidic mine drainage in particular can also be toxic to vegetation when recharging to the shallow groundwater system and soil water zones.

Effects of Mine Drainage and Metals on Aquatic Macroinvertebrates and Fish

Mine drainage is a complex of elements that interact to cause a variety of effects on aquatic life that are difficult to separate into individual components. Toxicity is dependent on discharge volume, pH, total acidity, and concentration of dissolved metals. pH is the most critical component, since the lower the pH, the more severe the potential effects of mine drainage on aquatic life. The overall effect of mine drainage is also dependent on the flow (dilution rate), pH, and alkalinity or buffering capacity of the receiving stream. The higher the concentration of bicarbonate and carbonate ions in the receiving stream, the higher the buffering capacity and the greater the protection of aquatic life from adverse effects of acid mine drainage (Kimmel, 1983). Alkaline mine drainage with low concentrations of metals may have little discernible effect on receiving streams. Acid mine drainage with elevated metals concentrations discharging into headwater streams or lightly buffered streams can have

a devastating effect on the aquatic life. Secondary effects such as increased carbon dioxide tensions, oxygen reduction by the oxidation of metals, increased osmotic pressure from high concentrations of mineral salts, and synergistic effects of metal ions also contribute to toxicity (Parsons, 1957). In addition to chemical effects of mine drainage, physical effects such as increased turbidity from soil erosion, accumulation of coal fines, and smothering of the stream substrate from precipitated metal compounds may also occur (Parsons, 1968; Warner, 1971).

Benthic (bottom-dwelling) macroinvertebrates are often used as indicators of water quality because of their limited mobility, relatively long residence times, and varying degrees of sensitivity to pollutants. Unaffected streams generally have a variety of species with representatives of all insect orders, including a high diversity of insects classed in the taxonomic orders of Ephemeroptera (mayflies), Plecoptera (stoneflies), and Trichoptera (caddisflies) (EPT taxa). Like many other potential pollutants, mine drainage can cause a reduction in the diversity and total numbers, or abundance, of macroinvertebrates and changes in community structure, such as a lower percentage of EPT taxa. Moderate pollution eliminates the more sensitive species (Weed and Rutschky, 1971). Severely degraded conditions are characterized by dominance of certain taxonomic representatives of pollution-tolerant organisms, such as earthworms (Tubificidae), midge larvae (Chironomidae), alderfly larvae (*Sialis*), fishfly larvae (*Nigronia*), cranefly larvae (*Tipula*), caddisfly larvae (*Ptilostomis*), and non-benthic insects like predaceous diving beetles (Dytiscidae) and water boatmen (Corixidae) (Nichols and Bulow, 1973; Roback and Richardson, 1969; Parsons, 1968). While these tolerant organisms may also be present in unpolluted streams, they dominate in impacted stream sections. Mayflies are generally sensitive to acid mine drainage; however, some stoneflies and caddisflies are tolerant of dilute acid mine drainage.

Fish are often used as indicators of pollution; however, they are not as useful as macroinvertebrates because of their greater mobility. Fish may temporarily swim through a non-lethal impacted area or away from a discharge of intermittent duration.

pH

Most organisms have a well defined range of pH tolerance. If the pH falls below the tolerance range, death will occur due to respiratory or osmoregulatory failure (Kimmel, 1983). Low pH causes a disturbance of the balance of sodium and chloride ions in the blood of aquatic animals. At low pH, hydrogen ions may be taken into cells and sodium ions expelled (Morris et al., 1989). Mayflies are one of the most sensitive groups of aquatic insects to low pH; stoneflies and caddisflies are generally less sensitive to low pH. Mayflies and stoneflies that normally live in neutral water experience a greater loss of sodium in their blood when exposed to low pH than do acid-tolerant species of stoneflies, such as *Leuctra* and *Amphinemura*, whose sodium uptake is only slightly reduced by low pH (Sutcliffe and Hildrew, 1989).

Acid waters typically have fewer species and a lower abundance and biomass of macroinvertebrates than near-neutral pH waters. Attempts have been made to specifically identify limiting factors, and two factors investigated are interruption of the food chain and direct effects of low pH levels on aquatic life. Macroinvertebrates are often grouped by their feeding habits, and assemblages of invertebrates in acidified waters appear to be related to food availability. The fauna of low pH streams is usually composed of shredders (organisms that eat leaves that fall into the stream), collectors (organisms that filter or gather particles of organic matter from the water), and predators. Low pH tends to eliminate species that feed on algae (scrapers or grazers). Low pH may inhibit growth of bacteria which help break down leaves to make them more easily digestible and which also serve as a food source. These observations led early investigators to theorize that low pH levels reduced the food sources for invertebrates, thereby indirectly reducing their numbers. This is partially true; however, more recent studies have shown that direct effects of low pH on aquatic life are more critical than indirect effects on food sources (Rosemond et al., 1992).

Cooper and Wagner (1973) studied the distribution of fish in Pennsylvania streams affected by acid mine drainage. They found fish species were severely impacted at pH 4.5 to 5.5; ten species showed some tolerance to pH 5.5 or less; 38 species were found at pH 5.6 to 6.4; and 68 species were found only at pH greater than 6.4 (Table 4.1). They found that a pH of 4.5 and total acidity of 15 mg/L accounted for complete loss of fish in 90% of streams studied. Although no concentrations of metals were taken into account, Cooper and Wagner indicated that the

Table 4.1 Order of appearance of 44 fish species in Pennsylvania streams with increasing pH levels. Sixty-eight additional species collected were never found at pH below 6.5 (Cooper and Wagner, 1973).

4.5	5.2	6.0	6.1
Ohio lamprey	Creek chub	Stoneroller	Cutlips minnow
		Silverjaw minnow	Fallfish
4.6	5.5	River chub	
Chain pickerel	Yellow perch	Common shiner	6.2
Golden shiner		Silver shiner	Redbreast sunfish
White sucker	5.6	Rosyface shiner	Rainbow darter
Brown bullhead	Bluntnose minnow	Mimic shiner	Variegate darter
Pumpkinseed	Blacknose dace	Northern hogsucker	Mottled sculpin
		Rock bass	
4.7	5.9	Smallmouth bass	6.4
Creek chubsucker	Brown trout	Greenside darter	Redside dace
Largemouth bass	Longnose dace	Fantail darter	Spotfin shiner
	Margined madtom	Johnny darter	Spottail shiner
5.0	Tessellated darter	Banded darter	Pearl dace
Brook trout	Slimy sculpin	Blackside darter	Green sunfish

absence of fish in acidified waters can be related to dissolved metals at certain pH levels. They also indicated that sulfates, a major constituent of acid mine drainage, did not become toxic to fish until concentrations exceeded the saturation level of several thousand mg/L.

The primary causes of fish death in acid waters is loss of sodium ions from the blood and loss of oxygen in the tissues (Brown and Sadler, 1989). Acid water also increases the permeability of fish gills to water, adversely affecting gill function. Ionic imbalance in fish may begin at a pH of 5.5 or higher, depending on the tolerance of the species; severe anoxia will occur below pH 4.2 (Potts and McWilliams, 1989). Low pH that is not directly lethal may adversely affect fish growth rates and reproduction (Kimmel, 1983).

Metals

Heavy metals can increase the toxicity of mine drainage and also act as metabolic poisons. Iron, aluminum, and manganese are the most common heavy metals which can compound the adverse effects of mine drainage. Heavy metals are generally less toxic at circumneutral pH. Trace metals such as zinc, cadmium, and copper, which may also be present in mine drainage, are toxic at extremely low concentrations and may act synergistically to suppress algal growth and affect fish and benthos (Hoehn and Sizemore, 1977). Some fish, such as brook trout, are tolerant of low pH, but addition of metals decreases that tolerance. In addition to dissolved metals, precipitated iron or aluminum hydroxide may form in streams receiving mine discharges with elevated metals concentrations. Ferric and aluminum hydroxides decrease oxygen availability as they form; the precipitate may coat gills and body surfaces, smother eggs, and cover the stream bottom, filling in crevices in rocks, and making the substrate unstable and unfit for habitation by benthic organisms (Hoehn and Sizemore, 1977). Scouring of iron flocculant increases turbidity and suspended solids and may inhibit fish feeding.

Aluminum rarely occurs naturally in water at concentrations greater than a few tenths of a milligram per liter; however, higher concentrations can occur as a result of drainage from coal mines, acid precipitation, and breakdown of clays (Hem, 1970). The chemistry of aluminum compounds in water is complex. Aluminum combines with organic and inorganic ions and can be present in several forms. Aluminum is least soluble at a pH between 5.7 and 6.2; above and below this range, aluminum tends to be in solution (Hem, 1970; Brown and Sadler, 1989).

Most information on the effects of low pH and aluminum on aquatic life is based on studies of acid precipitation, such as those summarized in Haines (1981), Morris et al. (1989), and Mason (1990). Of the three major metals present in mine drainage, aluminum has the most severe adverse effects on stream aquatic life. The addition of aluminum ions compounds the effect of low pH by interacting with hydrogen ions, further decreasing sodium uptake, and increasing sodium loss in blood and tissues. High calcium concentrations generally reduce mortality and

sublethal effects of low pH and elevated aluminum by reducing the rate of influx of hydrogen ions into the blood. Streams most susceptible to degradation from elevated aluminum, however, normally have low concentrations of calcium.

Stream investigations by the author have indicated that a combination of pH less than 5.5 and dissolved aluminum concentration greater than 0.5 mg/L will generally eliminate all fish and many macroinvertebrates. Fishflies, alderflies, and several genera of stoneflies, caddisflies, and true flies (particularly within the family Chironomidae) are tolerant of low pH and high dissolved aluminum. Mayflies are the aquatic insects most affected by a combination of low pH and acidic water. Some exceptions do occur, for example, the mayflies *Ameletus* and *Ephemerella funeralis* are tolerant of slightly acidic water, especially at low aluminum concentrations (less than 0.2 mg/L). Aluminum is most toxic to fish at pH between 5.2 and 5.4 (Baker and Schofield, 1982).

Streams with precipitated aluminum usually have lower numbers and diversity of invertebrates than streams with low pH and high dissolved aluminum. Precipitated aluminum coats the stream substrate, causing slippery surfaces and difficulty for insects to maintain position in the current. Aluminum precipitate can also be directly toxic to macroinvertebrates and fish. Rosemond et al. (1992) stated that deposition of aluminum hydroxide particles on invertebrates blocks surfaces important for respiratory or osmoregulatory exchange. Aluminum precipitate also eliminates most of the filter feeders, such as Hydropsychid caddisflies, which normally comprise a major portion of total stream macroinvertebrates. Precipitated aluminum can also accumulate on fish gills and interfere with their breathing (Brown and Sadler, 1989).

Iron is a common component of mine drainage which can have a detrimental effect on aquatic life. Like aluminum, iron can be present in several forms and combines with a variety of other ions. The impact of mine drainage containing elevated iron on aquatic ecosystems is complex. Little animal life may be found in streams with the lowest pH (under 3.5) and elevated dissolved iron concentrations. Alderflies, fishflies, dipterans, and aquatic earthworms will be present if the pH rises slightly. With further increases in pH, a more diverse assemblage of macroinvertebrates may be present, although total numbers may be lower than in nondegraded streams (Table 4.2 and Figure 4.1). Wiederholm (1984), Letterman and Mitsch (1978), and Moon and Lucostic (1979) presented results of research on the effects of mine drainage and elevated iron on aquatic life.

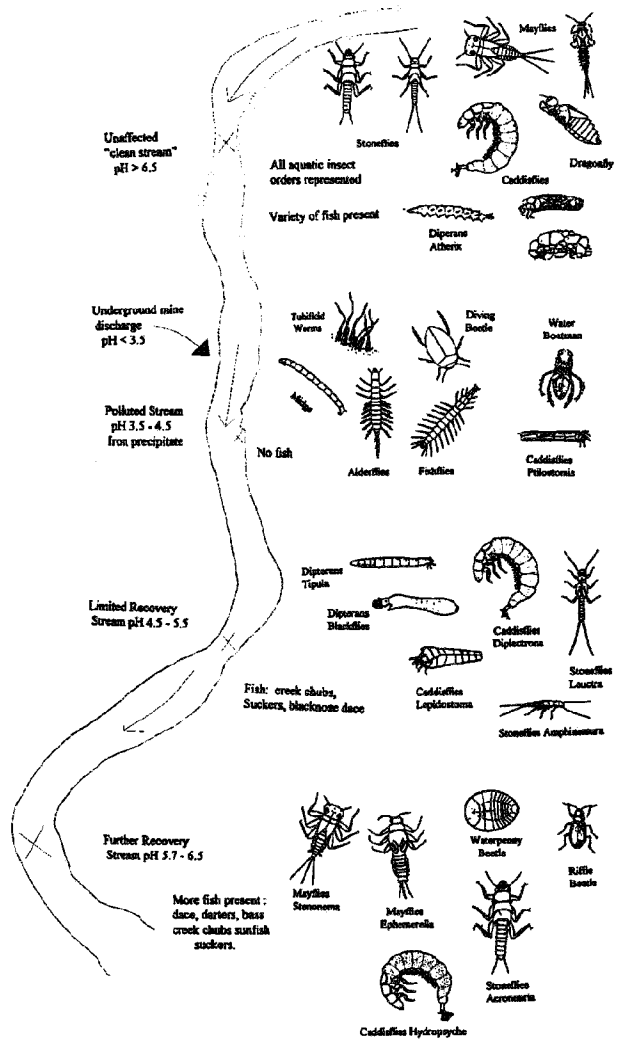

Figure 4.1 Macroinvertebrates and fish in polluted and recovery zones of a stream receiving acid mine drainage.

Iron precipitates at a pH greater than 3.5 and does not reenter solution at higher pH. Because iron can form precipitates at a lower pH than aluminum and can be present in streams with pH less than 4.5, separating the effect of iron from the effect of low pH is difficult. Precipitation of ferric hydroxide may result in a complete blanketing of the stream bottom, adversely affecting both macroinvertebrates and fish (Hoehn and Sizemore, 1977). The severity is dependent on stream

pH and the thickness of the precipitate. Generally, the effect of precipitated iron is less severe in alkaline conditions. Many fish and macroinvertebrates are tolerant of iron precipitate in alkaline water; however, total numbers and diversity are usually lower than in unaffected streams. Koryak et al. (1972) found that ferric hydroxide greatly diminished total biomass of benthic organisms and limited fish populations in streams with survivable pH levels. The caddisfly genus *Hydropsyche*, which is generally sensitive to low pH, can live in alkaline streams with iron precipitate. The Hydropsychid caddisfly *Diplectrona*, however, is tolerant of iron precipitate and pH less than 5.0. Mayflies are generally more tolerant of alkaline mine drainage than acid mine drainage. Mayflies such as *Ephemerella*, *Baetis*, *Attenella*, and *Acentrella* may be found in alkaline streams with iron precipitate. *Acroneuria* and *Paragnetina* stoneflies are tolerant of alkaline water with iron precipitate but are intolerant of acid (Table 4.2). Since iron precipitate particles often cover the bodies of macroinvertebrates that otherwise appear healthy, the iron precipitate itself appears to be less toxic than aluminum precipitate. Smallmouth bass, rock bass, creek chub, johnny and rainbow darter, white sucker, common shiner, and river chub are some fish species that can be found in alkaline water with iron precipitate.

Table 4.2 Representatives of macroinvertebrate, fish, and algae communities in unaffected streams, streams impacted by acid mine drainage, stream recovery zones, and streams with alkaline mine drainage and iron precipitate.

UNAFFECTED STREAM UPSTREAM OF DISCHARGE	A diversity of aquatic insect orders Abundance of EPT taxa (mayflies, stoneflies, caddisflies) and other orders Variety of fish species, depending on habitat
ACID MINE DISCHARGE pH <3.5 high dissolved iron	
STREAM pH 3.5 - 4.5 IRON PRECIPITATE	Elimination of most EPT taxa Dominance by midges (Chironomidae) Also present: alderfly (*Sialis*), fishfly (*Nigronia*), diving beetles (Dytiscidae), water bugs (Corixidae) Algae: *Euglena, Ulothrix, Pinularia, Eunotia* No Fish
LIMITED RECOVERY STREAM pH 4.5 - 5.5	More insect orders represented Stoneflies: *Leuctra, Amphinemura* Caddisflies: *Diplectrona, Lepidostomis, Polycentropus*; Blackflies (Simuliidae), Craneflies (Tipulidae) At higher pH range: Mayfly: *Ameletus*; Fish: creek chub, white sucker, blacknose dace, brook trout
RECOVERY ZONE STREAM pH 5.7 - 6.0	Additional EPT taxa: *Acroneuria, Stenonema, Ephemerella funeralis*; Elmid Beetles Algae: Diatoms, Flagellates, Green algae, *Oscillatoria*
FURTHER RECOVERY STREAM pH > 6.0	Variety of EPT taxa: *Ephemerella, Baetis, Isonychia, Acentrella, Attenella, Hydropsyche* Variety of fish species
ALKALINE OR NEUTRALIZED MINE DRAINAGE STREAM pH > 6.0 IRON PRECIPITATE	Variety of EPT taxa may be present; But usually low abundance *Ephemerella, Baetis, Acentrella, Paragnetina, Acroneuria, Leuctra, Cheumatopsyche, Hydropsyche,* Elmid beetles, *Corydalus* Variety of fish species, reduced numbers: creek chub, river chub, white sucker, johnny darter, rainbow darter, rock bass, smallmouth bass, pumpkinseed

Sources: Roback and Richardson, 1969; Parsons, 1968; Warner, 1971; Kimmel, 1983; and stream investigations by author.

Manganese is another metal that is widely distributed in mine drainage. Manganese can be present in a variety of forms and compounds and complexes with organic compounds. Manganese is difficult to remove from discharges because the pH must be raised to above 10.0 before manganese will precipitate. Manganese, therefore, is persistent and can be carried for long distances downstream of a source of mine drainage. Less information is available on the effects of elevated manganese concentrations on aquatic life than the effects of iron and aluminum. Perhaps this is because manganese in mine drainage is usually associated with other metals which may have a more deleterious effect or mask the effect of the manganese. Manganese discharge limits have traditionally been based on the objectionable discoloration effects of manganese at concentrations as low as 0.2 mg/L in water supplies rather than effects on aquatic life.

Kleinmann and Watzlaf (1988) summarized the results of manganese toxicology tests on fish and invertebrates. They concluded that manganese tolerance limits for fish reported in the literature varied widely and that the lowest toxic concentrations were reported in watersheds with very low levels of hardness. They reported that several researchers found that hardness concentrations as low as 10 mg/L protected fish from adverse effects of manganese. Bioassay tests on invertebrates produced tolerance rates for manganese ranging from 15 to 50 mg/L, depending on the test organism.

The less common precipitated form of manganese may be more toxic than the dissolved form. Werner et al. (1982) noted the presence of precipitated manganese hydroxide which formed a black coating over the substrate of a Pennsylvania stream receiving mine drainage. They reported that the precipitate along with siltation significantly lowered macroinvertebrate species diversity and changed the stream community structure.

Summary

Mine drainage effects on aquatic life vary widely, from elimination of all but the few most tolerant algae, macroinvertebrates, and fish, to little or no effect. The most severe effects are caused by high volume, low pH discharges with high concentrations of dissolved metals that drain into lightly buffered streams and produce accumulations of precipitated iron or aluminum. Little or no effect may occur from low volume or alkaline discharges with relatively low concentrations of metals that drain into moderate or highly buffered streams.

Water Uses and Man-Made Structures

"Mine drainage can be considered to be an unstable aqueous system undergoing continuous change. The composition reflects not only its origin but also what it encounters along its flow path and forms the most important criteria for the selection and design of control systems and/or treatment facilities. Subject to the location of the sample collection with respect to point of pyrite solubilization, such a solution has; been diluted, dissolved additional mineral components, undergone internal reaction which may have deposited ferric oxyhydroxides in its stream bed and possibly been mixed with other pollution sources, domestic, industrial, or agricultural." (Lovell, 1976).

Chemical Impacts on Potable and Industrial Water Supplies

The following is a quote from a 1937 report on the detrimental aspects of mine drainage: "...the acid water caused excessive corrosion of the federal navigation locks and dams, ships and barges, bridges and culverts, pipelines and plumbing. The acid, iron sulfate, and iron oxide (red water) often destroyed all fish and aquatic life, interfered with nature's self-purification of the streams sometimes perhaps favorably, in other cases detrimentally, made water unfit for drinking or household purposes, and caused unsightly reddish brown spots on fabrics in laundries and textile factories and scum in washbowls, sinks and tubs. The water was destructive, scale forming, and unsuitable for use in locomotive and power plant boilers, in manufacturing industries, and in municipal waterworks..." (Hodge,1937).

In areas where surface and groundwaters have been contaminated by mine drainage, treatment of water supplies becomes more difficult, more time consuming, and more expensive. Listed below are constituents which are typically elevated in mine drainage or in groundwater recharged by mine drainage and their properties which can render a municipal or domestic water supply unusable without treatment, unpalatable, or aesthetically offensive.

Iron - The taste threshold of iron in water has been given as 0.1 and 0.2 mg/L of iron from ferrous sulfate and ferrous chloride respectfully. It has been reported that ferrous iron imparts a taste at 0.1 mg/L and ferric iron at 0.2 mg/L. Staining of plumbing fixtures occurs at 0.3 mg/L. Certain animals are sensitive to minor

changes in iron concentration. Cows will not drink enough water (taste threshold 0.3 mg/L) if it is high in iron, and consequently, milk production is affected (Dairy Reference Manual, Third Edition, 1995).

pH - The hydrogen ion concentration can affect the taste of water. At a low pH water tastes sour. The bactericidal effect of chlorine is weakened as pH increases and it is advantageous to keep the pH close to 7. Water with a pH below 7.0 is corrosive to plumbing and can result in constituents such as copper, zinc, cadmium, and lead being dissolved in drinking water.

Sulfate - High sulfate levels in water may have laxative effects and cause taste and odor problems.

Total Dissolved Solids (TDS) - Excessive TDS in drinking water is objectionable because of possible physiological effects and unpalatable mineral tastes. Physiological effects related to TDS include laxative effects, effects on the cardiovascular system, and toxemia associated with pregnancy.

Manganese - Elevated manganese causes several specific problems when encountered in drinking water, such as unpleasant tastes, deposits on food, laundry staining, reduction in water main capacity, and discoloration of porcelain fixtures. Staining may occur at concentrations above 0.5 mg/L.

The major problem of most industrial water users is corrosion control. As discussed previously, increased acidity has been found to accelerate the corrosion of industrial water-using equipment, navigational equipment, buried transmission lines, and ordinary metal structures such as culverts, bridges, and pumps (Appalachian Regional Commission, 1969; and Skelly and Loy, 1973). Scale formation (incrustation) produced by increased water hardness reduces the heat exchange efficiency of boilers (Skelly and Loy, 1973). Elevated iron and manganese concentrations interfere with textile dyeing and metal plating (Appalachian Regional Commission, 1969).

Corrosion and Incrustation of Wells, Pipes, and Other Metal Structures

Damage to plumbing done by **corrosive** water represents a major expense to utilities and water users. The following is a list of indicators of corrosive water with respect to metal casings, screens, and other metal fixtures and conveyance devices: (Driscoll, 1986)

1. **Low pH**. pH below 7.0.
2. **Dissolved oxygen**. If dissolved oxygen in groundwater exceeds 2 ppm, corrosive water is indicated. Dissolved oxygen is likely to be found in shallow water table wells.
3. **Hydrogen sulfide**. Less than 1 ppm can cause severe corrosion and this amount can be detected by odor or taste. The presence of hydrogen sulfide can be detected readily from its characteristic rotten-egg odor.
4. **Total dissolved solids** Above 1000 ppm, the electrical conductivity of the water is great enough to cause serious electrolytic corrosion.
5. **Carbon dioxide** above 50 ppm.
6. **Chlorides** above 500 ppm.

As is evident by comparing the chemical signature of mine drainage with the list of corrosion indicators, the groundwater environment in areas affected by mine drainage (Chapter 1) has the potential to be highly corrosive. There are two recognized types of corrosion; chemical and electrochemical.

Chemical corrosion occurs when a particular constituent is present in water in sufficient concentration to cause rapid removal of material over broad areas. Chemical corrosion can cause severe damage regardless of the amount of total dissolved solids (Driscoll, 1986).

A second type of corrosion known as electrochemical corrosion is more prevalent. Two conditions are necessary for electrochemical corrosion to proceed; a difference in electrical potential on the surface of the metal(s), and water with enough dissolved solids content to act as a conductor. A difference in electrical potential can occur between two different metals or on the surface of the same metal in areas around joints, machine cuts, exposed threads, or breaks in surface coatings. (Driscoll, 1986)

Incrustation is a second major problem for wells, pumps and associated metal structures which is related to water quality. The kind and amount of dissolved minerals and gases in natural waters determine their tendency to deposit mineral matter as incrustation. The major forms of incrustation include; (1) incrustation from precipitation of calcium and magnesium carbonates or their sulfates; (2) incrustation from precipitation of iron and manganese compounds, primarily their hydroxides or hydrated oxides; and (3) plugging caused by slime-producing iron bacteria or other slime-forming organisms.

(Driscoll, 1986) Chemical incrustation usually results from the precipitation of carbonates, principally calcium, from groundwater in the proximity of the well screen. Other substances, such as aluminum silicates and iron compounds, may also be entrapped in the scalelike carbonates that cement sand grains together around the screen. The deposit fills the voids, and the flow of water into the well is reduced proportionally.

Iron and manganese incrustation is another common problem in pumping wells. During pumping, velocity-induced pressure changes can disturb the chemical equilibrium of the groundwater and result in the deposition of insoluble iron and manganese hydroxides. these hydroxides have the consistency of a gel, and may occupy relatively large volumes; over time, they harden into scale deposits.

Indicators of incrusting groundwater are:

1. **pH** - pH above 7.5
2. **Carbonate hardness**- If the carbonate hardness of the groundwater exceeds 300 ppm, incrustation due to deposition of calcium carbonate is likely
3. **Iron**- If the iron content of the water exceeds 2 ppm, incrustation due to precipitation of iron is likely.
4. **Manganese** - If the manganese content of the water exceeds 1 ppm, coupled with high pH, incrustation is extremely likely if oxygen is present (Driscoll, 1975).

Another common problem with well casings, screens, mains, and pipelines in the coal measures is the formation of **iron bacteria** in openings or adjacent areas due to elevated iron and/or manganese in the local groundwater. Crenothrix, Gallionella, and other iron bacteria utilize iron as a source of energy and store it in their microbial protoplasm. Problems are generally encountered at iron concentrations above 0.2 mg/L. These bacteria can become so numerous in the conveyance system that clogging can occur with resultant flow loss. Iron bacteria thrive best in the dark and are found most frequently in water containing little or no oxygen and a considerable amount of carbon dioxide along with dissolved iron. These bacteria obtain their energy by oxidizing ferrous ions to ferric ions. Precipitation of the iron and rapid growth of the bacteria create a voluminous material that quickly plugs any openings.

Durability of Concrete Structures

Two of the principal aggressive factors which affect the durability of concrete structures and are also a common by-product of mining in the eastern coal measures are sulfates and acidity. Problems resulting from **acid attack** to concrete are dependent on the following variables: (1) total acidity and pH of groundwater and (2) groundwater replenishment rate. When in contact with portland cement concrete, acid will attack the exposed surface and be neutralized by the alkalinity of the concrete. A given quantity of an acid will destroy a given mass of concrete, in proportion to the total alkalinity of the concrete. Without acid replenishment, the reaction stops. In static groundwater conditions acidity is the governing parameter, however the greater the anticipated movement of groundwater the greater is the replenishment rate of acid and the more important is the role of pH.

As a guideline, a pH of 5.0 and total acidity of 25 milligram equivalents per 100 grams of soil indicates a potentially aggressive groundwater situation. (Bealy, 1980). Such conditions would require a more comprehensive analysis of installation characteristics to determine if countermeasures are necessary to insure durability.

Sulfates in soil, groundwater, or mine effluents can be highly aggressive to portland cement concrete by combining chemically with certain constituents of the concrete, principally C_3A, to form calcium sulfoaluminate. This reaction is accompanied by expansion and eventual disruption of the concrete. If the concrete mass is dense, the action is superficial, such as rust on the surface of metal. If the concrete is porous, the action can be progressive through the mass. The stronger the sulfate concentration, the more active the corrosion (Table 4.3).

Table 4.3 Attack on Concrete by Waters Containing Various Sulfate Conc. (Bealy, 1980).

Relative Degree of SO_4 Attack	PPM Sulfate in Water Samples
Negligible	0 to 150
Positive	150 to 1500
Severe	1500 to 10000
Very Severe	10000 or more

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Chapter 5

PLANNING THE OVERBURDEN ANALYSIS

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Introduction

This chapter discusses when and where overburden analysis (OBA) is needed and how OBA can be used as one of the tools in the prediction of mine drainage quality. It also describes procedures for overburden sampling and sample handling. Sampling is addressed from a practical experience-oriented perspective, rather than theoretical.

The results of overburden analyses are generally used in two ways:

1. as a permitting tool and
2. as a management tool.

Applications of these tools are discussed in other chapters in this volume.

Purpose of OBA

Permitting Tool

As a permitting tool, OBA can be used to:

1. demonstrate that the proposed mining can be accomplished without causing pollution to surface or ground water;
2. assess the probable cumulative impacts of mining on the hydrologic balance; and,
3. aid in the design of the mining and reclamation plan to prevent or minimize damage to the hydrologic balance within and outside the proposed permit area.

Pennsylvania regulations require an OBA to be submitted for a mine site unless it is determined by the Department that "it has equivalent information..." (25 PA Code Chapter 87, §87.44). OBA is seldom waived for sites that meet any of the following criteria:

1. the proposed mine site lies within a High Quality, Exceptional Value, Wilderness Trout Stream, or other stream sensitive to mining impact;
2. the proposed mine site is in close proximity to a public water supply or mining has the potential to impact a public water supply or numerous private water supplies;
3. postmining water quality data in the watershed on the seam(s) of interest is poor or unavailable;
4. there is a history of acid mine drainage (AMD) in the local area, and the applicant is proposing to mine the same seams that caused AMD in the past;
5. alkaline materials: e.g., limestone or calcareous shale, sandstone, or siltstone, are proposed to be removed from the mine site.

OBA Waivers

When the proposed mine site does not meet any of the above criteria, waiving of the requirement for OBA may be considered. A waiver request must show that there is equivalent information available. The Department of Environmental Protection's Bituminous Surface Mine application requires that the request include:

1. a discussion of the relationship between the proposed mine site and the five categories discussed above;
2. an explanation of the existing hydrogeologic information that supports the waiver (for example, stratigraphy, water chemistry, and nearby overburden analyses); and
3. previous mining history on the watershed or adjacent areas (including percentage or relative acreages of mined and unmined portions of the watershed) and the postmining water quality associated with the proposed seams (including specific examples).

Other geochemical clues, such as water quality from previously mined areas, can often help support a request for a waiver of overburden analysis. These other prediction tools and how they are used are discussed in Chapters 8, 9, and 10.

Management Tool

As a management tool OBA can be used to:

1. calculate alkaline addition rates;
2. determine the distribution of pyritic zones which may require special handling or avoidance;
3. identify alkaline zones which can be incorporated into a mining plan to prevent acidic drainage; and,
4. determine mining feasibility, including potential environmental impacts, before investing a large amount of money in leasing (advance royalties) and permit application preparation.

With proper planning, performing OBA as a management tool also may satisfy permitting requirements if a decision is made to proceed with an application to mine.

Information Needed to Conduct an OBA

The site specific mining data needed to properly plan an OBA includes:

1. Mining limits:
   a. boundaries of the proposed area to be affected by coal removal;
   b. proposed maximum highwall heights;
   c. type of mining - for example, contour/block cut or hill top removal; and
   d. accessibility.
2. Geologic considerations such as coal seam identification, depth of weathering, and stratigraphic variation.
3. Information that is available in the permit files of the District Mining Offices, such as water quality data from previous permits or applications covering the same or adjacent areas.
4. OBAs from the same or adjacent areas.
5. Publications of the Pennsylvania Topographic and Geologic Survey, United States Geologic Survey (USGS), the former United States Bureau of Mines (USBM), US Army Corps of Engineers, and Previous Mine Drainage Pollution Abatement Watershed projects conducted under Operation Scarlift funded under Act #443, entitled the "Land and Water Conservation and Reclamation Act" from the late 1960s and early 1970s. These publications can include information such as:
   a. coal-bed outcrop maps,
   b. generalized stratigraphic sections,
   c. coal seam isopach maps,
   d. structure contour maps.

Particularly useful publications include "Map 61" the "Atlas of Preliminary Geologic Quadrangle Maps of Pennsylvania," (Thomas M. Berg and Christine M. Dodge), and Mineral Resource Reports M86, M89, M90, M91, M92, M93, M94, M96 and M98 which are about the coal resources of Greene, Allegheny, Butler, Fayette, Clarion, Washington, Westmoreland, Cambria and Blair, and Indiana Counties respectively. These publications are distributed by the Bureau of Topographic and Geologic Survey and are available from the State Book Store. Additional sources of information can be identified from the "Pennsylvania Geological Publications." This catalogue is published by the Bureau of Topographic and Geologic Survey and contains listings of many of the geologic reports written about Pennsylvania.

Old and current deep mine maps are available from the Office of Surface Mining, Appalachian Region Coordination Center, at 3 Parkway Center, Pittsburgh, PA; Pennsylvania Bureau of District Mining Operations, Division of Deep Mine Permitting in McMurray; and Pennsylvania Bureau of Deep Mine Safety in Pottsville and Ebensburg. These agencies have map repositories containing prints, originals, and microfilm. Copies of these documents are readily obtained. These repositories include the Works Progress Administration (W.P.A.) deep mine maps prepared in the 1930s. These maps cover nearly all the coal fields. Each map covers an area that is 1/9 of a 15' quadrangle. In addition to showing mining limits, deep mine maps frequently show structure contours. This information can be very helpful in planning OBA drilling.

Other considerations in developing an OBA drilling plan include:

a. Exploration equipment. It is important to understand the errors that are likely with different types of drilling equipment. These differences will have an impact on the ability to obtain unbiased representative samples. The choice of exploration equipment is also important in establishing costs.

b. The type of overburden analysis to be performed. This is important in knowing how much sample is required for the specific type of testing to be employed, and the time needed to analyze the samples.

c. Time constraints. For example, air rotary drilling is normally faster than coring.

d. Economic constraints. For example, air rotary drilling is generally less expensive than coring.

Preparing an OBA Proposal

The obvious and most frequently asked questions that operators and consultants have when preparing an OBA proposal are:

1. Should holes be drilled for OBA?
2. How many OBA holes are needed?
3. Where should they be drilled?

Once these details have been worked out, preliminary work can be started.

The first step in the development of an OBA proposal is to plan for the drilling. While there may appear to be savings associated with performing the drilling for the overburden analysis at the same time as the initial exploration drilling, it is generally preferable to exploratory drill the entire site first. This preliminary drilling enables the determination of cover heights and the lateral extent of the various lithologies. This information can then be used to better locate the overburden holes to represent lithologic variation and degree of weathering within the site. If research and exploration are done prior to drilling the OBA holes, it is less likely that there will be a need to drill additional OBA holes later in the permitting process.

Areal Coverage---Number of Holes per Ac (ha)

A rule of thumb developed in Pennsylvania in the 1980s to determine a suggested minimum number of overburden holes was:

$$\frac{\text{Number of ac (ha) to be mined}}{100 \text{ ac } (40.47 \text{ ha})} + 2 = \text{Number of Overburden Holes}$$

If the first part of the equation resulted in a fraction, it was rounded to the closest whole number. For example:

$$\frac{143 \text{ ac}}{100 \text{ ac}} + 2 = 3 \quad \text{or} \quad \frac{57.9 \text{ ha}}{40.5 \text{ ha}} + 2 = 3$$

$$\frac{49.99 \text{ ac}}{100 \text{ ac}} + 2 = 2 \quad \text{or} \quad \frac{20.2 \text{ ha}}{40.5 \text{ ha}} + 2 = 2$$

$$\frac{179 \text{ ac}}{100 \text{ ac}} + 2 = 4 \quad \text{or} \quad \frac{72.4 \text{ ha}}{40.5 \text{ ha}} + 2 = 4$$

This method included the assumption that, for mines where OBA was requested, at least 2 holes were needed to determine whether the drilling was representative. This two hole minimum is still in use. More recent data show that the actual sampling density for acid base accounting (ABA) drill holes is greater than the "rule of thumb." A recent survey of overburden hole coverage revealed that on average there was one hole for each 15.5 ac (6.3 ha) of coal removal for 38 sites (Table 5.1).

Table 5.1 Number of acres per OBA hole based on data from Brady et al., 1994.

n=38	coal acreage (ha)	number of ac (ha) per oba hole
mean	43.5 (17.6)	15.5 (6.3)
median	30.3 (12.3)	11.9 (4.8)
minimum	5.0 (2.0)	2.3 (0.9)
maximum	172.5 (69.8)	44.9 (18.2)
std. Dev.	38.0 (15.4)	10.6 (4.3)

A similar survey of 31 Small Operator Assistance Program (SOAP) applications received in the 1993 calendar year revealed that on average there was one hole for each 18.8 ac (7.6 ha) of coal removal, Table 5.2.

Table 5.2 Number of acres per OBA hole based on SOAP applications received in 1993.

n=31	coal acreage (ha)	number of ac (ha) per oba hole
average	72.6 (29.4)	18.8 (7.6)
median	55.0 (22.3)	15.7 (6.4)
minimum	6.0 (2.4)	3.0 (1.2)
maximum	220.0 (89.0)	53.5 (21.7)
std. Dev.	54.6 (22.1)	12.3 (5.0)

The above tables give an idea of the range of sampling intensity used in Pennsylvania. The ranges in the data are due to a multitude of factors. These include stratigraphic complexity of the site, shape of the site, and availability of other prediction tools. The data apply only to permit applications that had overburden analysis data. Approximately 30 to 40% of applications do not require submittal of overburden analysis

because of the availability or equivalent prediction data.

Operational Considerations

The overburden analysis drilling program must accurately represent the overburden to be encountered. Therefore, the overburden holes must be located within the limits of the proposed mining area. Some holes must be located at maximum highwall conditions, and the holes must represent all of the strata to be encountered by mining.

Other holes should be located under low and average cover conditions to provide representative sampling of the overburden where zones may be missing or which may have been altered due to surface weathering.

Stratigraphic Variation

It is important to provide enough drill holes to adequately represent the site, including any spatial lithologic variation. One of the first references to the minimum overburden hole spacing was contained in the West Virginia Surface Mine Drainage Task Force's "Suggested Guidelines for Surface Mining in Potentially Acid-Producing Areas" (1978), which recommended that all surface mining in potentially acid producing areas be within 1 km (approximately 3300 ft) of a sampled overburden analysis hole or highwall.

Donaldson and Renton (1984) and Donaldson and Eble (1991) indicated that although cores spaced up to 2 mi. (3 km) apart in the Pittsburgh coal were adequate to reflect major thickness and sulfur trends, this spacing was not adequate for mine design. They felt that lateral Pittsburgh coal bed sampling at intervals on the order of 1200 to 1400 ft (365 to 427 m) or less than 500 ft (152 m) for the Waynesburg coal along with geostatistics are necessary to determine small-scale sulfur content trends.

The Problem of Obtaining Representative Samples

The maximum thickness of each lithologic unit to be represented by one vertical sample interval will be discussed later under "Compositing and Laboratory Preparation." It is also discussed on pages 29 to 30 of Part 1 "Collection and Preparation of Sample" in the "Overburden Sampling and Testing Manual" by Noll et al. (1988).

Noll et al. (1988) do not however discuss the subtle complexity of ensuring accurate, non-biased, representative samples. It does stress that it is critical that 100% of the sample volume be included for a sample interval for compositing purposes, because of possible geochemical variations within the three foot (0.9 m) interval. The ultimate sample size used in Acid Base Accounting (ABA) is 1 g for total percent sulfur and 2 g for the neutralization potential (NP) test. Therefore, assuming no loss or contamination of the zone being sampled, only 1 g to 2 g are tested out of a 25,550 g sample (based upon a 4.5 in. (11.4 cm) diameter drill bit and using an average rock density of 170 lbs/ft^3 (2,723 kg/m^3)).

In reality, this 1 g to 2 g represents a lithologic unit in a drill hole which itself may extend laterally to 25 ac (10 ha) and up to a half a billion grams of material. To better comprehend this degree of representativeness, consider the following analogy: It is equivalent to evaluating the quality of an apple crop by examining one apple in a 7,000 acre (2,833 ha) orchard - for example, an average of 238,000 lbs of apples per ac and approximately 3 apples per lb. (U.S. Dept of Agriculture personal communication, 1996). There has been extensive literature, and, in fact, a complete science integrating geology and statistics to spatial sampling and the determination of optimal sampling patterns for estimating the mean value of spatially distributed geologic variables. For information on geostatistics the authors suggest Journel and Huijbregts (1981), Webster and Burgress (1984), and J.C. Davis (1986).

Fortunately, the geologic systems responsible for the deposition and alteration of the sediments and their chemical quality do not operate in a completely random fashion at the cubic centimeter level and, thus, do not produce overburden samples which are statistically independent. Although there are exceptions, most of the geologic systems, especially those which produce calcareous material, operate over large areas with some degree of order, and deposit laterally pervasive units (Caruccio et al., 1980). Lateral continuity has also been observed in high sulfur strata. Facies changes can provide variations in lithology and the degree of surface weathering can cause changes to the percent total sulfur and NP over short distances. Therefore, it is imperative to know the areal extent of any alkaline or acidic material, high energy paleodepositional environments (for example, channel sandstones), and the degree or depth of weathering. Adequate exploratory drilling is essential to the development of a representative overburden sampling plan.

A recent study suggested that the sulfur is not uniformly distributed in a homogeneous fashion, but is controlled by the nugget effect; i.e., distributed in clusters of hot spots similar to large chips or chunks of chocolate in a cake. If this is the case, accurately determining the mean percent total sulfur of a particular stratum may be difficult, which could in turn lead to under-predicting the potential to produce AMD (Rymer and Stiller, 1989). It could also result in under predicting the site's alkaline potential.

Concern over the nugget effect may be overemphasized. The concentration of total sulfur at a mine site may not be the critical factor of whether or not AMD will be produced. The acidity produced in laboratory experiments appears only to be strongly related to percent total sulfur for sulfur values above 1.0 parts per thousand (ppt) with acidity production being negligible for sulfur of lesser value unless there is a paucity of NP (Rose et al., 1983). Department experience has shown that, in the field, sulfur as low as 0.5% (and possibly somewhat less) can be a problem. As discussed in Chapter 11, the presence of significant NP appears to be a more critical factor, than percent sulfur.

The tendency for the mean percent total sulfur at a site to be skewed to the right is probably just a natural distribution of data involving the plotting of a quantity where the left boundary or minimum abscissa is zero, and there is essentially no right boundary. For example, most sulfur values in coal overburden are less than 0.5%; a rare few are as high as 10 to 20%. Pure pyrite has a percent sulfur of 53.4% (the maximum right-hand value). Thus, a few high values will skew data to the right. This is a commonly observed distribution in geologic data (Koch et al., 1980).

Regardless of the distribution of sulfur or carbonates at mine sites, the rule of thumb for the number of overburden holes sampled when combined with careful consideration of highwall heights, weathering zones, and stratigraphic variation, and the other techniques of mine drainage prediction, has proven to be effective. In order to identify these areas of the proposed mine site which may be different than the general mine site prior to drilling, it is helpful to look at the other geochemical clues which can provide insight into the presence of acidity or alkalinity producing materials. These can help define the extent and degree of variability of the overburden so that overburden holes can be located to adequately represent the entire site.

Sample Collection and Handling

Sample Collection

Overburden sampling is accomplished by drilling or direct collection of the sample from an open source such as a highwall. Four types of drilling methods are generally used to obtain overburden sample:

Air rotary rig: normal circulation - This type of drill is the most commonly used drill for the collection of overburden samples in Pennsylvania. Drilling in this manner uses air to blow the rock chips to the surface for collection. The most common pitfall with normal circulation air rotary drilling is that the individual samples of stratum can be contaminated by an overlying sample zone as the rock chips are blown up the annular space of the drill hole.

The rock chips traveling in this space can dislodge loose particles from an overlying source. Care should be taken to stop the downward progression of the drill stem after each interval has been sampled and allow any upper loose particles to blow out prior to continuing downward. Contamination of the sample can also occur at the surface due to the pile of ejected material that forms near the drill hole. These piled materials, if not removed during drilling, can sluff back into the open hole and the chip stream. This can be avoided by shoveling the materials away from the hole during the period when drilling is stopped to blow out the hole. Another option is to add a short length of casing to the top of the hole after the upper few feet have been collected. Samples are collected by placing a shovel under the chip stream. Care should be taken to clean the shovel of any accumulated materials from previous usage or sampling. This is particularly important in sampling of wet test holes where the ejecta consist primarily of mud. Before drilling the overburden hole, the driller should be instructed to clean the dust collector hood to remove any accumulated materials which may dislodge and contaminate the samples being collected.

Reverse Circulation Rotary Rig - This type of drill rig is less commonly used as a drilling platform for the collection of overburden samples, primarily because of availability. A reverse circulation rig uses a double-walled drill stem through which water or air is forced down the outer section of the drill stem and the cuttings/chips are forced up the inner section of the drill stem. The cuttings and water or air are brought into a separator and dropped near the rig where the samples can be collected. The samples are isolated from contact with overlying strata, so this type of drilling offers a much cleaner and quicker means of obtaining over-

burden samples. Further, the drilling does not need to be stopped to blow out the hole. If water is employed in the drilling process, the materials are also washed free of the fine dust coating which accumulates on the chips during drilling with air. This allows for much easier rock type identification and logging.

Diamond Cores - Diamond core barrels can be used on both types of rotary drilling platforms. Coring provides a continuous record of the lithology present and can provide the geologist with more information than can be obtained through the collection of rock chips (cuttings). Cores can provide a better overall view of the lithology underlying a proposed site by providing the geologist with the ability to judge rock color, gross mineralogy, grain size/texture, fossil content and relative hardness. This type of information is not always readily available from rock chips. Although a core provides an uncontaminated and better source of reliable lithologic data, coring is very time consuming and costly, especially if the entire overburden section is to be sampled by this means. Diamond cores can be used as a secondary means of data collection to isolate previously identified problem zones, or as a primary sampling tool in the area of the coal, i.e. the interval 5 ft above and below the coal horizon. The entire core section must be collected and processed for analysis to ensure representative sampling. A problem that can occur with coring is "core loss."

The problems of core loss during core drilling with a dedicated coring rig can be overcome or minimized by the driller and his helper by regulating the drilling speed, (i.e., rotational speed of the bit, and down pressure), diameter and type of core bit, amount of water, by minimizing the overbearing weight in the core barrel by emptying it prior to drilling the coal interval, and by keeping the equipment in good condition. Knowing what drilling adjustments to make can prevent blocking of the core barrel or causing the rock being cored to crumble and wash.

Successful coring is mostly dependent upon the experience of the on-site geologist, project engineer, or driller. Factors that are important include total years of core drilling experience, experience with the drill being used, and previous drilling experience in the same area, including exposure to the same rock formations and weathering characteristics (Personal Communication Clifford Dodge, William Marks, and Richard Beam). Having as much geologic data as possible (approximate depth to the coal, and extent of weathering) prior to drilling is also particularly useful. It is especially useful to have air rotary pilot holes to evaluate the site prior to the core drilling. These pilot holes allow particularly troublesome formations to be identified and avoided. Particularly troublesome conditions include highly fractured rocks or drilling into a joint or intersection of joints or fractures. Other problem areas include slickensided zones and areas indicative of paleoslump features. In some cases this may require re-drilling nearby, off of the joint or fracture zone (Personal Communication Clifford Dodge).

Other than encountering mine voids or solution channels, the first 10 ft (3 m) or so of unconsolidated soil and rocks as well as the transition through weathered rock into competent rock, is the zone most subject to core loss. Core recovery on the order of only 50 to 60% or less is not unusual. When drilling is done in the unweathered zone (sometimes indicated by an absence of iron staining) core recovery approaching 100% is the norm rather than the exception.

When coring the coal it is advisable to use a core barrel long enough to core the entire thickness of the coal and one that is not more than 20% full when first encountering the coal. It is preferable to have a nearly empty core barrel containing only 6 in. to 12 in. (15 to 30 cm) of overburden, before starting into the coal. The small amount of overburden aids in determining if the entire coal section has been sampled; i.e., knowing the starting and ending points of the coal. It also helps protect the coal from being crushed by the "ram" when extracting the coal from the core barrel (Personal Communication Clifford Dodge, Richard Beam, William Marks).

Besides actual core loss encountered while drilling, drilling data can be lost due to the improper handling of the cores. Possible problems include placing cores in the core boxes in the wrong order or upside down, or damage caused to the core during handling and shipping (Personal Communication Cliff Dodge).

Augering - Auger drilling is not recommended for general overburden sampling. It is typically used for unconsolidated or highly weathered materials. The auger lifts the materials on the auger screw. They are in constant contact with the overlying stratum, thus providing for intermixing. However, augering can be successfully used in homogeneous materials such as glacial till and/or old mine spoil.

Highwall Sampling - Direct collection of samples from an open source, such as a highwall within or near a proposed permit area, can be used for overburden analysis, provided several caveats are understood. First, samples may be weathered to such a degree that they do not represent the strata to be mined. Second, highwall sampling is limited by the availability and accessibility of highwalls. Therefore, care should be taken to collect only unweathered samples from the highwalls in close proximity to and representative of the proposed mining. It is recommended that open source (outcrop, highwall, etc.) samples be used primarily as a supplement to drilled samples.

Sample Description (Log)

For each sample or composite horizon collected, an accurate description of the gross lithology should be determined. This lithologic description should include the rock type, such as shale or sandstone, rock color as determined by comparison with the Munsell Rock Color Chart, texture/grain size, moisture conditions, and relative degree of weathering. Where applicable, a description of the gross mineralogy should be included with particular emphasis on the presence of any calcite ($CaCO_3$), siderite ($FeCO_3$), or pyrite (FeS_2). In addition, fossils should be noted and identified. The sample description must include the relative degree of fizz (effervescence) when dosed with a 10% solution of hydrochloric acid. A field fizz based on a scale of " none, slight, moderate, or strong" should be used. A dilute (10%) HCl solution is widely used by field geologists to differentiate calcium carbonate($CaCO_3$) from other carbonate rocks. If the purpose of the field fizz test is to replicate the laboratory tests, then a 25% HCl solution should be used. The field fizz determinations are highly subjective and should be made by the same individual for every sample on every hole for a particular site Extreme care must be exercised to be sure that the displacement of trapped air is not mistaken for CO_2 evolution. It is also important to identify if the fizz is from the matrix or from the cementing material. All of the above determinations, as well as the entire log of the test hole, should be made by a professional geologist.

Preparation of Samples

Field Preparation

The following procedures should be followed to ensure proper sample preparation in the field:

1. Use the drilling techniques previously discussed.
2. Samples should be immediately placed in airtight containers such as bottles or bags (plastic snap closing). This limits the exposure to air (oxygen), which can change the sulfur from the pyritic form to any of many secondary sulfate minerals.
3. The sample container should be immediately labeled with a permanent marker as to the interval which was sampled.
4. Field logs of the overburden holes should be kept to later help composite and log the represented lithologies at the site.
5. Each hole's individual sample containers should be immediately placed in a sealable mass container and labeled with hole number, mine name, and operator, if applicable, to avoid possible intermixing of samples from one hole to another from that site or from a different site.

Compositing and Laboratory Preparation

The purpose of compositing the 1 ft (0.3 m) noncore overburden samples is to reduce the cost of performing overburden analysis laboratory testing by minimizing the samples to be tested but not at the cost of sacrificing the precision needed to accurately predict postmining water quality. As with any well-intended cost-saving procedure, if not done properly, the real long-term costs might far outweigh the small cost saving.

The individual 1 ft (0.3 m) samples must be carefully logged under laboratory conditions to determine if successive zones are in fact the same. If the elements of sample description as described above are the same then the individual 1 ft (0.3 m) zones should be composited into a single composite sample. Table 5.3 shows the recommended maximum thickness for particular rock types in Pennsylvania. Sobek et al. (1978) suggest that most rock types should not be combined into composites representing more than 3 ft (0.9 m). They suggest that sandstone can be composited into 5 ft (1.5 m) increments. Experience in Pennsylvania has indicated that sandstone should be sampled at the same resolution of other rock types.

Some sandstones, such as portions with significant coal inclusions, may need to be sampled at a greater resolution. Where till from separate glaciations is present in the overburden, the different tills should be sampled separately. The reason for the 1 ft sample intervals above and below the coal is that these are frequently the highest sulfur strata present. Mixing of either of these strata with overlying strata can result in

Table 5.3 Maximum recommended sample thickness intervals based on lithology

Lithotypes	Composite Thickness	
	ft	m
limestone, mudstone, shale, siltstone, clay, claystone, coal, and sandstone	3.0	0.9
first one foot of strata above and below coal	1.0	0.3
mine spoil, tipple refuse, and glacial till or outwash	5.0	1.5

dilution of the zone and result in a falsely low percent sulfur, or make a thicker zone (e.g., 3 ft (0.9 m)) resemble a high sulfur zone, when in fact only the lowest third of the interval is high sulfur. The coal seam may also require greater sample resolution than the suggested 3 ft (0.9 m) if a portion of the coal will be left in the pit as pit cleanings or unmarketable coal. The coal that remains behind should be sampled separately.

As can be seen from Table 5.4, if too many 1 ft (0.3 m) intervals are composited or too large a vertical sampling interval is chosen, a high total sulfur (2.34%), potentially acid producing zone can be masked by dilution with adjacent low sulfur strata. The net effect is an underprediction of the potential for a site to produce acid mine drainage. Compositing one foot of high sulfur black shale with the overlying four feet of low sulfur sandstone results in a 0.48% total sulfur for the composited five foot zone, thus underpredicting the acid producing potential of the black shale.

Sobek et al (1978) suggested that for cores, a 5 inch (12.7cm) section out of the middle of a 1 ft interval can be assumed to be representative of that one-foot interval. The best way to ensure representativeness is to sample the entire interval. In order to avoid bias, one of the following two methods is recommended:

1. The entire core interval having the same log description as described above, whether it be a 1, 2, or 3 ft (0.3, 0.6, or 0.9 m) interval, must be entirely crushed and reduced in size via a riffle or rotating sectorial splitter until a suitable size fraction remains for analysis.

Table 5.4 Compositing of too many 1-ft (0.3 m) intervals can under-predict acid producing potential.

Thickness	Total %S	Lithology	Avg. %S of Interval
1'	0.01	sandstone	0.48
1'	0.01	sandstone	0.59
1'	0.01	sandstone	0.79
1'	0.01	sandstone	1.18
1'	2.34	black shale	

2. The entire core length should be bisected longitudinally using a core-splitter or saw. One-half of the core is retained for historical records and possible additional testing. The other half of the core is crushed for the entire sampling interval. After crushing, the entire sample is divided and reduced in size via a riffle or rotating sectorial splitter until a suitable size fraction remains for chemical analysis.

Purpose of Sample Preparation

The procedures for sample preparation are explained by Noll et al. (1988). The two main reasons for splitting and crushing are to provide:

1. an unbiased statistically representative sample of small quantity which can be easily used in a laboratory environment to make the necessary evaluations relative to total percentage sulfur and NP for acid base accounting or leaching tests; and,
2. samples of a small size fraction that maximizes surface area and minimizes the analytical time.

Conclusions

The use of OBA as a tool to predict mine drainage quality is useful only after careful planning that includes consideration of the caveats and limitations of the techniques being employed. Although it may seem like common sense, it is also necessary to carefully implement the plan. A properly planned and carried out overburden drilling program will help to ensure representative sampling of the strata which the mining will encounter.

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Chapter 6

LABORATORY METHODS FOR ACID-BASE ACCOUNTING: AN UPDATE

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Introduction

Laboratory methods for performing acid-base accounting overburden analysis (ABA) have been thoroughly detailed in previous publications. Sobek et al. (1978) formally presented a step-by-step laboratory protocol for performing ABA on mine overburden and is frequently cited as the source document. However, earlier publications described the application of ABA principals to mine overburden testing (West Virginia University, 1971; Grube et al., 1973; Smith et al., 1974; Smith et al., 1976). In 1988 Energy Center, Inc., under contract to the Department of Environmental Resources, Small Operator Assistance Program (SOAP), produced a detailed report on overburden sampling and testing (Noll et al., 1988). This latter document included a detailed description of considerations appropriate to planning an overburden analysis and to collecting the samples; it also added a boil step to the NP determination methodologies and provided a detailed description of methods for determining forms of sulfur.

This chapter focuses on aspects of the ABA procedures which have been somewhat controversial because of the effects that they can have on the reported results; it will not detail the laboratory protocols required to perform ABA.

Components of ABA

ABA is based on the premise that the propensity for a site to produce acid mine drainage can be predicted by quantitatively determining the total amount of acidity and alkalinity the strata on a site can potentially produce.

The maximum potential acidity (expressed as a negative) and total potential alkalinity (termed neutralization potential) are then summed. If the result is positive, the site should produce alkaline water, if it is negative, the site should produce acidic water. Sobek et al., (1978) defined any strata with a net potential deficiency of 5 tons per 1000 tons (ppt) or greater as being a potential acid producer. The maximum potential acidity (MPA) is stoichiometrically calculated from the percent sulfur in the overburden. The appropriate calculation factor is somewhat controversial. Sobek et al. (1978), noting that 3.125 g of $CaCO_3$ is theoretically capable of neutralizing the acid produced from 1 g of S (in the form of FeS_2), suggested that the amount of potential acidity in 1000 tons of overburden could be calculated by multiplying the percent S times 31.25. This factor is derived from the stoichiometric relationships in equation 6.1 and carries the assumption that the CO_2 exsolves as a gas.

$$FeS_2 + 2\ CaCO_3 + 3.75\ O_2 + 1.5\ H_2O \rightarrow Fe(OH)_3 + 2\ SO_4^{-2} + 2\ Ca^{+2} + CO_2(g) \quad (6.1)$$

Cravotta et al., (1990) suggested that, in backfills where CO_2 cannot readily exsolve, the CO_2 dissolves and reacts with water to form carbonic acid and that the maximum potential acidity in 1000 tons of overburden should then be derived by multiplying the percent S times 62.50.

The neutralization potential (NP) is determined by digesting a portion of the prepared sample in hot acid, and then by titrating with a base to determine how much of the acid the sample consumed. NP represents carbonates and other acid neutralizers and is commonly expressed in terms of tons $CaCO_3$ per 1000 tons of overburden (ppt). Negative NP values are possible, and are sometimes derived from samples of weathered rock that contain residual weathering products which produce acidity upon dissolution.

Interpretation of ABA data involves the application of numerous assumptions; some of the more significant assumptions often used are:

- all sulfur in a sample will react to form acid;
- all material in the sample which consumes acid during digestion in the lab will generate alkalinity in the field;
- the reaction rate for the sulfur will be the same as the dissolution rate for the neutralizing material.
- NP and percent sulfur values below certain threshold levels do not influence water quality.

As these assumptions imply, interpretation of ABA data is far more complicated than simply summing the MPA and NP values. Chapter 11 titled "Interpretation of Acid-Base Accounting Data" discusses these assumptions in more detail.

In addition to the percent sulfur and NP determinations, two other measured parameters in an ABA overburden analysis are paste pH and fizz. Other derived values are calculated from one or more of the measured parameters and from other information such as the sample thickness, density and areal extent. The derived values used may vary somewhat but typically include calculations of maximum potential acidity, tons of neutralization potential, tons of potential acidity, and tons net neutralization potential for each sample, as well as for the entire bore hole. The derived values are also discussed in the chapter of this document which deals with the interpretation of ABA overburden analysis.

Paste pH

The paste pH test is described in the previously referenced manuals on ABA protocol (Sobek et al., 1978; Noll et al., 1988), however, in Pennsylvania, it has fallen into general disuse over the past several years. A portion of the prepared sample is mixed with deionized water, and then tested with a pH probe after one hour. The paste pH test may indicate the number of free hydrogen ions in the prepared sample, but, since pyrite oxidation reactions are time dependent, the paste pH results provide little indication of the propensity of a sample to produce acid mine drainage. In fact, the paste pH of a unweathered, high-sulfur sample is likely to be near that of the deionized water, while a weathered sample with relatively low percent sulfur, but which includes a small amount of residual weathering products, may have a significantly depressed paste pH. Because of its limited usefulness in helping predict the potential for acid mine drainage production, the paste pH test often is no longer performed, and for mine permit applications in Pennsylvania, it is not a required component of ABA.

Percent Sulfur

Since acid mine drainage results from accelerated weathering of sulfide minerals, the amount of sulfur in a sample, or in an overburden column, is obviously an important component of ABA. As noted above, ABA uses the percent sulfur to predict the "maximum potential acidity" or MPA that a particular overburden sample or column could produce if all the sulfur reacts.

Sulfur determinations for ABA are often performed for total sulfur only, however, determinations for forms of sulfur are sometimes included. Sulfur generally occurs in one of three forms in the rock strata associated with coals in Pennsylvania: sulfide sulfur, organic sulfur, and sulfate sulfur. Sulfide sulfur is the form which reacts with oxygen and water to form acid mine drainage. The sulfide minerals most commonly associated with coals in Pennsylvania are pyrite and marcasite, both of which are FeS_2, chemically. Other sulfide minerals such as chalcopyrite ($CuFeS_2$) and arsenopyrite (FeAsS) may also be present in small amounts. Organic sulfur is that sulfur which occurs in carbon-based molecules in coal and other rocks with significant carbon content; since organic sulfur is tied up in compounds that are stable under surface conditions, it is not considered a contributor to acid mine drainage. Organic sulfur can represent a significant fraction of the total sulfur found in coal seams. Data from the Penn State Coal Data Base show that the average percent organic sulfur in several frequently mined coals in Pennsylvania ranges from a low of 0.55 % for the Upper Kittanning Coal to a high of 1.32 % for the Clarion Coal, with an overall average of 0.74%. Sulfate sulfur is often overlooked because in humid climates it generally is found in relatively small concentrations due to its high solubility. However, when present in Pennsylvania, sulfate sulfur often occurs in partially weathered samples as the reaction by-products of sulfide mineral oxidation. When solubilized, these weathering by-products are the source of the contaminants found in acid mine drainage, so when determinations for forms of sulfur are done, sulfate sulfur must be considered in the calculation of MPA. Alkaline earth sulfate minerals such as gypsum ($CaSO_4$) can also contribute to the sulfate sulfur fraction, but generally are not abundant in coal-bearing rocks in Pennsylvania. Where they are present, the alkaline earth sulfate minerals do not contribute to acidity.

Commonly used methods of performing total sulfur determinations are high temperature combustion methods (ASTM D4329), the Eschka Method (ASTM D3177) and the Bomb Washing Method (ASTM D3177). Of these methods, the high temperature combustion methods are the simplest and most frequently used and provide accurate, reproducible results.

Common methods used for determining forms of sulfur include ASTM D2492 and an EPA method. Noll et al., (1988) present an ASTM/EPA Combination method which the authors of that document felt combined the most desirable features of the other two methods.

Theoretically, the total of the sulfate and sulfide sulfur components should be a better indicator of the amount of reactive sulfur in a sample than should total sulfur. However, a laboratory study (Hedin and Erickson 1988) showed that total sulfur was related more strongly to leachate test results than was pyritic sulfur. Since pyritic sulfur is the form which contributes most significantly to acid mine drainage, these results indicate problems with pyritic sulfur determinations. A review of the methods for sulfur determinations described in Noll et al., (1988) reveals that the methods for total sulfur determinations have a relatively high degree of precision with few notable interferences and precautions, while the forms of sulfur determination methods described involve lesser degrees of precision and more numerous potential interferences and precautions. Stanton and Renton (1981) examined the nitric acid dissolution procedure, which is the cornerstone of the most frequently used methods for determining pyritic sulfur, including ASTM D2492; they found the procedure frequently does not succeed in digesting all the pyrite in a sample, thus underestimating the pyritic fraction of the sulfur in the sample. Brady and Smith (1990) compared total sulfur and forms of sulfur determinations performed by various laboratories. Their findings include:

- While the results generated by each laboratory were internally consistent in terms of the ratio of pyritic sulfur to total sulfur, there were significant differences between laboratories in the median percent pyritic sulfur/total sulfur. Where duplicate samples were available from different laboratories, differences were noted in the pyritic determinations, but total sulfur determinations were comparable.
- There was no significant difference in the percent pyritic sulfur/total sulfur between rock types (excluding coal). (This finding contradicts one of the primary reasons for doing determinations for forms of sulfur: that some rock types contain significant percentages of organic sulfur.)
- With one exception, all laboratories whose data was used in the study used a high temperature combustion method for determining weight percent total sulfur. The high temperature combustion results compared well on duplicate samples, while the pyritic results on the same samples did not.
- Standards are available from the National Institute of Standards for total sulfur but not for pyritic sulfur.
- A wide range of methods for determining pyritic sulfur were in use and individual laboratories had their own variations of the methods.
- One of the commonly used methods of pyritic sulfur determinations, ASTM D2492, was developed for use on coal and is probably not appropriate for determinations on rock overburden, according to ASTM Committee D-5 on Coal and Coke.

Figures 6.1 and 6.2 (data taken from Brady and Smith (1990)) compare total sulfur determinations and pyritic sulfur determinations of two different laboratories which performed analyses on duplicate samples. The high r^2 value for the total sulfur determinations indicate a strong correlation, and the low r^2 value for the pyritic determinations indicates a weak correlation.

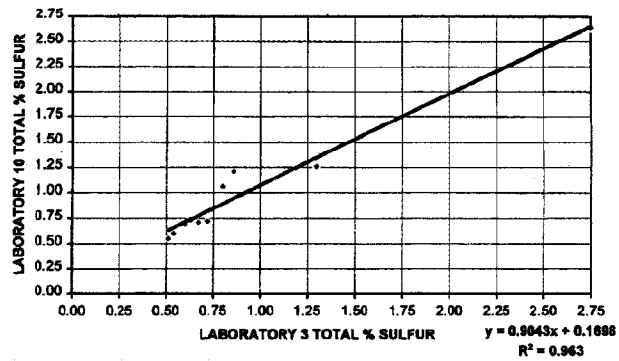

Figure 6.1 Comparison of percent total sulfur analysis results of duplicate samples analyzed by two different laboratories

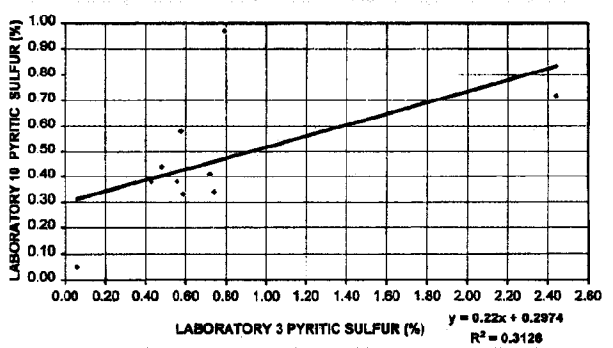

Figure 6.2 Comparison of percent pyritic sample analysis results for duplicate samples analyzed by two different laboratories

The above findings can be summarized as: Total sulfur determinations are typically simple to do, are reproducible, and can be calibrated and verified using available standards; pyritic sulfur determinations are done using a variety of methods (sometimes not standardized, and at least one of which is considered inappropriate for rock samples), produce results which are often not reproducible between laboratories, and cannot be calibrated and verified using available standards. Given these considerations, and that pyritic sulfur is the most abundant form in coal overburden (but not necessarily in the coal), total sulfur determinations currently provide the best basis for calculating MPA.

Fizz Rating

The importance of the fizz rating on ABA results is much underestimated and has often not received appropriate consideration. The fizz test is frequently presented as a minor part of the neutralization potential test; however the fizz test can have a large impact on the reliability and reproducibility of NP data, so it is discussed separately here. The fizz rating can be used as a check on the NP determination, since there should be a qualitative correlation between the two. More importantly, however, the fizz rating determines the volume and the strength of the acid which is used to digest the prepared sample, which in turn can affect the NP determination results (Evans and Skousen, 1995; Skousen et al., 1997). The NP result is then somewhat dependent on the fizz test results, and the fizz test results are a matter of human judgment.

The fizz test is performed by adding one to two drops of 25% HCl to a small amount of the prepared sample (Sobek et al., 1978). The degree of reaction is observed and recorded, according to a four-tiered system where the reaction is judged to be none or 0, slight or 1, moderate or 2, strong or 3. (Other systems with more levels have been used for reporting fizz results. However, given the obvious difficulties inherent to a test based on qualitative judgment, additional levels of judgment can only imply a precision which is not obtainable.)

There is an additional consideration which further complicates the subjective nature of the fizz test. Thresholds for NP and percent sulfur are often used in interpreting ABA. The theory behind using thresholds is that strata which produce NP or percent sulfur values below the thresholds are thought to have little impact on postmining water quality. However, these same strata often represent the greatest mass of the overburden and can "dilute" the effects of the strata with significant NP and percent sulfur if they are included in the calculations of total NP and MPA for the site. In Pennsylvania a threshold value of 30 is often used for NP. A threshold value of a 1 (slight fizz) is also often used. The fizz threshold tends to label a 0 or no fizz as being "bad" and higher fizz ratings as being "good." Strata identified as having a 0 fizz will not be counted as contributing potential alkalinity to postmining water quality which could result in a negative permitting decision. Even with the best intentions of the lab personnel performing the test, one cannot expect objective and reproducible results from a subjective test with a particular outcome pre-labeled as either good or bad. This is not to suggest that the use of thresholds is inappropriate, but to point out another precaution concerning reported fizz test results.

Evans and Skousen (1995) suggested a two-tiered fizz rating system which would combine the 0 and 1 fizz ratings into a single category and a 2 or 3 fizz rating into a second category. They reported that during a round robin sample testing study conducted by representatives of West Virginia University, Consolidation Coal Company (Consol), and the Pennsylvania DER (now DEP) on samples processed at the Penn State Materials Research Laboratories, the fizz ratings varied significantly between laboratories for certain samples. The laboratories then used different normalities and volumes of acid to perform the NP determinations on those samples, as dictated by the fizz ratings. The NP values varied considerably, and generally were higher when a larger volume of acid was used to digest the samples. When the Consol lab ran the NP determinations for each sample twice, with a different volume of acid each time, the determination that was made with the higher volume of acid produced a higher NP in each case. The differences were often great enough to change the interpretation one would make regarding the alkaline-producing potential of the sample. Table 6.1 displays fizz and NP data generated by the WVU and Consol laboratories during the round robin test and shows how fizz rating, acid volume and acid normality can affect NP results. Most of the samples included in Table 6.1 were selected for the study because visual observation suggested that they were siderite-rich; therefore, the differences in the fizz results and NP determinations between laboratories are probably more representative of what one would expect for siderite-

Table 6.1 Fizz test results and NP determinations for replicate overburden samples.

	West Virginia University*			Consol**		
SAMPLE NUMBER	FIZZ	SOBEK NP	GEOCHEM NP	FIZZ	NP1	NP2
NP-01	1	20	18	1	--	50
NP-02	1	8	8	3	--	445
NP-03	0	11	8	1	--	27
NP-04	3	926	930	3	--	936
NP-05	3	710	710	3		724
NP-07	1	25	30	0	20	6
NP-09	2	288	266	0	136	26
NP-10	1	13	13	0	58	22
NP-11	1	11	10	0	97	29
NP-13	0	17	14	0	51	23
NP-14	0	14	7	0	7	4
NP-15	1	11	11	0	85	14
NP-18	1	15	14	0	93	25

***Digested samples in accordance with both Sobek and Geochem recommendations; autotitrated to pH 7.0.**
****NP1 results based on digestion in 80 ml of 0.1N HCl. NP2 results based on digestion in 20 ml of 0.1N HCl for 0 fizz, 40 ml of 0.1N for 1 fizz, and 80 ml of 0.5N for 3 fizz. Manually titrated to pH 7.0.**

rich samples as opposed to samples with low siderite content. Skousen et al., (1997) reported that when three different laboratories performed fizz determinations on replicates of 31 samples, all three laboratories assigned the same fizz rating to only 13 of the 31 samples.

Reducing the number of tiers in the fizz test should reduce the amount of judgment required and consequently the subjectivity of the test. However, running the NP test with a reduced number of fizz test possibilities means that some samples would be digested in different volumes of acid than they would using the methods in Sobek et al. (1978) and Noll et al. (1988). Users of NP data need to be aware that changing the volume of acid used to digest a sample can change the NP results.

Skousen et al. (1997) described a protocol for a quantitative method of rating overburden samples based on the percent insoluble residue. Twenty ml of 10% HCl is added to 2.0 g of the prepared sample which has been dried in an oven. The solution is agitated until evolution of CO_2 is observed to cease. The solution is passed through a weighed filter, the filter plus residue are then dried and weighed, and the percent insoluble residue is calculated. The rating is then used to determine the volume and strength of acid used in the NP digestion; for that purpose the carbonate rating numbers are considered to be equivalent to the fizz rating values described in Sobek et al. (1978) and Noll et al., (1988). The NP and fizz determinations reported in Skousen et al., (1997) were run on replicates of the overburden samples, but the percent insoluble residue test was only run by one of the labs. As noted by the authors of that study, the method needs to be further tested to validate the proposed rating system and to provide a yardstick for comparing NPs based on the fizz test to those based on the percent insoluble test. One potential problem with the percent insoluble residue test is that, for some samples, the results may vary significantly when the percent HCl used in the digestion is changed (Keith Brady, personal communication). The samples studied by Skousen et al. (1997) were subjected to X-ray diffraction and characterized as belonging to one of four groups, based on their mineral and elemental content: Fe, Ca, S, and Si. When the percent insoluble residue test was performed on replicates of some of the samples using differing percents HCl, the results changed significantly for the iron-rich samples (Fe group) which included the samples with relatively high siderite content. (See Table 6.2.) The results for one of the carbonate-rich samples (Ca2) also changed significantly. These results raise questions concerning which % HCl should be used to achieve results which rate the carbonate in the samples in an accurate and reproducible way.

Given the difficulties which the current fizz rating system introduces into NP determinations, a reproducible, objective carbonate-rating test could significantly

Table 6.2 Comparison of percent insoluble residue to %HCl used to digest the sample.

(Samples which were digested with all three % HCl were tested at the DEP laboratory in Harrisburg, PA. For the samples digested in 10% and 50% HCl, the 10% digestion was done at West Virginia University and the 50% digestion was done at the PA Geologic Survey. Samples which were digested twice in the same percent HCl were duplicate samples.)

%HCl	Ca1	Ca2	Ca3	Fe1	Fe2	Fe3	Fe4	Fe6	Si1	Si13	Si15
10	13	39	34.1	97.5	97.7	97.8	99.2	77	99.2	85	96.8
10	-	-	-	-	-	-	-	69	-	86	-
25	-	13	-	-	-	-	-	54	-	86	-
25	-	-	-	-	-	-	-	45	-	85	-
50	4.7	13	25	26.4	17.9	22.5	23.8	32	80.9	85	89.5
50	-	-	-	-	-	-	-	33	-	86	-

improve the reproducibility of NP data. Until such a test is refined, individuals who generate and interpret ABA data need to be much more aware of the influence of the fizz test values on the NP determinations. Where fizz test results and NP values seem to be at odds, further testing would be prudent.

When a carbonate rating system other than the familiar four-tiered fizz test is used, data interpretation will have to be adjusted and interpretive rationales will have to be "recalibrated."

Neutralization Potential (NP)

The first step of the NP test is to conduct a qualitative fizz test on a small amount of the prepared sample as described earlier in this chapter. Based on the fizz test results, an appropriate volume and normality of HCl is selected then added to 2.0 grams of the prepared sample. (See Table 6.3.) Reagent water is added to bring the total volume to 100 ml (Noll et al., 1988). (Note that there are variations between the methods described in Noll et al. (1988) and in Sobek et al. (1978). This discussion is based on the methods described by Noll et al.) The solution is boiled for approximately 5 minutes, which is intended to dissolve potential neutralizers in the sample. After the solution is cooled, it is titrated with NaOH to a pH of 7.0; the end point is to be held for 30 seconds. The NP in terms of tons per thousand tons of rock (ppt) is then calculated from that amount of acid that was neutralized by the sample.

Carbonate minerals, such as calcite and dolomite, are known to be the major contributors to groundwater alkalinity in the coal regions of Pennsylvania. The acid-digestion step of the NP test is suspected of dissolving various silicate minerals, which results in an NP determination that overstates the amount of carbonate minerals in a sample. Lapakko (1993), working with rock samples from metals ore in Minnesota, reported that silicate minerals such as plagioclase dissolve and neutralize acid at relatively low pH values such as those which occur in acid mine drainage or during a NP titration; however, he also noted that since this dissolution will only take place at low pH values, it is unlikely to help maintain a drainage pH of acceptable quality. His test results, based on leaching studies, also indicated that the rate of acid neutralization by silicate minerals was not adequate to maintain a drainage pH of 6.0 or above.

Siderite ($FeCO_3$) has long been suspected of interfering with the accuracy of NP determinations and of complicating the interpretation of the data (Meek, 1981; Morrison et al., 1990; Wiram, 1992; Leavitt et al., 1995). Siderite is common in Pennsylvania coal overburdens. Samples with significant amounts of siderite can make it difficult to hold the final end point

Table 6.3 Volume and Normality of HCl used to do NP digestion based on the sample fizz rating. (After Sobek and others (1978) and Noll and others (1988).)

FIZZ RATING	HCl VOLUME	HCl NORMALITY
None (0)	20 ml	0.1N
Slight (1)	40 ml	0.1N
Moderate (2)	40 ml	0.5N
Strong (3)	80 ml	0.5N

of the titration with NaOH (Noll et al., 1988). If iron in solution from the siderite is not completely oxidized when the titration is terminated, then the calculated NP value will be overstated, since complete oxidation of the iron would produce additional acidity. An uncertain titration end point can obviously affect the reproducibility of the NP results. Skousen et al. (1997) also found that laboratories tended to assign different fizz ratings to replicates of samples with high siderite content. As noted in the earlier section of this chapter which dealt with fizz ratings, assigning different fizz ratings to the same sample can change the acid volume and strength used in the NP digestion step, which will affect the NP results.

Meek (1981) and Morrison et al., (1990) proposed adding a hydrogen peroxide step to the NP determination procedures to eliminate the problems with the method caused by siderite. Morrison and Scheetz (1994) performed ABA tests on four samples using both the method described in Noll et al. (1988) and their modified approach. Under the modified method, after the sample was digested in acid, it was filtered into a vacuum flask. The filtering was done to ensure that the H_2O_2 did not oxidize pyrite or other solids in the undigested portion of the sample. The solution was then transferred to a 400 ml Pyrex beaker, and the vacuum flask was rinsed with 125 ml of deionized water. Five to 7.5 ml of 30 wt % H_2O_2 was added to the solution which was then boiled for three to five minutes. After cooling, the solution was then titrated to pH 7.0 with NaOH. The NP for each sample was lower when the modified method was used, and was significantly lower for the three samples known to contain a significant amount of siderite.

Evans and Skousen (1995) found that NP values were not appreciably different when samples were analyzed both with and without the hydrogen peroxide step; however they found that reproducibility between laboratories did improve when the hydrogen peroxide step was used. They also found that when the hydrogen peroxide step was performed without filtering the solution, the results sometimes did not compare well with other ABA methods, probably due to the oxidation of pyrite in the residue by H_2O_2. In fact, oxidation of pyrite with H_2O_2 has been used as a method of predicting the acid-producing potential of overburden (O'Shay, et al., 1990). Morrison and Scheetz (1994) used samples known to include a significant amount of siderite (determined by X-ray diffraction) in their comparative study, which may be why their results showed that the hydrogen peroxide step reduced NP.

Skousen et al. (1997) subjected 31 overburden samples of known mineralogy (determined by X-ray diffraction) to four variations of the NP test. The variations were defined by the authors of that paper as: 1) **(Sobek)**, the standard Sobek method (Sobek et al., 1978); 2) **(Boil)**, a method that includes boiling of the sample for five minutes during the digestion step (Noll et al., 1988); 3) **(H_2O_2)**, the same as the boil method except that after digestion the sample is filtered and treated with H_2O_2 before titration; 4) **(SobPer)**, the same as the Sobek method except that H_2O_2 is added to the sample (no filtration) after the first titration. Among their findings the authors concluded:

- The four variations on the NP test produced similar results for samples containing little pyrite or siderite.
- The SobPer method gave lower NP values than the other methods for samples which included significant amounts of pyrite, due to oxidation of the pyrite by H_2O_2 in the unfiltered samples.
- Compared to the other three methods, the H_2O_2 method provided: The lowest NP values for samples with significant siderite content; the best reproducibility between the laboratories which participated in the study; results which were the most consistent with soxhlet leachate results.
- Autotitration at a slow setting is preferable to hand titration, especially for samples with significant siderite content.

Skousen et al. (1997) briefly describe a method to perform NP determinations with the H_2O_2 step. If the hydrogen peroxide step performs according to its intent, it should generally decrease the NP's of strata with a significant siderite content, but should not appreciably affect the NP values of strata that do not include significant amounts of siderite. It should also lead to better reproducibility of NP data between laboratories, especially for samples with significant siderite content.

Other Methods of Determining Carbonate Content

The NP test has been adapted and widely used to approximate the carbonate content of mine overburdens largely because it is relatively quick, inexpensive, and easy to perform. However, as noted in this chapter, it may not always provide results which are accu-

rate and reproducible. Other methods of determining carbonate content have occasionally been used in Pennsylvania on high risk-sites or on sites where the NP test provided questionable results.

Morrison et al. (1990) suggested CO_2 coulometry as an alternative method for determining carbonate content of overburden samples and reported promising results, however, the method has not been widely adopted for characterizing overburden samples to date.

X-ray diffraction, which can give detailed information on the overburden mineralogy, has been used on a few sites in Pennsylvania. In cases where X-ray diffraction has been used and where fizz test ratings and NP results seemed in conflict and suggested the presence of siderite (results which showed significant NP values for samples which did not fizz), the X-ray diffraction results verified the presence of the siderite.

In situations where NP data provide ambiguous results and/or where mining presents a risk to significant uses of nearby groundwater or surface water sources, tools such as X-ray diffraction and CO_2 coulometry are available and should be considered to verify the NP results.

Conclusions

Three aspects of ABA overburden analysis laboratory techniques create problems with reproducibility and accuracy of data.

Difficulties in performing forms of sulfur determinations can lead to unreliable results if pyritic sulfur determinations are used to calculate MPA instead of total sulfur determinations. Since pyritic sulfur is typically the largest component of total sulfur in coal overburdens, and since total sulfur determinations can be done more reliably, MPA calculations should be based on total sulfur and not pyritic sulfur.

The importance of the qualitative fizz rating in ABA has often been overlooked. The fizz rating can significantly affect the outcome of NP determinations. Since the fizz rating is a qualitative test, reproducible results can be elusive, and where multiple labs performed fizz tests on replicates of samples reproducibility was poor (Evans and Skousen, 1995; Skousen et al., 1997). The fizz rating determines the normality and volume of acid which is used to digest the sample; when the normality and volume of acid changes, so does the NP result. Reducing the subjectivity of the fizz test by reducing the number of choices in the rating system from 4 to 2 as suggested by Evans and Skousen (1995) could result in more consistent NP determinations. However, when the number of fizz rating possibilities are reduced, some samples are digested in a larger volume of acid than they would under the traditional way of performing the tests, resulting in higher NP determinations. The interpretive rationale applied to ABA data will have to be "recalibrated" if a carbonate rating system other than the traditionally used four-tiered system is ultimately adopted

The quantitative method of rating carbonate content of overburden samples by determining the percent insoluble residue, as described by Skousen et al. (1997), requires additional testing to determine if it could be used as a more objective option than the fizz test for rating carbonate content. The percent HCl used to digest the samples may significantly affect the percent insoluble residue for siderite-rich samples.

Siderite, a common mineral in Pennsylvania coal overburdens, can interfere with NP determinations, generally resulting in values that are high relative to the amount of calcium carbonate in the sample. Adding a hydrogen peroxide step (such as described by Skousen et al., (1997)) to the NP determinations reduces the interference of siderite and does not appreciably affect NP determinations for samples without significant amounts of siderite. NP determinations run with the hydrogen peroxide step provide better reproducibility between laboratories and produce results which better represent the true carbonate content of the rock.

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Chapter 7

KINETIC (LEACHING) TESTS FOR THE PREDICTION OF MINE DRAINAGE QUALITY

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Introduction

The tests described in this chapter consist of the simulation of mine drainage production from samples of strata to be affected by mining, followed by chemical analyses of effluent quality produced from these simulated conditions. These tests are referred to as kinetic tests because they incorporate dynamic elements of the physical, chemical, and biological systems and processes which control the production of acidic or alkaline mine drainage. Specifically, these tests are designed and conducted to deal with the reaction kinetics, the rates and mechanisms of the chemical reactions which lead to the production of acidic or alkaline mine drainage. A thorough discussion of reaction kinetics may be found in Barrow (1973, chapter 16 & 17), Lehninger (1975, chapter 8) and Stumm and Morgan (1970, chapters 2, 4 and 10).

While some kinetic tests may be done in the field to promote a better approximation of the physical, chemical and biological systems; these tests are usually done in a laboratory environment with a variety of apparatus including leaching columns, humidity cells and soxhlet reactors.

The group of test procedures generically referred to as kinetic tests for the prediction of mine drainage quality may be contrasted to the group of tests labeled as "static" tests for the prediction of mine drainage quality. The term static may not be as fitting a descriptor, because static tests are not completely motionless, stable, or undynamic; but they do not typically incorporate reaction kinetics except in a theoretical manner. For example, in the acid-base accounting technique of Smith et al. (1974) and Sobek et al. (1978), the neutralization potential (NP) test is a measure of the amount of calcium carbonate in the sample (adapted from the work of Jackson, 1958) rather than an actual alkalinity concentration. This NP number is compared to the maximum potential acidity (MPA) which is calculated from the percent total sulfur in the sample, using stochiometric relationships. Therefore, of the three types of scientific evidence: theoretical, empirical, and experimental; the MPA component of acid-base accounting is theoretical, while the actual acidity and alkalinity concentrations in the effluent from a leaching column are experimental evidence.

A major advantage of kinetic tests for the prediction of mine drainage quality is that, since these types of tests produce an effluent of simulated mine drainage quality, the effluent may be tested for the same water quality parameters as the actual mine drainage to be produced from the proposed mining operation. The water quality parameters typically included in the leachate analyses are pH, acidity, alkalinity, sulfates, iron, manganese and aluminum. These are the same water quality parameters typically monitored as required by NPDES permit conditions for an active mining operation. If the physical, chemical, and biological conditions of the kinetic tests are representative of those found in the mine environment, the concentrations of the water quality parameters in the leachate may be used to predict or estimate the concentrations of these parameters in the actual mine drainage from the proposed mining operation.

Unfortunately, there are several potential disadvantages of some kinetic tests for the prediction of mine drainage quality. A major problem with these types of tests is the interpretation of the results of the experimental process and the extrapolation to the actual environment of the proposed mine site. It is easy to be fooled by the laboratory results, where test procedures are simplified or some component of the physical, chemical, or biological systems is either underestimated or overestimated. Then, the apparently precise laboratory analyses may not be accurate, and in fact, may be meaningless. Further, it is difficult enough to test a single representative sample of a lithologic unit. Some kinetic tests attempt to combine numerous strata in the same test apparatus to simulate

the configuration of the active mine or backfilled mine spoil. That is a very difficult, if not an impossible task, within the average laboratory kinetic test apparatus.

What follows in the remainder of this chapter is:

(1) a chronology and synopsis of scientific literature on these kinetic tests as they have developed throughout the past 45 years,

(2) an evaluation of the factors to be considered involving physical, chemical, and biological processes, and

(3) general guidelines for test procedures, data interpretations, and recommendations for further research to develop standard methods.

The two major sections of this chapter are the chronology of the development of kinetic tests for mine drainage, and the evaluation of physical, chemical, and biological factors in kinetic tests. These two sections may be treated in an integrated manner or taken separately. The reader who is merely searching for a summary of kinetic test design and performance may want to review the nine general principles in the summary and recommendations section of the chapter.

In compiling the information contained in this chapter, more than 275 pieces of scientific literature have been cited. These references and related information have been compiled in a computer data base which may be sorted chronologically or by key words. A copy of this bibliographic data base may be obtained from the authors.

Chronology of the Development of Kinetic Tests for Mine Drainage

This section of the chapter is an attempt to summarize the development and use of kinetic tests in mine drainage research, and applications to mine sites by university researchers, state and federal agencies, and the mining industry and their consultants. Most of the literature cited pertains to surface coal mining in the Appalachian coal fields of the eastern United States, but a significant amount of the references are associated with metal mining activities in the western United States, Canada, and elsewhere. Many of these works have been primarily oriented toward the development of techniques for the pre-mining prediction of mine drainage quality with a reasonable degree of accuracy and precision. However, very significant developments in kinetic tests have also occurred in acid mine drainage abatement studies, and in contrasting efforts by the metal mining industry to optimize acid production in heap leaching operations.

An effort has been made by the writers to locate and include a representative sample of the scientific literature on this subject, but this chapter does not purport to be a comprehensive bibliography on kinetic tests. The format of this section is an approximate chronological order of studies on various types of kinetic tests (i.e., leaching columns, humidity cells, Soxhlet reactors, etc.) intertwined together, in order to demonstrate, that like most scientific developments, there has been an effort to converge on the truth by refining successes and eliminating failures through time. Unfortunately, this chronology also demonstrates that after more than forty years of research, some of the early failures are still being repeated and promoted today; and some of the early successes have been repeated and refined through time, but have not achieved sufficient widespread acceptance to be uniformly applied by the majority of the workers in the field. Perhaps M. K. Hubbert's classic paper, "Are We Retrogressing in Science?" (1963) is relevant to some of this research.

A summary of the chronology follows on the next few pages. The entire chronology is presented in Appendix A at the end of this chapter due to its length and the large number of references and figures used in its construction. Examples of leaching columns, humidity cells, and Soxhlet reactors are shown in Figures 7.1, 7.2, and 7.3. For other graphic and written descriptions of kinetic test apparatuses, refer to Appendix A. The 45-year chronology on the development of kinetic tests for the prediction of mine drainage quality commences in 1949 and concludes in 1994 for reasons described below. A few earlier references may be found, but probably the most significant early work on this subject started in this country with the leaching columns of S. A. Braley at the Mellon Institute in Pittsburgh in 1949. The chronology outlines the post-World War II awakening to the impacts that acid mine drainage from coal surface mining in the Appalachian Basin was having on the surface waters and ground waters of the northern Appalachian Region. This period of awareness and assessment of the problem lasted through the 1950s and 1960s. During this time, state and federal regulatory and research agencies and university researchers, particularly in Pennsylvania, Ohio and West Virginia, began to develop a variety of laboratory and field kinetic tests for AMD prediction including leaching columns, humidity cells, Soxhlet

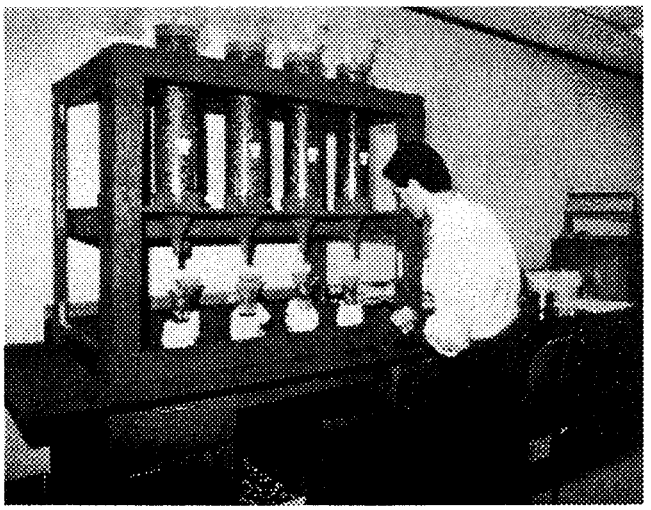

Figure 7.1 Leaching columns (from Bradham & Caruccio, 1995).

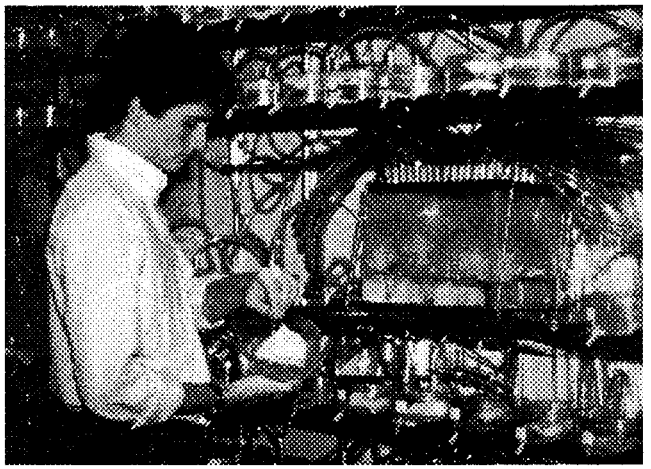

Figure 7.2 Humidity cells (from Bradham & Caruccio, 1995).

reactor techniques, and field scale tests. These kinetic tests were refined and applied throughout the Appalachian Coal Basin during the 1970s and into the 1980s, principally by researchers at the Pennsylvania State University, West Virginia University, and the University of South Carolina.

The Arab oil embargo of 1973, and perhaps other economic factors, led to a boom in coal mining in the United States that lasted throughout the remainder of the 1970s and into the 1980s. Proposed surface mining operations were spreading out from previously mined watersheds into unmined watersheds, where AMD impacts were threatening high quality streams and public water supplies. In a landmark 1977 Environmental Hearing Board decision of Pennsylvania case law, (Harman Coal Company), which was affirmed by Commonwealth Court in 1978, the courts determined that pursuant to 25 Pa. Code Section

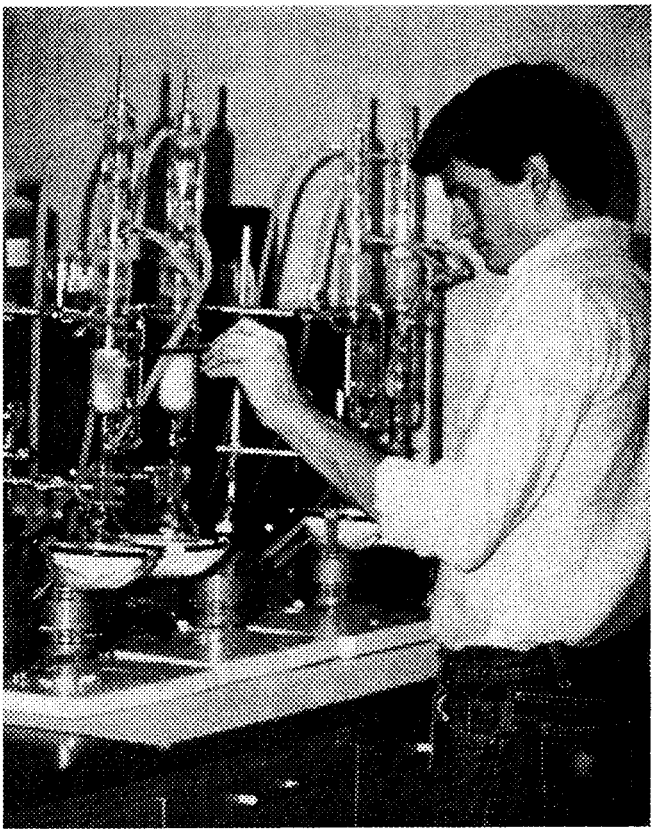

Figure 7.3 Soxhlet reactor (from Bradham & Caruccio, 1995).

99.35(a) it is a permit applicant's responsibility to affirmatively demonstrate that there is no presumptive evidence of potential pollution from the proposed mining activities.

A significant milestone during this period was the enactment of the Federal Surface Mining Conservation and Reclamation Act of 1977 (SMCRA). Prior to that law, some state regulatory agencies required predictions or assessments of AMD potential in mining permit applications, but overburden analysis tests were not routinely required. SMCRA and associated federal regulations required that permit applicants determine the Probable Hydrologic Consequences of proposed mining activities, including the chemical analyses of the coal and overburden strata for AMD potential. Pennsylvania obtained primacy under SMCRA in 1980 and the Pennsylvania mining regulations, 25 Pa Code Chapters 86 through 90, were promulgated to meet requirements in the federal and state laws. While some overburden analyses were required prior to primacy, the OSM approved program and corresponding DER policy and procedures established relatively routine overburden analysis requirements under certain criteria. Section 86.37(a)(3) of the regulations requires

that, "The applicant has demonstrated that there is no presumptive evidence of potential pollution of the waters of the Commonwealth." The federal and state regulations requiring the chemical testing of coal, overburden, and underclay samples as part of the surface mining permit application created a major demand for the development, routine use, and interpretation of kinetic and static tests to predict mine drainage quality by the regulatory agencies, mining industry consultants, and commercial laboratories. This demand forced a search of available laboratory methods used in AMD research and other sciences, that might be used to obtain accurate and precise results. It also initiated the adaptation of some test methods from a university research study environment to the routine sample production environment of commercial laboratories. Unfortunately, the rapid growth in the development and application of these tests was accompanied by significant confusion in the interpretation of test results and apparent contradictions among some test predictions. The scientific and legal controversies surrounding the various static and kinetic overburden analysis methods in use at that time prompted state and federal regulatory and research agencies and other researchers to conduct comparisons of test results in an attempt to determine whether any of the available overburden analysis methods produced accurate and precise premining predictions of postmining water quality. Several of these comparative studies were published between 1986 and 1992, and additional work in this area continues today to determine the best predictive test methods.

In other areas of the United States, outside of the Appalachian Coal Basin, including Illinois, Montana, Minnesota, Utah, and Washington, kinetic test methods were being developed and applied in mine drainage work for coal mines, metal mines, and associated tailings deposits throughout the 1980s. In fact, some of the very best kinetic test studies were done by the metal mining industry to optimize acid leaching and metal recovery from mine waste dumps, commencing in approximately 1975. In Canada, particularly British Columbia, research on static and kinetic tests to evaluate AMD potential was ongoing during the late 1970s and 1980s, primarily for metal mines and associated tailings deposits.

Significant collaboration among state and federal regulatory and research agencies, the mining industry, and university researchers on solving mine drainage problems occurred in the mid-1980s in West Virginia with the Acid Mine Drainage Technical Advisory Committee (AMDTAC) and from the late 1980s to the present in Canada with the Mine Environment Neutral Drainage (MEND) program. Both of these groups and their participating scientists and engineers have made significant advances in the field of mine drainage prediction (including the use of kinetic tests) and mine drainage abatement.

During the 1990s, very extensive work on the evaluation of critical parameters and performance of kinetic tests, particularly humidity cells and leaching columns, has been done by researchers at the USBM Pittsburgh, Salt Lake City, and Spokane Research Centers, and other researchers in university research programs. The 45-year chronology concludes with the publication of the proceedings of the Third International Conference on the Abatement of Acidic Drainage in Pittsburgh in 1994, because this conference was the focal point on the status of mine drainage prediction throughout the world, among other things. At least 45 of the 186 papers presented included kinetic test developments, evaluations, and applications. These 1648 pages of conference proceedings are an accurate indicator of the current state of the art, science, or confusion surrounding kinetic tests for the prediction of mine drainage quality.

The 45-year chronology was written for the following four reasons:

(1) it documents the historical development of kinetic tests for mine drainage prediction and practical applications of the test results on mine sites in the Appalachian coal fields and elsewhere,

(2) it provides the reader with a fairly complete list of references on the origin and development of the various kinetic tests for mine drainage prediction in the event that additional research is contemplated, or additional, more detailed information on the test developments and field applications is needed,

(3) it demonstrates that most of the kinetic test methods in use today were substantially developed and applied more than 30 or 40 years ago, including leaching columns (Braley, 1949), humidity cells (Hanna and Brant, 1962), Soxhlet reactors (Pedro, 1961), and field scale tests with actual precipitation (Glover and Kenyon, 1962),and

(4) it depicts the present state of confusion concerning the use and interpretation of specific kinetic test procedures for mine drainage prediction, and

promotes a concerted effort to converge on a practical solution to the problems in the near future.

After at least 45 years of kinetic test developments, at least 45 technical papers on kinetic test developments and applications were presented at the 1994 AMD conference in Pittsburgh. To witness many of these presentations and later review the more than 1600 pages of proceedings for the preparation of this chapter was mind-boggling and frustrating. A tremendous amount of kinetic test information now exists, but the variety of test apparatus and procedures in use is so great that it is very difficult to interpret the results and make meaningful comparisons of data from different studies in similar or different lithologic settings. If, after 20 years of personal experience with kinetic tests and other aspects of AMD research, the authors of this chapter struggle to make sense out of much of this data; it should be no wonder that mine operators and consultants new to the subject of AMD prediction would shy away from kinetic tests because they don't know which apparatus or procedure to use, nor how to interpret the results.

Notwithstanding the millions of dollars of research expended, is the state of affairs in kinetic test development and application really much better off now than it was 20 years ago? Hopefully, researchers and research users will unite and develop a consensus on kinetic test procedures and interpretation for mine drainage prediction, in order to facilitate the meaningful comparison of test results from rock sample to rock sample, mine to mine, state to state, and nation to nation, in order to make sound decisions. We will remain optimistic that researchers and research users will ultimately develop a consensus on kinetic test procedures and interpretation for mine drainage prediction within the next few years. In the interest of advancing that process, the following discussion of essential physical, chemical and biological factors is offered.

Evaluation of Physical, Chemical, and Biological Factors in Kinetic Tests

The kinetic tests described in the 45-year chronology above, incorporate physical, chemical, and biological processes and constraints. The scientific literature on physical, chemical, and biological controls on AMD production and other natural or man-induced acidity- and alkalinity-generating processes is much more voluminous and long-term than the 45-year chronology. Consequently, the role of these physical, chemical, and biological factors in natural systems is largely understood, and these factors must be considered and incorporated in the design, operation, and interpretation of kinetic tests for AMD prediction, or the laboratory data will have little or no relevance to the real world.

Physical factors include: the size, shape, and structure of the apparatus used to conduct the tests; the volume, texture, and particle size distribution of the sample to be tested; and the volume, pathway, and resultant saturation conditions (e.g. saturated zone, capillary fringe or relative humidity of pore spaces) of the fluids introduced into or removed from the apparatus for analysis.

Chemical factors include: the mineralogical composition of the rock sample, the composition (i.e. concentration of cations and anions) of the influent and effluent fluids; the solubility controls on the acidity- and alkalinity-generating processes, the interrelationships between these processes and other constraints affecting the reaction kinetics, and the composition of gaseous phases (e.g. partial pressures of oxygen and carbon dioxide) in the fluids and void spaces within the kinetic test apparatus.

Biological factors include: the presence and relative abundance of bacteria (e.g. *Thiobacillus*,) that catalyze the AMD producing reactions; the availability of nutrients and other life-supporting ingredients; and the interrelationships among controls on the biological system, such as temperature and pH, which determine whether various organisms flourish, barely survive, or die.

A complete discussion of all of the chemical reactions associated with acidity and alkalinity production is not included in this chapter because those reactions are explained elsewhere in this volume and in many other references. However, it is useful to briefly review the controls and range of acidity, alkalinity, sulfate, and metals concentrations which may be found in nature, particularly mine environments, in order to demonstrate the variations in mine drainage composition associated with the range of geologic settings in Pennsylvania and elsewhere, and to place some expectations on the variations in leachate composition from kinetic tests.

Excellent explanations of the series of chemical reactions by which AMD is produced from pyrite and other iron sulfide minerals, are found in Lovell (1983), Barnes and Romberger (1968), Singer and Stumm

(1968, 1970), Kleinmann et al. (1981), Evangelou (1995) and Chapter 1 (this volume). Singer and Stumm (1970) simplify the explanation by describing an indicator reaction and a propagator reaction, in a process where the rate determining step is the oxidation of ferrous iron, and where the presence of iron-oxidizing bacteria catalyzes the oxidation by a factor greater than 10^6. As pyrite is formed in a reduced depositional environment, it is unstable in the oxidizing conditions of most surface and underground mines. However, secondary mineral phases formed from pyrite weathering, such as jarosite, alunite, and melanterite, are capable of dissolving or precipitating in mine environments. Additional information on these and other secondary mineral phases is found in Nordstrom (1982) and Cravotta (1994). According to Lovell (1983), of the various iron sulfates which are several orders of magnitude more water-soluble than pyrite, melanterite has a solubility of 156,500 mg/L, while coquimbite has a solubility of 4,400,000 mg/L. Lovell (1983) also lists ranges of component concentrations in Appalachian acid mine drainage where pH may be as low as 1.4, and maximum concentrations for the following parameters are: acidity of 45,000 mg/L, total iron or ferrous iron of 10,000 mg/L, aluminum of 2,000 mg/L, and sulfate of 20,000 mg/L.

According to Krauskopf (1967, p. 35): "The lowest recorded pH's in nature are found in solutions in contact with oxidizing pyrite; values even less than zero have been recorded from such environments". An outstanding example of this phenomena is the study by Alpers and Nordstrom (1991) at the Iron Mountain mine in Shasta County, California that is producing some of the most acidic and metal-rich mine drainage in the world. Alpers and Nordstrom (1991, p. 323) state:

> "Oxidation of pyrite is well known to cause acidification of surface and ground waters. Minimum pH values tend to be in the range of 1.5 to 2.5 for natural waters infiltrating disseminated sulfide deposits, base metal tailings, and sulfidic waste rocks, where some degree of neutralization by gangue minerals accompanies pyrite oxidation. However, within massive sulfide deposits and in sulfide-rich tailings and waste rock, extremely high aqueous concentrations of sulfate, iron, and other metals can develop, accompanied by pH values less than 1.0. In at least one extreme case, at Iron Mountain, California, pH values less than 0.0 have now been documented."

The most extreme values reported by Alpers and Nordstrom (1991) for a ground-water seep from a stalactite of melanterite or rhomboclase collected within the underground mine were a field pH of -1.0, sulfate of 760,000 mg/L, and total iron of 111,000 mg/L.

In Pennsylvania coal mine drainage, some of the most extreme concentrations of acidity, iron and sulfate have been found at the Leechburg Mine refuse site in Armstrong County, and at surface mine sites in Centre, Clinton, Clarion and Fayette Counties as shown in Table 7.1. The acidity concentrations of seeps from Lower Kittanning Coal refuse at the Leechburg site exceed 16,000 mg/L (Table 7.1), while the sulfate concentration of one sample exceeds 18,000 mg/L. At the Stott surface mine site on the Clarion Coal in Centre Co., a 35 gpm (132.5 lpm) post-mining discharge had an acidity concentration over 9,700 mg/L with an iron concentration of almost 2,000 mg/L (Table 7.1). A pit water sample at the Lawrence site in Fayette County was found to have an acidity concentration greater than 5,900 mg/L and an iron concentration greater than 2,000 mg/L (Table 7.1). Schueck et al. (1996) report on detailed AMD abatement studies conducted at a backfilled surface mine site in Clinton County, where a monitoring well that penetrated a pod of buried coal refuse produced a maximum acidity concentration of 23,900 mg/L and a mean acidity concentration of 21,315 mg/L based on 13 samples. The maximum concentration of iron was 5,690 mg/L and the maximum sulfate concentration was 25,110 mg/L in the same monitoring well, as reported in Schueck et al. (1996). Toe of spoil seeps at the Clinton County site have acidity and sulfate concentrations greater than 3,500 mg/L and 3,700 mg/L, respectively.

The alkalinity production process has a dramatically different set of controls, and the resultant maximum alkalinity concentrations are typically one or two orders of magnitude less than the maximum acidity concentrations found in mine environments. The carbonate rocks which produce significant alkalinity or bicarbonate concentrations in groundwater, surface-water, and mine drainage samples (i.e., coal surface mines, stone quarries, and coal and noncoal underground mines) are limestones and dolomites and the principal carbonate minerals are typically calcite (calcium carbonate) and dolomite (calcium-magnesium carbonate).

Table 7.1 High Concentrations of Acidity and Related Water Quality Parameters in AMD at Bituminous Coal Mine Sites in Pennsylvania.

Site Name	SMP #	County	Township	MP ID	Date	pH	Conduct.	Alkalinity	Acidity	Iron	Mn	Al	SO_4	TSS	Flow	Type of Sample
					Sampled		umhos/cm	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	(gpm)	
Leechburg	03-92-01	Armstrong	Kiskiminetes	8	6/29/94	2.4	N.D.	0.0	**16594.0**	> 300.0	16.5	> 500.0	11454.0	10.0	1.0	Seep
Leechburg	03-92-01	Armstrong	Kiskiminetes	8	10/26/94	2.4	N.D.	0.0	**16718.0**	> 300.0	19.3	> 500.0	18328.0	74.0	2.0	Seep
Leechburg	03-92-01	Armstrong	Kiskiminetes	1	6/29/94	3.1	N.D.	0.0	**1368.0**	> 300.0	13.9	82.3	1896.0	34.0	200.0	Deep Mine Discharge
Leechburg	03-92-01	Armstrong	Kiskiminetes	3	5/3/96	2.0	9800	0.0	**10383.5**	2200.0	3.3	N.D.	14565.2	14.0	3.5	Diversion Ditch Discharge
Trees Mills	65880112	Westmoreland	Salem	MP-1	11/29/90	2.5	2700	0.0	**3616.0**	190.4	13.5	73.1	1497.8	10.0	13.0	Deep Mine Discharge
Lawrence	3376SM15	Fayette	Springfield	1063-5	1/18/82	2.2	11000	0.0	**5938.0**	2060.0	73.0	146.0	3600.0	N.D.	0.0	Pit Water
Lawrence	3376SM15	Fayette	Springfield	Breakout	12/14/81	2.6	5500	0.0	**1840.0**	166.0	89.0	85.0	2700.0	N.D.	25.0	Surface Mine Discharge
Blue Lick	56880109	Somerset	Brothersvalley	N.D.	3/28/96	2.9	N.D.	0.0	**2594.0**	> 300.0	35.7	180.0	2701.0	5.0	N.D.	Seep
Stott	14673012	Centre	Rush	B1P	6/27/84	2.7	25000	0.0	**9732.0**	1959.8	205.3	N.D.	4698.0	N.D.	35.0	Surface Mine Discharge
Stott	14673012	Centre	Rush	B1P	5/15/89	2.8	9400	0.0	**4520.0**	4880.0	149.5	N.D.	5139.4	N.D.	40.0	Surface Mine Discharge
Stott	14673012	Centre	Rush	A5P	5/8/93	2.8	5400	0.0	**1450.0**	215.8	44.3	N.D.	2886.1	N.D.	1300.0	Surface Mine Discharge
Orcutt	33803040	Jefferson	Union	S-2	10/2/86	3.2	9536	0.0	**4784.4**	6118.4	510.0	N.D.	7500.0	22.0	0.0	Spoil Piezometer
Orcutt	33803040	Jefferson	Union	S-2	10/16/86	3.9	8040	0.0	**5179.6**	2848.0	349.0	N.D.	11120.0	43.0	0.0	Spoil Piezometer
†Fran	4674SM21	Clinton	Keating	K-23	7/28/92	2.2	N.D.	0.0	**23900.0**	5690.0	79.0	2240.0	25110.0	N.D.	0.0	Monitoring Well
††Old 40	3671BSM19	Clarion	Monroe	C 1	11/12/85	2.2	15000	0.0	**10000.0**	3200.0	260.0	550.0	14000.0	N.D.	0.0	Monitoring Well
††Old 40	3671BSM19	Clarion	Monroe	C 1	4/7/87	1.9	17000	0.0	**9200.0**	2200.0	120.0	370.0	6800.0	N.D.	0.0	Monitoring Well
††Old 40	3671BSM19	Clarion	Monroe	C 1	9/15/87	1.8	14000	0.0	**8600.0**	2400.0	< 1.0	440.0	8200.0	N.D.	0.0	Monitoring Well
††Old 40	3671BSM19	Clarion	Monroe	C 5	3/4/86	2.0	12800	0.0	**9400.0**	2400.0	62.0	480.0	10000.0	N.D.	0.0	Monitoring Well
††Old 40	3671BSM19	Clarion	Monroe	C 5	12/10/86	2.0	13100	0.0	**10000.0**	44.0	92.0	380.0	10000.0	N.D.	0.0	Monitoring Well
††Old 40	3671BSM19	Clarion	Monroe		6/7/83	2.4	6000	0.0	**5000.0**	700.0	90.0	180.0	3300.0	N.D.	22.5	Spoil Drain
††Old 40	3671BSM19	Clarion	Monroe		3/13/89	2.2	5000	0.0	**4400.0**	1200.0	75.0	250.0	4000.0	N.D.	4.5	Spoil Drain
††Old 40	3671BSM19	Clarion	Monroe		10/12/83	3.1	3200	0.0	**1100.0**	260.0	55.0	26.0	2100.0	N.D.	4.5	Seep
††Old 40	3671BSM19	Clarion	Monroe		6/4/86	2.6	3140	0.0	**1200.0**	1900.0	140.0	58.0	1900.0	N.D.	0.0	Seep
Zacherl	2769BSM28	Clarion	Clarion		9/17/81	2.3	N.D.	0.0	**9870.0**	2860.0	136.6	583.0	7600.0	N.D.	N.D.	Toe-of-spoil Discharge

* N.D. = No Data

† data from Schueck et al (1996)

†† data from Dugas et al (1993)

Very thorough discussions of the chemical reactions of carbonate mineral dissolution and precipitation and associated solubility and chemical equilibria controls are found in Stumm and Morgan (1970), Krauskopf (1967), Garrels and Christ (1965), Freeze and Cherry (1979), Plummer et al. (1978) and White (1988). According to Krauskopf (1967, p. 52-55), the solubility of calcium carbonate is controlled by the pH of the environment, changes in temperature and pressure, and organic matter activity and decay. Freeze and Cherry (1979, p. 106) state that the solubility of carbonate minerals is dependent on the partial pressure of carbon dioxide (PCO_2), and list the solubilities of calcite and dolomite at partial pressures of 10^{-3} bar and 10^{-1} bar as an indication of the range of values that are relevant for natural groundwater. The solubility for calcite in water at 25° C, pH 7, 1 bar total pressure, and a PCO_2 of 10^{-3} bar is 100 mg/L, while the solubility at a PCO_2 of 10^{-1} bar is 500 mg/L according to Freeze and Cherry (1979, p. 106), using data from Seidell (1958).

However, these relationships may be more complex than they initially appear if the carbonate minerals do not dissolve congruently and the solution contains constituents other than "pure water" (e.g. if the starting solution is saturated with gypsum) according to Rose (1997), who calculated the range of bicarbonate concentrations for calcite dissolution in pure water from 83 mg/L at PCO_2 of 10^{-3} to 370 mg/L at PCO_2 of 10^{-1} using the methods (i.e. Case 4) described in Garrels and Christ (1965). Figure 7.4 from White (1988) shows solubility curves for calcite as a function of carbon dioxide partial pressure, and Rose and Cravotta (Chapter 1, this volume) depict bicarbonate and alkalinity concentration for a similar range of PCO_2, based upon Case 2 of Garrels and Christ (1965, p. 81). Additional diagrams of calcite and dolomite solubility at various carbon dioxide partial pressures are found in Faust (1949), Runnells (1969) and other sources.

Barrow (1973, p. 10) states that the term partial pressure denotes the pressure exerted by one component of a gaseous mixture, in accordance with Dalton's law of partial pressures. According to Stumm and Morgan (1970, p. 180-181) a partial pressure of carbon dioxide of $10^{-3.5}$ bars corresponds to atmospheric conditions, and "The distribution of the dissolved carbonate species at a given temperature is defined entirely by PCO_2." Concerning the partial pressures of carbon dioxide in the subsurface conditions of soil air, soil water, and groundwater; Brady (1974, p. 16, 257) and Hem (1970, p. 45) describe that carbon dioxide in soil air is often several hundred times more concentrated than the 0.03% commonly found in the atmosphere, as much as 10% for example. Also, water moving through soil dissolves some of this carbon dioxide, affecting pH, solubility, and weathering of minerals in the soil and underlying rock. Additional information on limestone dissolution, carbon dioxide partial pressures and the kinetics of chemical reactions involved in the neutralization of acidic water by limestone is found in Cravotta et al. (1994a), Pearson and McDonnell (1974, 1975a, 1975b, 1977, 1978) and Ziemkiewicz et al. (1995).

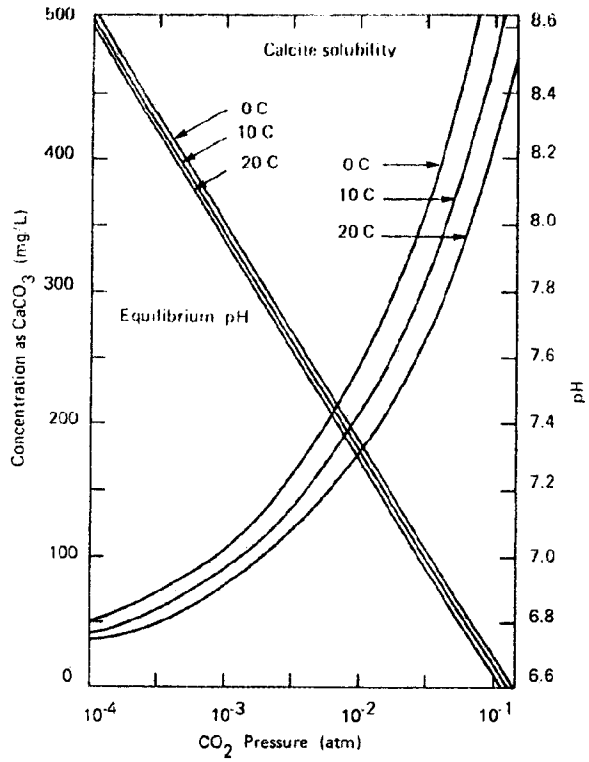

Figure 7.4 Solubility curves for calcite as a function of carbon dioxide partial pressure (from GEOMORPHOLOGY AND HYDROLOGY OF KARST TERRAINS by William B. White. Copyright © 1988 by Oxford Univ. Press, Inc. Used by permission of Oxford Univ. Press, Inc. See pp. 128-131 for equilibrium conditions related to figure).

Davis and DeWiest (1966) indicate that most groundwaters have pH values between 5.0 and 8.0 but that pH values as high as 11.0 have been reported for alkali-spring water in desert regions. Hem (1970) refers to two reported analyses of high pH spring waters in areas of ultramafic rocks, with values of 11.6 and 11.7. According to the National Academy of Sciences-National Academy of Engineering Committee on Water Quality Criteria (1972, p. 54) alkalinities of natural waters rarely exceed 400 to 500 mg/L (as $CaCO_3$).

However, in discussing the chemistry of seawater, Harvey (1957) indicates alkalinity may reach 2,600 mg/L, but rarely exceeds that value. Considering the portion of the alkalinity represented in bicarbonate concentrations, Hem (1970, p. 158) states: "The bicarbonate concentration of natural water generally is held within a moderate range by the effects of carbonate equilibria. ... Most surface streams contain less than 200 mg/L, but in groundwater somewhat higher concentrations are not uncommon". Very high bicarbonate concentrations in groundwaters of the Alto Guadalentin aquifer in the Murcia province of Spain are reported by Ceron and Pulido-Bosch (1996), who consider the high levels of carbon dioxide gas in the groundwater to be a pollutant because increases in the PCO_2 over time have been related to over-exploitation of the aquifer. They report a range of bicarbonate concentrations from 495 to 1890 mg/L with a median of 1010 mg/L for 23 samples from wells in the El Saladar area. The groundwater sample with the maximum bicarbonate concentration had an alkalinity concentration of approximately 1,550 mg/L and also had a sulfate concentration of 1,283 mg/L, chloride of 426 mg/L, calcium of 667 mg/L, magnesium of 244 mg/L, sodium of 181 mg/L, and a PCO_2 of 1.497 bars. Davis and DeWiest (1966, p. 107) indicate a general range of 10 to 800 mg/L for bicarbonate concentrations of groundwaters and state that "concentrations between 50 and 400 ppm are most common". Additional groundwater alkalinity data are in Brady et al. (1996).

Typical bicarbonate and alkalinity concentrations associated with limestones and dolomites in Pennsylvania are found in Langmuir (1971), Shuster (1970) and Shuster and White (1971). Langmuir (1971) reported bicarbonate concentrations ranging from 81 to 438 mg/L for wells and springs in limestone of central Pennsylvania. Shuster (1970) reported a maximum bicarbonate concentration of 292 mg/L from springs in carbonate rocks in central Pennsylvania. Examples of maximum and other relatively high alkalinity concentrations in mine drainage, groundwater and surface waters associated with surface and underground mines in Pennsylvania limestones and dolomites, bituminous and anthracite coals are shown in Table 7.2. The highest natural alkalinity concentration found in PA DEP mining permit file data and reported in Table 7.2 is 626 mg/L in a spring located near the cropline of the Redstone Coal in Fayette County. Thick sequences of carbonate strata, including the Redstone Limestone and the Fishpot Limestone underlie and overlie the Redstone Coal.

The alkalinity of quarry pit waters and underground mine waters in the Ledger Dolomite/Elbrook Limestone sequence in Chester County, the Kinzers Formation in York County, the Valentine Limestone in Centre County, and the Vanport Limestone in Armstrong County, typically range from 150 to 250 mg/L as shown in Table 7.2. It might be expected that underground mine sumps, groundwater inflow, and active deep mine discharges would have higher alkalinity concentrations and higher PCO_2 than surface mine waters open to the atmosphere, but that is not evident in the water samples shown in Table 7.2, apparently due to the properly functioning ventilation systems within the underground mines.

Some stream samples in the bituminous coal region exhibit alkalinities greater than 250 mg/L, and some springs, wells, and abandoned mine discharges have alkalinity concentrations greater than 300 mg/L as shown in Table 7.2. Curiously, the Wadesville shaft pumped discharge in the Southern Anthracite Field typically has alkalinity concentrations greater than 350 mg/L (including a sample from 1986 with 414 mg/L alkalinity), but there are no known major carbonate lithologic units in this stratigraphic section. Another curiosity is that some of the highest alkalinity concentrations shown in Table 7.2 are accompanied by equivalent or greater sulfate concentrations, so that bicarbonate may not be the dominant anion in some of these highly alkaline groundwaters and mine waters. An excellent example of this is found in research on the chemistry of pore gas and groundwater at a reclaimed bituminous coal mine in Clarion County by Cravotta et al. (1994a p. 371), who report a maximum alkalinity of 750 mg/L in an unsaturated zone lysimeter 15 ft (4.57 m) below the land surface, and a sulfate concentration of 3,600 mg/L in the same groundwater sample.

Given the ranges and extreme values of pH, acidity, alkalinity, iron, aluminum, and sulfate reported above, it is reasonable to expect that kinetic tests for AMD prediction should be capable of producing leachate with acidity and sulfate concentrations of several thousand to tens of thousands mg/L, and metals concentrations of several hundred mg/L from worst-case AMD-producing rock samples, and leachate with alkalinity concentration of several hundred mg/L from best-case carbonate rock samples. All of these expectations are possible, as shown in Figure 7.5, even with the use of a relatively crude kinetic test apparatus like that shown in Figure 7.11 in Appendix A.

Table 7.2 High Concentrations of Alkalinity in Mine Drainage, Groundwater and Surface Waters at Limestone and Dolomite Mines and Bituminous and Anthracite Coal Mines in Pennsylvania

Formation	SMP #	County	MP ID	pH	Alkalinity mg/L	Acidity mg/L	Iron mg/L	Mn mg/L	Al mg/L	SO_4 mg/L	TSS mg/L	Type of Sample
Waynesburg 1	30813009	Greene	DM-2	7.8	379.0	0.0	0.12	0.04	N.D.	165.0	17.0	Deep Mine Discharge
Waynesburg 2	30813009	Greene	SP-1A	7.9	296.0	0.0	0.49	0.09	< 0.1	124.0	N.D.	Stream
Redstone	26910115	Fayette	8	7.4	626.0	0.0	1.65	1.05	< 0.5	1440.0	12.0	Spring
Redstone	65930104	Westmoreland	8	8.1	338.0	0.0	0.66	0.33	0.5	181.0	< 3.0	Spring
Lower Freeport	17910103	Clearfield	I-511	7.8	238.0	0.0	0.01	0.01	N.D.	458.0	0.3	Deep Mine Discharge
Blue Lick	56880109	Somerset	Pit Sump	6.8	166.0	0.0	2.86	0.52	< 0.5	220.0	24.0	Pit Sump
Blue Lick	56880109	Somerset	SP15	7.9	276.0	0.0	< 0.3	< 0.05	< 0.5	436.0	< 3.0	Spring
Blue Lick	56880110	Somerset		7.7	138.0	0.0	1.12	0.86	< 0.5	494.0	10.0	Stream
Blue Lick	56880111	Somerset		6.9	226.0	0.0	0.81	0.83	< 0.5	1102.0	10.0	Stream
Lower Bakerstown	56920105	Somerset	L. Pit Water	7.3	118.0	0.0	2.63	5.87	1.2	566.0	8.0	Pit Pool
Vanport	3840105R	Armstrong	15	7.8	274.0	N.D.	0.01	1.13	N.D.	1645.0	1.0	Seep
Vanport		Lawrence	W-29	7.5	324.0	< 2	2.10	0.07	N.D.	40.0	4.0	Well
Wadesville	54713002	Schuylkill	N.D.	6.7	414.0	0.0	3.61	3.37	< 0.5	1038.0	26.0	Deep Mine Pumped Discharge
Wadesville	54713002	Schuylkill	1	6.9	370.0	0.0	1.95	3.42	< 0.5	884.4	< 3.0	Deep Mine Pumped Discharge
Valentine 1	4775SM10	Centre	172	7.5	226.0	0.0	< 0.01	< 0.01	< 0.135	145.0	< 2.0	Pit Water Outfall
Valentine 2	1479401	Centre	174	7.5	146.0	0.0	0.29	< 0.01	0.4	105.0	2.0	Pumped Pit Water
Valentine 3	14900301	Centre	175	7.6	102.0	0.0	2.07	0.05	3.9	44.0	100.0	Raw Pit Water
Valentine 4		Centre		8.0	164.0	0.0	0.22	< 0.01	0.59	68.00	94.00	Deep Mine Discharge
Ledger		Chester	167	8.0	284.0	0.0	0.04	0.01	< 0.135	41.0	4.0	Pit Sump
Loyalhanna	3472SM7	Westmoreland	502	7.7	152.0	0.0	< 0.3	< 0.05	< 0.5	143.2	< 3.0	Pit Water
Kinzers		York	299	7.7	190.0	0.0	0.09	< 0.01	< 0.135	N.D.	< 3.0	Underground Sump
Kinzers		York	300	7.6	178.0	0.0	0.20	0.02	< 0.135	N.D.	< 3.0	Fault
Kinzers		York	301	7.2	170.0	0.0	41.70	2.74	29.0	N.D.	576.0	Inflow
Kinzers		York	302	8.0	172.0	0.0	0.26	< 0.01	0.3	N.D.	< 3.0	Pumped Surface Discharge

* N.D. = No Data

The acidity concentration of 37,042 mg/L shown in Figure 7.5 was produced from a leaching column test on a sample of lower Freeport coal from Somerset County, Pennsylvania which had a total sulfur content of 6.44% and a pyritic sulfur content of greater than 5.5%. The leaching column tests on this coal sample from the Pennsylvania State University Coal Research Section sample repository (PSOC-317) also produced a pH of 1.71, a sulfate concentration of 44,000 mg/L, and a total iron concentration of 1605 mg/L in leachate samples collected during the 35-day leaching study. The leaching column apparatus and tests procedures were developed by Hornberger, Parizek and Williams (1981) as shown on Figure 7.11, and the resulting data, graphical and statistical analyses of variations in sulfur content, abundance of framboidal pyrite, and leachate chemistry are reported in Hornberger (1985). In these leaching column tests, precautions were taken to encourage and confirm the presence of *Thiobacillus* bacteria populations, and the leaching columns were maintained at a constant temperature of 25° C. in an incubator for the duration of the leaching study.

In order to produce the alkalinity concentration of 1,012 mg/L shown in Figure 7.5, a sample of Valentine Limestone from a quarry near Pleasant Gap in Center County, Pennsylvania was placed in a separate leaching column identical to that shown in Figure 7.11. Carbon dioxide gas was bubbled through the contact water during this test conducted in the Land and Water Research lab at Penn State University. The Valentine Limestone sample had a neutralization potential (NP) test result of 987.95 ppt $CaCO_3$ equivalents. Hence the limestone sample should be composed approximately of 98.8% calcium carbonate or calcite. This value is consistent with limestone purity data reported in O'Neill (1964, 1976) and Rones (1969) who show several analyses of the chemical composition of the Valentine Limestone in the same locale ranging from 96.8% to 98.6% calcium carbonate. Additional chemical composition data on the Valentine Limestone, Vanport Limestone, and other Pennsylvania limestones is shown in Chapter 8 (this volume). It can be interpreted using Figure 7.4, that the partial pressure of carbon dioxide in the leaching column was much greater than 10^{-1} bar in order to produce the alkalinity of 1,012 mg/L, (see White, 1988; Chapter 1, this volume).

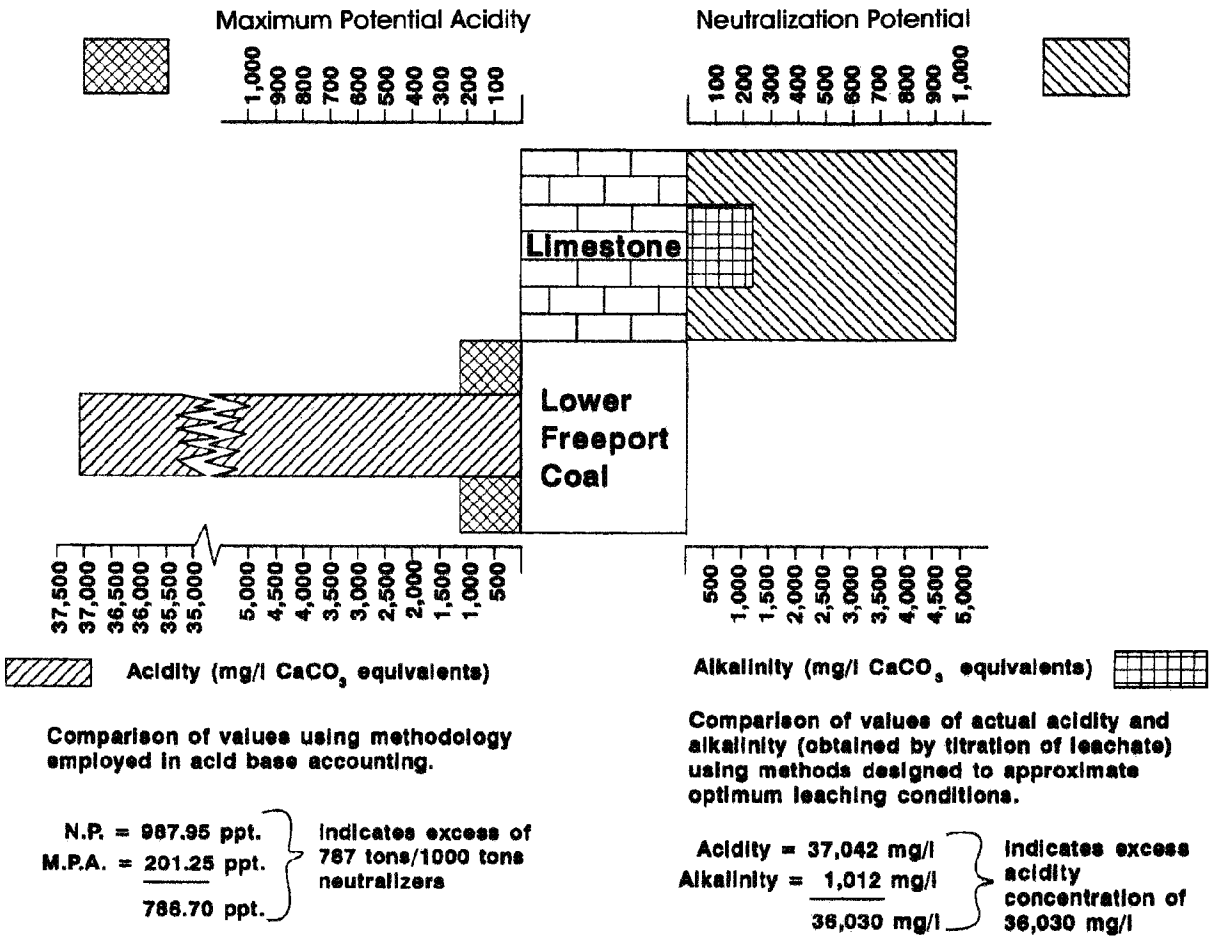

Figure 7.5 Comparison of acidity and alkalinity concentrations from leaching tests with acid-base accounting data from rock samples containing high sulfur and high neutralization potential.

Leaching tests on the same Valentine Limestone sample, without the introduction of additional carbon dioxide, produced alkalinity concentrations of less than 100 mg/L. Adjusting the partial pressure of carbon dioxide as a gas mixture within the leaching column to approximately 10^{-1} bar should be expected to produce alkalinity concentrations of approximately 350 mg/L for the Valentine Limestone sample and similar, relatively pure carbonate minerals.

Figure 7.5 was originally developed by the authors to depict the dramatic differences in the reaction kinetics of the acidity-producing and alkalinity-producing systems, and demonstrate why users of static tests for AMD prediction, like acid-base accounting, must be cautious. Interpretations of data on documented or implied excesses in neutralizers do not automatically translate to definite excesses in alkalinity over acidity concentrations in the mine environment. In this example, a potentially acidic stratum with 6.4% total sulfur content produced acidity concentrations many times greater than the alkalinity concentrations produced by an equivalent weight of rock that is 98.8% pure carbonate. However, the relative stratigraphic positions of these potentially acidic and potentially alkaline strata in the consolidated overburden and in the surface mine backfill, and the sequence and interactions of acidic and alkaline rocks encountered in the groundwater flow system may greatly influence the alkalinity and acidity concentrations of the resultant mine drainage. In the context of this chapter on kinetic tests, Figure 7.5 illustrates why properly designed kinetic tests may be helpful in predicting mine drainage chemistry, especially where static test results are inconclusive or subject to misinterpretation. The remaining discussion in this section of the chapter outlines specific physical, chemical and biological factors to be considered in kinetic test design, performance, and data interpretation.

Size, Shape, and Structure of the Kinetic Test Apparatus

The chronology section of this chapter (see Appendix A) reviews a wide range of kinetic test apparatus used during the past 45-years. Relatively simple leaching columns with a wide variety of diameters and heights and some more complex leaching columns of various dimensions are described. For example, the leaching columns described in Appendix A range in diameter from 1.3 in (3.30 cm) (Hood and Oertel, 1984) to 10 ft (3.08 m) (Murr et al., 1977). The range of size and shapes of humidity cells described in the chronology is apparently not as great as that of the leaching columns, but the complexity of the humidity cell apparatus and peripheral equipment varied substantially from the early work of Hanna and Brant (1962) to the CARWA of Harvey and Dolhopf (1986) and some other recent work with large arrays of humidity cells. Other types of kinetic test apparatuses with substantial complexity of external form and internal structure have been utilized, such as the Warburg respirometer used by Lorenz and Tarpley (1963) and the Soxhlet reactors used by Renton et al. (1973), Sobek et al. (1982), and other researchers.

The Principle of Simplicity (Occam's Razor; see Bross 1981, p. 58 for additional information) may be applicable here, in that the kinetic test apparatus should not be more complicated than it absolutely needs to be, especially considering that multiple arrays of these apparatuses are frequently used concurrently to test multiple rock samples from a proposed mine site. However, the kinetic test apparatus may need some complexity in external form or internal structure to allow fluids and gases (i.e. oxygen and carbon dioxide) to enter, circulate through, and exit the apparatus, in a manner that is representative of weathering conditions of the mine environment.

The relationship between the dimensions of the kinetic test apparatus and the dimensions of the rock samples being tested must be considered in order to prevent adverse interactions between the sample and the container. For example, in some leaching column studies, including Hood and Ortel (1984), and some studies to compare numerous overburden analysis procedures including Bradham and Caruccio (1990, 1995), problems with airlocks within the leaching columns are discussed. These types of problems or artifacts of kinetic test apparatus and procedures must be prevented or minimized because they may skew the test results. In the mine environment, the rock samples within spoil piles and surface mine backfills are not typically in containers when they weather in contact with rainwater and groundwater. Hence, the interaction between the container and the sample should not be a major factor in the test results. According to Potter (1981) and Cathles and Breen (1983, p. E-1) "Solution flow within the column is a critical operating parameter and to avoid undue wall effects the column diameter (I.D) should be four times the largest particle diameter in the aggregate of particles being leached." Murr et al. (1977) developed scaling factors considering the ratio of column diameter and column height and maximum rock size within the column in order to scale solution and air flow rates within the columns. The range of leaching column diameters studied by Murr et al. (1977) were 0.10 m, 0.39 m, and 3.08 m. The large columns were actually stainless steel tanks 40 ft (12.19 m) high and 10 ft (3.08 m) in diameter as further described in Cathles et al. (1977). Additional information on stainless steel leaching columns and elements of leaching theory and practice is contained in Murr (1980).

Another group of studies has evaluated humidity cell performance and parameters including Bradham and Caruccio (1995), Pool and Balderama (1994), and White and Jeffers (1994). In addition, within the last ten years, there have been a number of studies comparing various test methods to determine which is the best AMD predictor, including Caruccio and Geidel (1986a), Erickson and Hedin (1988), Ferguson and Erickson (1986, 1987, 1988), and Bradham and Caruccio (1990, 1995). While most of this discussion and scientific debate has been useful, it may be more productive now to focus on similarities among the various kinetic test methods rather than the differences between them. For example, there are some kinetic tests which have combined features of leaching columns and humidity cells; so that the name or type of kinetic test apparatus may not be as important as the factors affecting the design, performance, and data interpretation of kinetic tests. In the remainder of this chapter, references to specific kinetic test apparatus will be avoided whenever practical, because the following physical, chemical, and biological considerations should be incorporated in any kinetic test.

Particle Size Distribution and Composition of Rock Sample

The mineralogic composition and size distribution of rock materials within a backfilled surface mine are important factors in determining whether the mine spoil

produces concentrations of acidity or alkalinity. Several factors interact to determine the sizes of blocks or particles or rock materials within the backfill, and the corresponding size and distribution of the voids which serve as pathways and storage spaces for the various fluids and gasses contained in and moving through the backfill. These factors are:

(1) the blasting practices used to fragment and cast consolidated overburden strata,

(2) the effects of heavy equipment used to remove overburden strata and conduct backfilling and grading operations,

(3) the fundamental properties of the various lithologic units (i.e. mineralogic composition, grain size, hardness, degree of cementation, porosity, linear sedimentary features (e.g. bedding planes), and

(4) linear structural features (e.g. joints and fractures), within the overburden strata.

The same types of factors are operational within a kinetic test apparatus, but on a different scale. Occasionally, the kinetic test apparatus and type of material being tested may be large enough to use mine spoil or mine refuse samples with rock sizes (particle sizes) as large as those found in the mine environment. Examples include the studies by Renton et al. (1984, 1985) using field barrels of coal refuse samples, and the large tank studies of Cathles et al. (1977) and Murr et al. (1977) using the 10 ft (3.08 m) diameter by 40 ft (12.19 m) high stainless steel tanks for copper ore tailings and leach dump samples. In addition, Caruccio and Geidel (1983) and Geidel et al. (1983) conducted field particle size studies of sandstone and shale samples in 4 ft (1.22 m) by 8 ft (2.44 m) field tubs, to evaluate variations in acid production from 5 different classes of particle sizes ranging from less than 1 in (2.54 cm) to greater than 8 in (20.32 cm) in diameter.

Usually, for the purposes of pre-mine prediction of AMD potential, the rock samples will be obtained from exploration drill holes, and the particle size distribution of the rock sample used in the kinetic test will be determined by the type and method of drilling equipment and by any subsequent crushing or other sample preparation equipment and procedures. As most exploration drilling for coal surface mines is done by air-rotary methods, a maximum particle size of approximately ½ in (1.27 cm) and a nominal or mean particle size of approximately ¼ in (0.635 cm) should be expected for most overburden lithologic units, except where drilling equipment tends to pulverize some lithologies (e.g. coal) into finer grained particles. Therefore, the kinetic test apparatus and procedures should be designed to perform optimally on the particle size distribution produced by air-rotary drilling methods; unless further sample preparation is warranted for other purposes. Some consideration should be given to whether core drilling of overburden analysis test holes is warranted in some circumstances because air rotary drilling methods may mix particles from different lithologic units encountered during drilling and cause interferences in overburden analyses such as the NP test. In addition to preventing sample mixing and resultant chemical analysis problems, core drilling provides for (1) better definition of lithologic descriptions and stratigraphic intervals, and (2) greater control of sample preparation procedures and the resultant particle size distribution of the sample used for kinetic tests.

The particle size distribution of an overburden sample may be determined through a sieve analysis of the sample. In soil classification and analysis, a mechanical analysis is conducted using a series of sieves and other physical methods (e.g. settling, suspension) to separate soils into sand, silt, and clay-sized particles as described by Brady (1974), Terzaghi and Peck (1967), Folk (1968), and others. There are a number of different grain-size classification systems in use, but most of them typically consider particles greater than 2.0 mm to be gravel and particles less than 0.002 mm to be clay sized. The USDA system classifies particles less than 0.002 mm as clay, silt from 0.002 through 0.05 mm, sand from 0.05 through 2.0 mm, and gravel greater than 2.0 mm. The particle size distribution of soils or unconsolidated overburden units, such as glacial till, may then be plotted on a triangular diagram depicting the percentages of sand, silt, and clay-sized particles. Examples of these diagrams are found in Flint (1971, p. 157) for glacial tills, and Terzaghi and Peck (1967) and Brady (1974) for some soils.

As most consolidated rock overburden strata should yield a relatively large percentage of gravel-sized particles in samples obtained from air-rotary drilling (or crushing to a nominal ¼ in (6.35 mm), it is probably not necessary to conduct a complete mechanical analysis to obtain an estimate of the particle size distribution for most kinetic test samples. However, a relatively crude mechanical analysis may be useful to determine the percentages of coarse and fine particles in a few size classes for some specific kinetic test purposes, or in general for different overburden lithologic units. For

example, where samples have been crushed to a nominal ¼ in (6.35 mm) by a jaw crusher, a U.S. series #10 sieve would separate the size fraction less than 2 mm, to retain the gravel-sized particles of nominal ¼ in (6.35 mm); and a #200 sieve with a 74 micron opening would retain the sand-sized grains, and pass the finer silt and clay-sized grains. Alternatively, a #270 sieve equals 53 micron openings which approximates the sand/silt size interface. Additional information on these sieve sizes and procedures is found in soils texts such as Scott and Schoustra (1968, p. 7) and Bowles (1970, p. 35). It could be expected that sandstone overburden samples would possess a relatively large percentage of coarse particles and relatively few fines, especially where the sample is indurated, well-cemented sandstone; and that overburden samples from more fine-grained rocks, like shales and underclays, would possess larger percentages of silt and clay-sized particles.

The presence of a relatively large percentage of fine-grained particles in an overburden sample may have positive and negative effects upon the kinetic test results. According to Bradham and Caruccio (1990), the fine-grained nature of the Canadian metal mines tailings that they tested in leaching columns, caused high specific retention of fluid and created air locks within the columns which skewed the results. In addition, the particle size distribution at the conclusion of the kinetic test may be different (i.e. more fine) than the original particle size distribution of the sample, due to particle decomposition during the test.

Another potential problem is that sorting by grain size can bias a sample. Several studies have shown a disproportionate percentage of total sulfur in the finer-grained portion of a sorted sample. Geidel et al. (1983) evaluated pyritic sulfur contents of 5 particle size fractions (i.e. ranging from greater than 6 in (15.2 cm) to less than 1 in (2.54 cm) of a sandstone sample and a binder sample from a West Virginia surface mine. They found the pyritic sulfur content of the binder increased from 0.28% to 0.74% with decreasing particle size, while the sandstone sample exhibited a general decrease in pyrite sulfur from 0.26% to 0.14% with decreasing particle size. However in field leaching tests (i.e. using plastic lined tubs 8 ft (2.44 m) x 4 ft (1.22 m) x 2 ft (0.61 m) connected to 30 gal (113.56 l) plastic barrels) using natural precipitation, the smallest size fraction of sandstone produced the highest acid loads for the sandstone samples, and the smallest size fraction of the binder produced nearly 10 times the total acid load of the larger particle sizes of binder. The cumulative acid load of the less than 1 in (2.54 cm) binder sample was approximately four times larger than the cumulative acid load of the same size fraction of sandstone sample as shown on plots of the acidity data in Geidel et al. (1983). In a study of more fine grained coal refuse from a West Virgina preparation plant, Renton et al. (1984) initially screened the refuse sample to exclude particles greater than 5/8 in (1.59 cm) diameter, and subdivided the sample into 6 size classes. The largest particle size class ranged from 0.375 in (0.953 cm) to 0.625 in (1.59 cm), while the smallest size class was less than 0.0016 in (0.004 cm). There was a general increase in total sulfur content from 2.58% to 3.90% with decreasing particle size in the coal refuse sample.

Notwithstanding the potential operational problems with some fine-grained samples and some types of kinetic test apparatus, variations in the surface area available for reaction may have dramatic effects upon the chemical reactions of acidity and alkalinity production. According to Brady (1974, p. 43) concerning silt and clay-sized particles in soil:

> "Surface area is the characteristic most affected by the small size and fine subdivision of silt and especially clay. A grain of fine colloidal clay has about 10,000 times as much surface area as the same weight of medium-sized sand. The specific surface (area per unit weight) of colloidal clay ranges from about 10 to 1,000 square meters per gram. The same figures for the smallest silt particles and for fine sand are 1 and 0.1 square meters per gram. Since the adsorption of water, nutrients, gas, and the attraction of particles for each other are all surface phenomena, the significance of the very high specific surface for clay is obvious."

Morin and Hutt (1994a) found that the fine (i.e. less than ¼ in (6.35 mm)) size fraction dominates the surface area of typical waste rock, and recommended expressing rates as mass of acid per gram per week, or mass per unit surface area per week. The fine particles have more surface area per unit mass, and reactivity is proportional to surface area, according to Rose (1997). Additional information on particle size and surface area effects of iron sulfide and carbonate minerals in kinetic tests is found in Lapakko et al. (1995).

Numerous studies have examined the potential effects of pyrite surface area and crystallinity upon AMD production and related topics of pyrite morphol-

ogy (particularly the framboidal form) and depositional environments including Caruccio et al. (1977), Reyes-Navarro and Davis (1976), Rickard (1970), Love and Amstutz (1966), Pugh et al. (1981, 1984), Hornberger (1985), McKibben and Barnes (1986), and Chapter 1 (this volume). According to Rose and Cravotta in Chapter 1 "Kinetic studies indicate that the rate of acidic generation depends on the surface area of pyrite exposed to solution, and on the crystallinity and chemical properties of the pyrite surface."

The consideration of surface area available for reaction in kinetic tests leads to the evaluation of the ratio of the surface area to the volume of leachate, which may be the most important factor in kinetic test design, performance, and data interpretation. This factor will be discussed in the succeeding section on water handling procedures.

Volume and Placement of Overburden Samples in Kinetic Test Apparatus

The volume of sample needed to conduct kinetic tests is related to the size of the kinetic test apparatus and a function of representative sampling considerations. The relationship between the dimensions of the kinetic test apparatus and the dimensions of the rock samples being tested was discussed in a previous section of this chapter in the context of preventing adverse interactions between the sample and the container, particularly where the container was too small or confining. A corollary to that principle is that the amount of sample typically available for the kinetic test should be a determining factor in the dimensions of the apparatus. For example, while the 30-gal (113.56 l) field barrels used by Renton et al. (1984, 1985) were ideally suited to testing representative samples of large volumes of coal refuse; it is unlikely that this apparatus would be suitable for testing the volume of sample available from an air-rotary drill hole intercepting a 2 ft (0.61 m) thick black shale unit. The mass of rock chips and fines from a 5 5/8 in (14.29 cm) diameter air-rotary drill hole, typically used for blast hole drilling and overburden analysis sampling, is approximately 12 kg of sample per foot of rock drilled. According to overburden sample collection procedures outlined by Sobek et al. (1978), Noll et al. (1988), and Chapter 5 (this volume, rock samples from air-rotary drilling methods should be collected at 1 ft (0.305 m) intervals; but several feet of successive samples of the same lithologic unit may be combined or composited for testing purposes. As some significant lithologic units may only have 1 ft (0.305 m) thickness, and representative splits of the sample are typically needed for other overburden tests, including NP and total sulfur content, a sufficient amount of the sample should be allocated for kinetic tests. Generally, the volume of sample available for kinetic tests should be at least 1,000 g for each lithologic unit to be tested.

Where the available volume of rock sample is greater than that needed for the kinetic test, a riffle splitter should be used to obtain a representative split of the sample in the desired volume. That split should be physically representative of the particle size distribution of the available sample, and chemically representative of the mineralogical and bulk chemical composition of the lithologic unit being tested. If the sample has been subjected to a mechanical analysis to determine the particle size distribution (as described in the preceding section of this chapter), the coarse and fine fractions should be recombined by passing them through a riffle splitter or similar device to restore the original particle size distribution of the sample prior to kinetic testing because of the potential to have an unequal distribution of pyrite content in different size fractions.

In kinetic tests where a representative sample from a single lithologic unit is being tested, the method of placement of the sample within the kinetic test apparatus may not be critical, except for the particle size distribution concerns and related potential operational problems (e.g. air locks) described above. Where representative samples from more than one lithologic unit have been combined in the same kinetic test apparatus, particularly when there has been an attempt to construct layers of samples to simulate the configuration of the backfilled spoil, the placement of the sample becomes much more problematic. Chapter 1 and Evans and Rose (1995) describe the significance of microenvironments within coal mine spoil in the production of AMD. Rose and Cravotta state in Chapter 1: "Within a mass of broken pyritic rock in the unsaturated zone, water fills fine pores and occurs as films on grain surfaces. Flow rates of water vary widely as a result of channeling along open pathways vs. near stagnation in water films or fine pores. Also, the abundance of pyrite varies widely from one fragment to another. Because of these factors, the chemical environment within spoil can be very heterogeneous. Small volumes with high pyrite, access to the gas phase, and slow flow of water are expected to develop high acidities compared to volumes lacking pyrite, or with complete water saturation. In addition, *T. ferrooxidans* may attach itself to

pyrite surfaces and create its own microenvironment favorable to oxidation. For all these reasons, it seems likely that no simple characterization of chemical conditions (pH, O_2, Fe^{3+}, etc.) is possible for unsaturated spoil. The solution leaving a mine spoil is a mixture of AMD generated in a variety of microenvironments within the spoil."

The differences in scale between the backfilled surface mine site and the typical kinetic test apparatus are many orders of magnitude apart. However, the potential to have similar microenvironments within the kinetic test apparatus is significant, based upon potential variations in particle size, mineralogy, void spaces, and flow paths. The potential problems are further complicated if different minerals with significant potential acidity and potential alkalinity are combined in the same kinetic test apparatus. Another potential problem with the volume and placement of multiple overburden samples in a kinetic test is that approximately 95% of the total volume of overburden may be relatively inert, with respect to significant acidity or alkalinity production. Then the approximately 5% of sample volume containing minerals with significant acidity or alkalinity potential may become dilluted or misplaced within the test apparatus. In some large kinetic test apparatuses like the 40 ft tall tanks of Cathles et al. (1977) and Murr et al. (1977), it may be possible to create layers of different lithologic units and simulate waste dump, spoil pile, or surface mine backfill behavior of different lithologic units. Actually, while it is possible to construct a replica of a ship in a bottle, it is improbable that the conditions of a stratified surface mine backfill can be replicated in a test tube or even the average sized leaching column.

Water Handling Procedures

The importance of the ratio of the surface area of sample to the volume of leachate from a kinetic test was mentioned in an earlier section of this chapter. Obviously, the volume of leachate or effluent from a kinetic test is related to the volume of influent fluid and other factors including water handling procedures during the test and interactions among the solid sample, fluids, and gaseous phases within the kinetic test apparatus. The importance of water handling in kinetic tests cannot be overstated because the final analytical result of the test will be a set of numbers, usually concentrations of acidity, alakalinity, sulfate, and metals (e.g. iron, manganese, aluminum), of the effluent water samples, which will be used to predict the quality of mine drainage waters located within or emanating from mine sites. The bulk chemistry and mineralogy of the rock samples being tested are no doubt important in the laboratory and in the field setting, but the kinetic test results are expressed in and based upon effluent water quality parameters.

Distilled, deionized water will be the influent in most laboratory kinetic tests for mine drainage prediction, while natural rainfall will be the influent in most field-scale kinetic tests, like those described in Emrich (1966), Glover and Kenyon (1962), Renton et al. (1984, 1985), Pionke et al. (1980), and Pionke and Rogowski (1982). There is probably no good reason to use synthetic precipitation or simulated AMD instead of distilled, deionized water in these laboratory kinetic tests, providing that the physical, chemical, and biological conditions of the test facilitate the oxidation and weathering of pyrite or other iron disulfide or iron sulfate minerals, and the dissolution of carbonate minerals, if present in the rock sample. It is not difficult to achieve these conditions in the average laboratory setting. Distilled deionized water is abundantly available in most laboratories, and will very quickly change from pH 7 to pH 5.7 when exposed to air in atmospheric carbon dioxide concentrations, according to Krauskopf (1967, p. 40) and Hem (1970, p. 91). If an abundance of calcareous minerals is present in the sample and the partial pressure of carbon dioxide within the kinetic test apparatus is greater than atmospheric conditions, influent distilled deionized water (actually a weak carbonic acid of pH 5.7), will generate an effluent of significantly higher pH and alkalinity as carbonate minerals dissolve, to produce more bicarbonate anions in the contact water. Conversely, if an abundance of pyrite or other potentially acidic minerals is present in the sample, and oxygen and iron oxidizing bacteria are readily available, the influent distilled deionized, pH 5.7 water, will readily generate an effluent of significantly lower pH and higher acidity, metals, and sulfate concentrations, indicative of acid mine drainage production.

The volume of influent water must be sufficient to obtain enough effluent water for all desired laboratory analyses, and must be in proportion to the volume of rock sample used in the kinetic tests. Further, the volume of water should simulate or approximate the hydrologic conditions of rainfall, surface water, or groundwater that will be operative in the mine environment. A principal objective of many kinetic test procedures is to perform a short term laboratory simulation of many years of weathering in the mine

environment. However, frequent leaching episodes with relatively large volumes of water may simulate the conditions of a tropical rain forest (i.e. abnormally high infiltration rates) rather than the mine environment within the humid Appalachian Coal Basin or the more arid conditions of the western United States. If the ratio of the volume of influent water to volume of rock sample is much greater than will occur in the mine environment, the concentrations of cations and anions in the leachate will probably be much less (i.e. more diluted) than in the actual mine drainage. For example, the fluid volume to sample volume ratio of 4:1 used in the ASTM Water-Shake Extraction Procedure (1983) floods the sample in a manner that is not representative of most surface mine backfills, which is one of several significant reasons why this technique did not work well for AMD prediction. Therefore, the volume of influent water in kinetic tests is critical for determining dilution of the mass of leached constituents.

This portionality consideration is analogous to the concept of pollution load and other relationships between flow and concentration (Gunnerson, 1967; Smith, 1988, and Hornberger et al., 1990) where high-flow hydrologic conditions produce low concentrations of water quality parameters, and low-flow conditions produce high concentrations. The extremely acidic Iron Mountain mine drainage samples reported in Alpers and Nordstrom (1991) are seepage drip waters within the underground mine and a floor drainage sample, which was representative of the effluent from the portal during low-flow conditions. The worst case samples were "drippings of groundwater seeps from stalactites of either melanterite or rhomboclase under humid, warm conditions" (p. 326), which produced a pH of -1.0, total iron concentration of 111,000 mg/L, and sulfate concentration of 760,000 mg/L; while the floor drainage/portal effluent sample had a pH of 0.48, total iron concentration of 20,300 mg/L and sulfate concentration of 118,000 mg/L. No doubt, if the mine drainage from the Iron Mountain mine was sampled after commingling with the waters of a receiving stream, the total iron and sulfate concentrations would be much lower, following dilution and/or precipitation of the iron, further emphasizing the relationship between flow or water volume and the resulting concentrations of water quality parameters.

The USBM has evaluated the major parameters associated with humidity cell tests to determine their effect on the test precision or repeatability according to Pool and Balderama (1994, pp. 330-331), who reported on two of these parameters, effluent volume and airflow rate and stated:

> "These data indicate that the degree of drying, and the amount of effluent recovered from these tailings affected the amount of acid generated.... The optimum amount of leachant, to generate the most acid, is dependent on the amount required to replace evaporation and control the chemical and biological environment. For these tailings, to produce the most acid approximately half the weight of the sample was added as leachant with a subsequent recovery of only a third of the sample weight as effluent."

It appears that for optimum kinetic test performance, the volume/weight of influent water in any single leaching episode should not be greater than 1 times the rock sample weight; (and normally not greater than 0.5 times the rock sample weight) regardless of whether the apparatus is a humidity cell, leaching column or other device (Bradham and Caruccio, 1995). In fact, in field leaching column tests using actual precipitation as the influent water (Emrich, 1966; Glover and Kenyon, 1962; Renton et al., 1984, 1985; and Pionke and Rogowski, 1982), approximately 45 in (1.14 m) of influent would be used in an entire year, based upon average precipitation rates for Pennsylvania. Renton et al. (1984, 1985) used 35-gal (132.49 l) plastic barrels, filled with 300 lbs (136.08 kg) of rock samples; so the ratio of the rainfall volume to rock sample volume was much less than 1:1 for these rainfall-induced leaching episodes (i.e. approximately 5 gal (18.93 l) of water to 35 gal (132.49 l) of rock, equals 1:5).

The importance of the relationships among the volume of rock sample, surface area of the rock sample, volume of the influent water, amount of water consumed/lost during testing, and volume of effluent from kinetic tests have been discussed above. Now, the effects of water in saturating, humidifying, weathering, and flowing through the rock sample in kinetic tests should be given additional consideration. These factors and associated physical, chemical, and biological interrelationships will affect kinetic test performance and extrapolation to hydrologic conditions in the mine environment.

Overburden rock materials in spoil piles in active surface mine sites will weather when infiltrating rainwater and groundwater pass through the spoil pile, but most of the spoil would not be completely saturated all of the time. In typical backfilled surface mine sites, some of the spoil positioned high in the backfill will be

unsaturated most of the time; some of the spoil located close to the pit floor/underclay may be saturated most of the time; and some spoil in an intermediate position may be alternately saturated and unsaturated as groundwater levels rise and fall within the backfill. The hydrogeologic setting of the mine site (i.e. groundwater recharge area, transition area, or groundwater discharge area) should be considered in determining the appropriate kinetic test procedures. For the above reasons and others that will follow, rock samples in kinetic tests should usually not be completely submerged for the duration of the test. Watzlaf (1992) evaluated pyrite oxidation in saturated and unsaturated coal waste samples in leaching columns using influents of distilled, deionized water and recycled AMD (i.e. previously collected leachate laden with ferric iron). The cumulative loads of sulfate, acidity, iron, manganese and aluminum produced from 189 days of leaching were much greater (i.e. 1 to 3 orders of magnitude) for unsaturated conditions, regardless of whether the influent was distilled water or recycled AMD. Watzlaf (1992, p. 203) concluded that:

> "Saturation of the pyritic coal refuse significantly reduced the rate of pyrite oxidation. The sulfate load produced by the unsaturated columns after 189 days would take 118 years to be generated under saturated conditions in the columns receiving the deionized water leachant...
>
> Theoretical calculations, column leaching, and experience from the metal mining industry show the disposal under saturated conditions can significantly reduce contaminant concentration from pyritic material. A field scale study is needed to demonstrate the utility of this approach."

The effectiveness of submergence of the rock samples in kinetic tests is also discussed in Leach (1991) and Caruccio et al. (1993) who describe:

> "... a series of weathering tests using columns whereby samples of acid producing sandstone and shale would be weathered under vadose conditions, the zone of fluctuating water table and the zone below the water table... The results clearly show that submerging acid producing material below the water table have a dramatic effect on inhibiting acid production." (p. 11)

Within the unsaturated zone of a kinetic test apparatus or a surface mine backfill, the humidity in the void spaces and episodes or cycles of infiltrating water facilitate weathering of the rock sample and the production of acidity or alkalinity in the leachate. The effects of humidity on pyrite oxidation have been evaluated by Borek (1994, p 31) who states:

> "Humidity is an important factor in pyrite oxidation as it has been shown that pyrites weather differently depending on the humidity. The formation of oxidation products is also determined by humidity. These observations suggest that if pyritic waste materials are not in direct contact with water (i.e. high and dry), the exclusion of water is not guaranteed. High humidity conditions can contribute the water needed for pyrite oxidation."

Borek (1994) quantified "the amounts of weathering products formed during abiotic chemical pyrite oxidation of six pyrite samples (i.e. three sedimentary pyrites, and three hydrothermal pyrites) under four relative humidity conditions (i.e. 34%, 50%, 70% and 79%); using Mossbauer spectroscopy to determine the types and amounts of weathering products formed." The principal weathering products identified included two ferrous sulfates, melanterite and rozenite.

Generally, Borek (1994, p. 44) found that:

> "While the amount of product was found to be dependent on the humidity and time, the type of product produced seems dependent on the mode of pyrite formation. The physical properties of pyrite, such as crystal structure, may need to be introduced as contributing factors in oxidation and should be examined like other factors (e.g. oxygen partial pressures, temperature, etc.)."

However, Borek (1994, p. 39) also stated: "Two hydrothermal pyrites (Iron Mountain and Noranda) produced no detectable weathering products at any humidity tested. However, both pyrites are believed to be responsible for contaminating water at their field sites." Unfortunately, there was an absence of iron-oxidizing bacteria in these laboratory experiments.

Incredibly, the Mossbauer spectra of hydrothermal pyrite samples from Iron Mountain, California showed no significant difference (i.e. no weathered/oxidized products) from before weathering and after 250 days in 79% relative humidity conditions; while the actual mine drainage from the Iron Mountain mine reported by Alpers and Nordstrom (1991) had a pH less than 0, sulfate greater than 100,000 g/L, and iron greater than 20,000 mg/L.

The water-handling procedures in kinetic tests, especially within unsaturated zones, and the interactions among the kinetic test apparatus, the rock sample, and the water conditions during the test, are most important for a variety of reasons. According to Caruccio et al. (1993 p. 6): "The physical configuration of the testing method may impact the leachate quality more so than the chemistry of the sample. These artifacts in leachate production may be more directly related to the mechanics of the test rather than reflect the chemistry of the rock." They evaluated artifacts of humidity cells (weathering cells), large and small leaching columns, and Soxhlet reactors, and considered a variety of factors including humidity, ambient temperature, leachant temperature, particle size, infiltrating wetting fronts, capillary zones, porosity, permeability, effects of air locks, effects of submergence, presence of iron-oxidizing bacteria, and leaching interval. Humidity cells and the large leaching columns each had certain factors or features which approximated the hydrologic conditions in the mine environment. The ideal kinetic test probably contains some features from both of these methods.

Leaching Cycles

The procedures and elapsed times that occur when water is introduced into kinetic tests, circulated through and/or stored in a test, and withdrawn from the apparatus as leachate will be referred to as a leaching cycle. Within that cycle, the amount of time allocated to circulation and/or storage may be referred to as the residence time, analogous to the elapsed time between groundwater recharge and discharge in a groundwater flow system. Some kinetic test procedures flush accumulated weathering products from the unsaturated zone with relatively small storage times; other kinetic test procedures may leave some components of the water in storage (i.e., in saturated or unsaturated zones) for longer amounts of time within the leaching cycle. Numerous kinetic test procedures described in the 45-year chronology section of this chapter including Caruccio and Parizek (1967), Geidel (1979), and Rose and Daub (1994), used 1-week leaching cycles, with a variety of differences in procedures within the 1-week cycles. Hornberger et al. (1981, 1985) found significantly higher acidity, sulfates, and metals in 1-week contact samples than 1-hour contact samples from the same leaching columns; presumably due to longer residence time of the water within the test apparatus.

Bradham and Caruccio (1995) evaluated variability in leachate quality from humidity cells, Soxhlet extractors and leaching columns due to the factors of leaching interval, leachate temperature, storage conditions (i.e. the conditions of temperature and humidity under which the rock samples are stored between leachings), particle size, and particle sorting efficiency. They found that storage condition and leaching interval were the factors that had the most significant influence on contaminant production from Soxhlet reactors and humidity cells, while particle size effects played a subordinate, although important role in controlling leachate quality. However, in comparing leachate quality from leaching columns and humidity cells, Bradham and Caruccio (1995) concluded that particle size effects were the dominant factor. The leaching interval and associated time factors may also be critical, depending on whether the kinetic test is an acidity generating system or an alkalinity generating system, according to Geidel (1979) who found that the results of more frequent intervals may produce opposite results in terms of rates of alkalinity and acidity production.

The total number of leaching cycles, therefore the total duration or elapsed time of a kinetic test, varied greatly within the procedures outlined in the 45-year chronology. From the scientific and technical standpoint of accuracy, precision and predictability, the number of leaching cycles, and the total duration of the kinetic test must be sufficient to simulate weathering and natural hydrologic conditions of the mine environment, and to guarantee acceptable reproducibility and repeatability of test results with the same rock samples and same kinetic test conditions. From the standpoint of economics and practicality, the number of leaching cycles and duration of the kinetic test should be short enough to be compatible with time and cost constraints of typical mine permitting. Hopefully, both goals can be satisfied within the same kinetic test.

Gas Handling Provisions (oxygen and carbon dioxide)

The significance of oxygen and carbon dioxide in acidity and alkalinity production in the mine environment and in kinetic tests to predict mine drainage quality has been noted throughout this chapter and elsewhere. Without sufficient oxygen and aeration of the rock samples, pyrite oxidation and weathering will be impeded and AMD production will not reach its full potential. Without sufficient carbon dioxide, the dissolution and maximum solubility concentration of car-

bonate rocks will be reduced dramatically, and alkalinity production will not reach the full potential of the carbonate rocks. This section of the chapter will briefly summarize studies on pore gas composition in mine environments and the effects of oxygen and carbon dioxide upon effluent quality in the field and laboratory settings.

The composition of gases within void spaces and backfilled surface mine spoil located in Pennsylvania and elsewhere has been studied by Jaynes et al. (1983), Lusardi and Erickson (1985), Cravotta et al. (1994a), Guo et al. (1994), Guo and Parizek (1994) and others. Jaynes et al. (1983) found that decreases in oxygen concentration with depth were strongly correlated with increases in carbon dioxide concentrations with increasing depth, but that most of the mine site remained well oxygenated (i.e., oxygen greater than 10%) down to 12 m depth throughout the 2-year study. The highest carbon dioxide concentrations reported were 16.61% at 7 m depth. Cravotta et al. (1994a, p. 368) reported that:

> "Partial pressures of O_2 and CO_2 in spoil are expected to vary depending on the predominant reactions involving the gases, relative rates of the reactions, and rates of gas exchange with surrounding zones (Jaynes et al. 1984a,b; Lusardi and Erickson 1985). In general, where pyrite-oxidation and carbonate-dissolution reactions are active, P_{O_2} will decrease and P_{CO_2} will increase. Data on pore-gas compositions at the mine indicate that P_{O_2} decreases from about 21 volume percent (vol %) at the land surface to less than 2 vol % at 10.7 m below the surface, with corresponding increases in P_{CO_2} with increasing depth in all three areas."

Guo et al. (1994, p47) found oxygen concentrations deep within mine spoil to be greater than 18% at a Clearfield County, Pennsylvania surface mine site, and they state:

> "The field data and a simple model show that thermally induced air convection can be a dominant process maintaining high O_2 concentration in deep mine spoil...
>
> The major hypothesis of this paper is that the thermal anomalies generated by acid-forming, exothermic, pyrite oxidation reactions induce thermal convection that causes significant transport of O_2 into mine spoil."

In a related area of research concerning oxidation concentrations and transport processes within metal mine leach dumps and reclaimed coal surface mine sites, mathematical models have been developed and tested to simulate pyrite oxidation rates and AMD production. Cathles and Apps (1975) and Cathles (1979) describe models of waste dump leaching processes that incorporate air convection, heat balance, temperature dependent oxygen kinetics, and bacterial catalysis. Modeling of pyrite oxidation in reclaimed coal strip mines by gas diffusion processes is described by Rogowski et al. (1983), Jaynes et al. (1984a, 1984b) and Jaynes (1991). According to Jaynes (1984a) the air convection mechanism of oxygen movement used by Cathles and Apps (1975) represents reasonable assumptions for coarse waste dumps, but they believe that diffusion processes would dominate within backfilled coal mine spoil. However, Guo et al. (1994, p. 54) concluded that the: "Results of both field investigation and analytical calculation suggest that the high O_2 concentration (18% or higher) observed in mine spoil cannot be the result of diffusion but, instead, is caused by advection, probably due to thermal convection."

Additional information on oxygen transport is found in Guo and Cravotta (1996). Pyrite oxidation in laboratory kinetic tests has been studied by USBM researchers for more than 60 years including Leitch et al. (1930), Lorenz and Tarpley (1963), Watzlaf and Hammack (1989), Hammack and Watzlaf (1990) and Watzlaf (1992). Oxidation rates of pyrite (with and without bacterial catalysis) were measured by Lorenz and Tarpley (1963) using a Warburg Respirometer, which facilitated the measurement of oxygen consumption during the kinetic test. Hanna and Brant (1962) used the Warburg Respirometer to evaluate oxygen uptake during laboratory weathering of pyrite materials in differing lithological units and particle sizes, in order to compare the oxidation potential of these samples to the results of laboratory leaching methods from the humidity cell type of apparatus they developed. Hammack and Watzlaf (1990) measured abiotic and biotic oxidation rates of pyrite in leaching columns, wherein certified gas mixtures ranging from 0.005% to 14.5% oxygen (plus 5% carbon dioxide and the remainder nitrogen gas) were introduced into the leaching columns via compressed gas cylinders and a gas humidifier. Watzlaf (1992) studied pyrite oxidation in saturated and unsaturated coal waste in leaching columns to determine the effects of dissolved oxygen in

water and the presence of ferric iron upon the pyrite oxidation. According to Watzlaf (1992):

> "To limit pyrite oxidation, oxygen levels must be reduced from an atmospheric level of 21% (0.21 atm) to extremely low levels. It has been shown that the biotic rate of pyrite oxidation is not limited unless pore gas oxygen is reduced to less than 1% (0.01 atm) (Carpenter, 1977; Hammack and Watzlaf, 1990). With current reclamation practices, limiting oxygen to less than 1% is not feasible. At the current time, the only practical method to reduce oxygen to levels low enough to limit pyrite oxidation is by saturating the pyritic material with water (p. 192).... In an unsaturated system, pyrite oxidation has been found to be independent of oxygen levels down to about 1% (Myerson 1981 and Hammack and Watzlaf 1990). Pore gas oxygen levels in surface mine spoil or in coal refuse piles are almost always above 1% .... In a saturated system, pyrite would oxidize at a very low rate that is dependent on the amount of dissolved oxygen and ferric iron in the contacting water. Once dissolved oxygen is consumed, the rate of diffusion of pore gas oxygen through water becomes limiting. (p. 203)"

Watzlaf (1992) also compiled data on pyrite oxidation rates from other studies (expressed in mg of sulfate per gram of pyrite per hour) ranging from 0.06 to 0.16, including data from Braley (1960), Clark (1965), Nicholson et al. (1988), and Hammack and Watzlaf (1990). Cravotta (1996, p. 90) provides a more recent compilation and comparison of pyrite oxidation rates from laboratory experiments ranging from 0.02 to 0.96 (expressed in the same units as above) including data from Rimstidt and Newcomb (1993), Moses and Herman (1991), McKibben and Barnes (1986), and others. These significant studies, including the work of Moses et al. (1987) and Cravotta (1996), evaluated differences in pyrite oxidation rates on the basis of particle size (surface area), pH of initial solution, and availability of oxygen and ferric iron.

In a practical guide to acid mine drainage prediction, Hyman et al. (1995) further summarized laboratory and field studies on the placement of potentially acidic materials below the water table and state that "The dissolved oxygen in the water is too low to create appreciable amounts of CMD (contaminated mine drainage)" p. 25. According to Cathles (1980, personal communication), the dissolved oxygen in groundwater in contact with pyritic materials would not typically be capable of producing an effluent pH less than 3.8; therefore mine drainage with a lower pH emanating from a sealed deep mine, for example, is indicative of an air leak in the system that is augmenting the dissolved oxygen in the groundwater.

Concerning the role of gases in laboratory kinetic tests, Hyman et al. (1995, p. 11) state, "Gas phases, such as oxygen and carbon dioxide, that occur in field conditions may not be represented appropriately in the laboratory test conditions." Gas handling provisions in kinetic test design and operation should account for: (1) percentages of oxygen and carbon dioxide within the test apparatus that are representative of field conditions of the mine environment (e.g., pore gas composition of a backfilled surface mine) and (2) mechanisms to circulate the gas mixture through the apparatus to ensure that chemical reactions (oxidation and dissolution) may take place and promote weathering of the rock samples. From the discussion on pyrite oxidation above, it appears that there should be more than enough oxygen available for pyrite oxidation in the normal laboratory setting if the kinetic test apparatus is open to the air and the rock samples are not entirely saturated within the apparatus. However, the amount of carbon dioxide needed to facilitate significant dissolution of carbonate minerals is more than can be achieved under normal atmospheric conditions, as described in a previous section of this chapter. Therefore, carbon dioxide generally needs to be added to or concentrated within the kinetic test apparatus to enrich the carbon dioxide concentration within the gas mixture unless interactions of minerals (e.g. pyrite) and fluids will increase the PCO_2. If the partial pressure of carbon dioxide in the gas mixture is $10^{-3.5}$ bars (i.e. atmospheric conditions) within the kinetic test apparatus, the maximum alkalinity/bicarbonate concentrations in the leachate will be less than 100 mg/L, even with pure limestones and dolomites. If there is too much carbon dioxide in the gas mixture (e.g. greater than 10^{-1} bars, PCO_2 typically found in groundwater systems and pore gas of surface mine backfills) the bicarbonate and alkalinity concentrations may be greater than 500 mg/L, for example, as shown on figure 7.4 (see also Chapter 1, this volume). To ensure a representative and realistic gas mixture in kinetic tests for mine drainage prediction, it may be necessary to have the kinetic test apparatus fitted with gas ports to enable the constant or intermittent introduction of a controlled gas mixture (for carbon dioxide enrichment) into the apparatus. For example, a gas mixture of 10% oxygen,

10% carbon dioxide and 80% nitrogen in a compressed gas cylinder would probably supply adequate and representative amounts of oxygen for pyrite oxidation and carbon dioxide for carbonate mineral dissolution.

Most of this section of the chapter on gas handling provisions in kinetic tests has emphasized the composition of gases, but the circulation of gases during the test, or air flow is also important. Pool and Balderrrama (1994) evaluated the effects of air flow rate upon humidity cell tests and found that:

> "Changes in air flow rate and effluent volume affected the amounts of sulfate and acid reporting to effluent. Increased air flow rate resulted in more moisture removal and increased acid generation. (p. 1)... In the absence of air flow, evaporation was nearly zero.(p. 9).... The important parameters which affect the acid production in the constant temperature humidity cell apparatus were the pct water removed and the amount of effluent recovered. The pct water removed was controlled by airflow through the cell and across the sample surface, and the amount of effluent recovered was dependent on the amount of leachant used and the airflow." (p. 13)

Biological Considerations in Kinetic Tests

The importance of the role of bacteria in AMD production has been known for more than forty years, and significant early work on this subject in field and laboratory settings is described in Leathen and Braley (1954), Leathen et al. (1953a,b, 1956), Temple and Delchamps (1953), Braley (1954), Silverman and Lundgren (1959), Silverman et al. (1961), Unz and Lundgren (1961), Lorenz and Tarpley (1963), and Razell and Trussell (1963). Braley (1954) discusses the studies at the Mellon Institute that were funded by the Pennsylvania Department of Health to investigate the role of bacteria in acid mine drainage formation. Hanna and Brant (1962) describe the design and performance of a humidity-cell type of laboratory "acid generator apparatus," which they developed in Ohio to study, among other factors, "the effects of bacteria on the acid production process." Lorenz and Tarpley (1963), at the USBM Coal Mining Research Center in Pittsburgh, studied pyrite oxidation in laboratory kinetic tests. They compared oxidation rates with and without the introduction of the iron-oxidizing bacterium, *Ferrobacillus ferrooxidans*, utilizing the bacterial culture medium, growth and harvesting procedures developed by Silverman and Lundgren (1959).

The dramatic effect of iron-oxidizing bacteria populations on AMD production has been described in Singer and Stumm (1970), Brierley (1982), Kleinmann et al. (1981), and elsewhere. Singer and Stumm (1970) found that the rate-determining step in AMD production is the oxidation of ferrous iron wherein the bacteria catalyze the reaction by a factor greater than 10^6. Kleinmann et al. (1981) describe three stages to the AMD production process involving four chemical reactions wherein Stage 1 occurs at a pH above approximately 4.5 with high sulfate but little or no acidity; Stage 2 occurs between pH 2.5 and 4.5 with increasing acidity and low ferric to ferrous iron ratio; and Stage 3 occurs at a pH below approximately 2.5 with high acidity, sulfate, total iron and ferric to ferrous iron ratios. The most significant differences between these stages is the increasing influence of *Thiobacillus ferrooxidans*, to the point that reaction 3 proceeds at a rate totally determined by the activity of *T. ferrooxidans*. Concerning Stage 3, Kleinmann et al. (1981) state that a "vicious cycle of pyrite oxidation and bacterial oxidation of ferrous iron results from the combined effects of reactions 3 and 4."

Concerning the metal mining and dump leaching industry, Brierley (1982, p 44), stated that, while the relatively large-scale leaching of copper was well established by the eighteenth century, the miners did not realize until about 25 years ago "that bacteria take an active part in the leaching process." Brierley also states "Today bacteria are being deliberately exploited to recover millions of pounds of copper from billions of tons of low-grade ore."

There are a number of genera and species of bacteria relevant to acidic drainage production and leaching processes. A large portion of the scientific literature on this subject is devoted to the bacterium, *Thiobacillus ferrooxidans*. According to Brierley (1982), bacteria of the *Thiobacillus* genus are essential to the leaching of metals from sulfide minerals, but other microorganisms may have important roles including *Thermothrix, Leptospirillium* and *Sulfolobus* genera. *Ferrobacillus ferrooxidans*, which has been referred to earlier in this chapter, was subsequently reclassified as a strain of *Thiobacillus ferrooxidans*. Another bacterium, *Metallogenium*, is discussed in Kleinmann and Crerar (1979). All of these bacteria vary in their acidophilic (acid loving) and thermophilic (heat loving) preferences or tolerances, therefore ranges in temperature and pH in natural or constructed/controlled environments may determine which bacteria are present or

absent. According to Brierley (1982, p. 44): "The bacteria involved in the leaching of metals from ores are among the most remarkable life forms known. The microorganisms are said to be chemolithotrophic ("rock-eating"); they obtain energy from the oxidation of inorganic substances. Many of them are also autotrophic, that is, they capture carbon for the synthesis of cellular components not from organic nutrients but from carbon dioxide in the atmosphere."

As stated in Chapter 1, these bacteria, "produce enzymes which catalyze the oxidation reaction, and use the energy released to transform inorganic carbon into cellular matter." While these bacteria require oxygen and carbon dioxide for their metabolism, it appears that relatively low percentages of these gases are sufficient for their survival because, *T. ferrooxidans* obtains carbon autotrophically from atmospheric carbon dioxide (i.e. 0.035%). Brierley (1982) and Cathles and Apps (1975, p. 619) report that "the bacterial oxidation rate of ferrous iron is essentially independent of oxygen concentration in the air until the concentration falls below 1%."

T. ferrooxidans thrives in the temperature range between 20 and 35 ° C, according to Brierley (1982), who classifies the bacterium as moderately thermophilic. Murr et al. (1977, p. 222) report that "The optimum temperature for sulfide leaching catalyzed by *T. ferrooxidans* is 35° C, and that biological oxidation appears to cease at around 55°C (see also Bryner et al., 1967). In large scale leaching column experiments with low-grade copper waste rock, Murr et al. (1977, p. 222) found that... "the population of *T. ferrooxidans* began to decline at approximately 45° C." In related leaching column studies, field measurements of actual industrial sulfide waste dumps, and mathematical models developed to simulate waste dump performance, it has been assumed that, "the bacteria become sick at about 50° Centigrade and finally die or become inactive at about 55° Centigrade" (Cathles (1979); Cathles et al. (1977); and Murr et al (1977)). According to Cathles (1979, p. 185)... "low grade sulfide waste dumps are only very rarely (if ever) observed to have internal temperatures greater than 65°C." In addition Cathles et al. (1977) state: "The fact dumps always appear to operate at temperatures below 55°C is thus direct evidence of the importance of bacteria in at least one step of the leaching process." From some evidence collected by Murr et al. (1977) it appears that a high-temperature microbe, like *Sulfolobus*, was present to account for bacterial oxidation and catalysis of reactions at temperatures somewhat greater than 50° C.

Brierley (1982, p. 47) states that:

> "The most robust of the leaching microorganisms are the extremely thermophilic and acidophilic species of the genus *Sulfolobus*. These bacteria flourish in acidic hot springs and volcanic fissures at temperatures that can exceed 60 degrees C. Some strains of *Sulfolobus* have been observed in springs at temperatures near the boiling point of water."

Some kinetic tests for AMD prediction have incorporated special equipment or procedures in the test to control and/or monitor temperature during the tests; others simply rely upon room temperature in the laboratory or ambient temperature in the field to provide acceptable temperatures for the AMD reactions to take place. Hornberger et al. (1981) placed leaching columns in an incubator within the laboratory and maintained temperatures within the incubator at a constant 25°C. That temperature was selected because 25°C and 1 atmosphere pressure are standard conditions frequently used in studies of chemical reactions as described by Hem (1970, p. 22), Garrels and Christ (1965, Chapter 9) and others. The temperature of 25°C is also within the range between 20°C and 35°C where *Thiobacillus* bacteria flourish (see Brierley, 1982). Cathles and Breen (1983) coiled ¼ in (6.35 mm) copper tubing around their leaching columns and circulated distilled, deionized water from a constant temperature bath through the coils. Fiberglass pipe insulation was used to jacket the column to prevent heat loss and the column was fitted with three thermocouple ports to constantly measure temperature within the column. Temperatures of 35°C and 50°C were selected by Cathles and Breen (1983) because of optimum and upper limits of "non-thermophilic, iron-oxidizing" bacteria performance reported in previous studies (Murr, 1980 and Murr et al., 1977). The effluent solutions from the 50°C column experiments were more concentrated in iron than the 35°C column experiment. Room (laboratory) temperature at 73°F. equals 22.8°C, and is within the range of *Thiobacillus*.

In addition to the fact that optimum temperature for *Thiobacillus* bacterial catalysis of reactions is 35°C, there are other reasons why it may be advantageous to maintain temperatures at 35°C rather than 25°C. Concerning the effect of temperature on chemical reaction rates, Hem (1970, p. 32) states: "The generalization is

commonly made that a 10°C change in temperature changes the rate of reaction by a factor of about 2. The term "reaction" here includes biochemical processes as well as inorganic reactions.

While this increased temperature may be advantageous in optimizing pyrite oxidation, it may be disadvantageous if carbonate minerals are present in the kinetic test, as the solubility of calcite decreases with increasing temperature. Some kinetic test procedures operate at significantly higher temperatures, specifically Soxhlet reactors heat to boiling, then cool to condense water. These test procedures and others including oven drying at 105° C, probably kill bacteria populations between leaching episodes. The fact that there are relatively few sterile natural environments without bacteria has been documented by Bass-Becking et al. (1960), who define the limits of the natural environment in terms of pH and oxidation-reduction potentials (Eh).

The iron-oxidizing bacteria are typically abundant in mine environments, and they can be readily adapted to survive and flourish in a kinetic test apparatus in a laboratory setting without great difficulty. According to Brierley (1982, p. 48):

> "The dumps are not inoculated with the leaching bacteria. The organisms are ubiquitous, and when conditions in the rock pile become suitable for their growth, they proliferate. Rock samples collected near the top of a leach pile typically harbor more than a million bacteria of the species *T. ferrooxidans* per gram."

It appears that there is almost no lower limit to the pH where iron-oxidizing bacteria will survive, but there is some debate and uncertainty on the effects of a pH regime below approximately 2.0 upon *T. ferrooxidans*. Nordstrom and Potter (1977) and Kleinmann et al. (1981) report a 0.8 pH tolerance level of *T. ferrooxidans*. However, laboratory tests indicate that the bacterial oxidation of ferrous iron slows below pH 1.5 (see Silverman and Lundgren (1959), Schnaitman et al. (1969) and), Chapter 1, this volume). Alpers and Nordstrom (1991, p. 327) describe the most extreme conditions of natural acidity developed from pyrite oxidation yet reported (including published documentation of mine water with a pH less than 0), but state that the Iron Mountain, California site contains optimal conditions for all five hydrogeochemical factors required for production of acid mine waters, including iron-oxidizing bacteria (p. 332).

It also appears that there is an upper pH limit where the acidophilus, iron-oxidizing bacteria will not survive, but there is similar debate and uncertainty on the effects of the higher pH regime upon *T. ferrooxidans*. According to Wadell, Parizek, and Buss (1980), the bacteria tend to die off at pH of 5.5 as shown on Figure 7.6. Lovell (1983), Wadell et al., (1980), and others (Chapter 13, this volume) have advocated the development and maintenance of an alkaline environment in mine spoil in order to inhibit pyrite oxidation, including bacterial catalysis. However there is some doubt that the *T. ferrooxidans* actually die off above pH 5.5, according to Rose (1997), who states: "At near-neutral pH, the *T. ferrooxidans* attach directly to the pyrite surface and create a microenvironment at the attachment point where they carry on their chemistry. However, the reaction is much slower than that in solution at a more acidic pH." Additional information on *T. ferrooxidans* survival in this higher pH regime is found in Ehrlich (1962; 1990), who demonstrated tolerance up to pH 6.98 in synthetic buffered media. Kleinmann and Crerar (1979) found the bacteria in a mine drainage-contaminated stream in southwestern Pennsylvania at pH 6.4. "Such presence does not imply acid-producing activity, but it does indicate that the bacteria are available should a suitable environment appear," according to Kleinmann and Crerar (1979, p. 383).

Most of the discussion in this section of the chapter has involved the importance of the presence of iron-oxidizing bacteria upon AMD production in field and laboratory settings, within certain ranges of temperature and pH. In contrast, a brief discussion on promoting the absence of bacteria in mine environments or laboratory settings will follow. As described earlier in the water handling section of this chapter, it is almost beyond belief that the Iron Mountain pyrite samples, "displayed no significant weathering over time in any relative humidity" (Borek, 1994, p. 31) in the absence of iron-oxidizing bacteria in the laboratory; while the Iron Mountain pyrite weathering in the presence of bacteria in the mine environment (i.e. field conditions) produces the most extreme conditions of natural acidity developed from pyrite oxidation including pH less than 0.0.

The use of alkaline addition materials (e.g. limestone crusher fines and lime plant fluedust) to promote an alkaline mine environment and thereby inhibit the bacterial oxidation of pyrite, has been evaluated in laboratory kinetic tests by Rose and Daub (1994), and

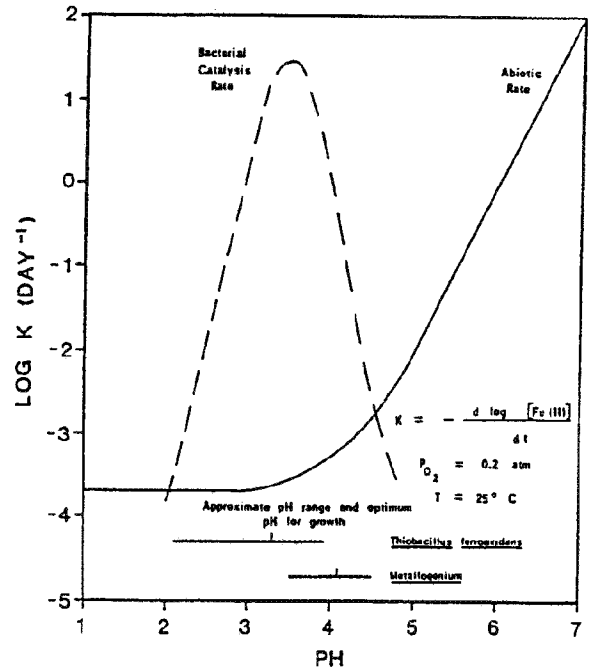

Figure 7.6 Reaction rate as a function of pH for the oxidation of ferrous iron (from Waddell et al., 1980).

in surface mine environments by Waddell et al. (1980), Dugas et al. (1993), Evans and Rose (1995), Rose et al. (1995), Perry and Brady (1995), and Williams et al. (in press).

There also have been significant efforts to use bactericides (e.g. Sodium lauryl sulfate and other anionic detergents) to inhibit, control or minimize AMD production at mine sites, including the work of Walters (1965), Dugan (1975), Walsh and Mitchell (1975), Kleinmann and Crerar (1979), Kleinmann et al. (1981) and Parisi et al. (1994). Additional information on these bactericidal controls is found in Chapter 15.

From all the above discussions on biological considerations in kinetic tests, it should be obvious that iron-oxidizing bacteria must be allowed to be active in the kinetic test apparatus if the test conditions and results are expected to be representative of pyrite oxidation potential in the mine environment. In some laboratory kinetic test procedures, the presence of iron-oxidizing bacteria is guaranteed by the use of relatively formal inoculation procedures including the work of Lorenz and Tarpley (1963), Cathles and Breen (1983), and others. In field scale kinetic tests, it is not necessary to inoculate the rock samples with iron-oxidizing bacteria because they are ubiquitous in the mine environment (Brierley, 1982).

Some kinetic test procedures have ensured the presence of iron-oxidizing bacteria in the laboratory by wetting the rock sample with mine drainage collected in the field. Hornberger et al. (1981, 1985) demonstrated that *Thiobacillus* bacteria can survive from the field to laboratory leaching columns, including rock crushing and other sample preparation procedures, by simply wetting the rock samples with pit water at the surface mine site, and keeping the samples moist through storage in plastic bags until placement in the leaching columns. Numerous studies have informally inoculated the rock samples in laboratory kinetic tests by adding AMD from a deep mine or surface mine to the kinetic test apparatus during the initial wetting of the rock sample or at some other point in the test, including the work of Smith et al. (1974), Poissant (1986), and Poissant and Caruccio (1986).

Regardless of how the iron-oxidizing bacteria have arrived in the laboratory kinetic test apparatus, their presence and relative abundance in the sample may be determined and quantified using a culture medium and a Most Probable Number method (see Standard Methods, Greenberg, et al. Eds. (1980, p. 802)). Bacteria populations determined by this MPN method in AMD studies are reported in Murr et al. (1977),Cobley and Haddock (1975), Olem and Unz (1976, 1977), Cravotta (1996), and other references. These techniques may be used to document that adequate biological considerations have been included in the kinetic test, and that the test conditions and results are representative of the mine environment.

Summary and Recommendations

The role of physical, chemical and biological factors in mine environments and in kinetic tests has been described in the preceding sections of this chapter and numerous examples are given in the chronology in Appendix A. Most of these factors must be incorporated into the design, operation and interpretation of kinetic tests for AMD prediction, or the laboratory data will have little or no relevance to the real world. Given the ranges and extreme values of pH, acidity, alkalinity, iron, aluminum, and sulfates found in mine environments as shown in Tables 7.1 and 7.2, it is reasonable to expect that kinetic tests for AMD prediction should be capable of producing leachate with acidity and sulfate concentrations of several thousand to tens of thousands mg/L, and metals concentrations of several hundred mg/L from worst- case AMD producing rock samples, and leachate with alkalinity concentrations of several hundred mg/L from best-case carbonate rock

samples. If the concentrations of acidity, alkalinity, sulfates, and metals in the leachate from a kinetic test are equivalent to the concentrations of these parameters in the mine environment, the interpretation of the test results will be more straightforward than applying a dillution factor or some other transformation of the leachate data. Also, if the leachate data will be subjected to some further graphical or mathematical analysis (e.g. converting the concentration data to mg acidity/g sample/day and plotting the cumlative acidity), it may be helpful to refer back to the original concentration data and find a range of concentrations that can be directly related to post-mining discharge concentrations in the field.

Therefore, a major objective of kinetic tests for mine drainage prediction should be to simulate the quality of effluent from the rocks to be mined with a reasonable degree of accuracy and precision. The following nine general principles of kinetic test design and performance constitute a summary and guidelines of the major factors to be considered in that simulation:

1. The size, shape and structure of the kinetic test apparatus should be as simple as is practicable, given that multiple arrays of these devices may be needed to concurrently test multiple rock samples from a proposed mine site. Yet, the apparatus may need some complexity in external form or internal structure to allow fluids and gases (i.e. oxygen and carbon dioxide) to enter, circulate through and exit the apparatus in a manner that is representative of the weathering conditions of the mine environment.

2. The dimensions of the kinetic test apparatus should be in proportion to the particle size distribution and volume of the rock sample to be tested, so that there are no adverse interactions (e.g. airlocks or other testing artifacts) between the sample and its container. For example, with a columnar shaped apparatus, the inside diameter of the column should be at least several times greater than the largest particle diameter within the volume of rock samples.

3. The goals of sampling for kinetic testing should be to obtain rock samples that are representative of the physical (i.e. particle size distribution) and chemical (i.e. mineralogic composition) characteristics of the consolidated overburden strata, or backfilled mine spoil, or waste dump to be simulated in the test. If the rock samples are obtained from air rotary drilling procedures typically used in overburden analysis testing, the particle size distribution within the kinetic test apparatus will probably not be truly representative of the particle size distribution within the mine spoil. Consideration should be given to the percentage of relatively coarse (i.e. gravel sized) particles and relatively fine grained particles in the sample. A greater percentage of fine particles increases the surface area available for reaction, which is a critical parameter in the production of acidity or alkalinity.

4. Multiple lithologic units should not be combined in the same kinetic test apparatus, in composite samples, or especially not in layers, unless the potential acidity or alkalinity of the individual lithologies is already known from similar kinetic tests, static tests or equivalent geochemical information. If more than one lithologic unit is contained in the same kinetic test apparatus, the method of placement of the sample within the apparatus becomes more problematic, and the effect of microenvironments with the apparatus should be evaluated.

5. The volume of influent water minus the volume of water consumed during the kinetic test determines the volume of effluent water or leachate. These volumes of water should be properly proportioned to the volume of rock sample being tested and should simulate or approximate the hydrologic loading conditions (i.e. amounts of rainfall, surface water or groundwater) that will be encountered in the mine environment. The ratio of the surface area of rock sample to the volume of leachate may be the most important parameter in kinetic test design, performance and data interpretation.

6. Rock samples in kinetic tests usually should not be in a completely saturated condition for the duration of the test, because pyrite oxidation rates will be greatly diminished when the samples are submerged, and the kinetic test effluent water samples may not be indicative of the concentrations of acidity, sulfate, and metals that will be produced in the actual mine environment. To simulate the weathering conditions of a surface mine or mine waste dump, the rock samples should be in a partially saturated, or intermittently saturated and unsaturated condition during the test, which approximates the effects of episodes of infiltrating rainfall and the groundwater flow system within the mine environment. In these unsaturated zones within the kinetic test apparatus, weathering of the rock samples will be enhanced by alternating wetting and drying cycles, and the effects of humidity, water flow and air flow through the voids or pore spaces.

7. The pore gas composition within the kinetic test apparatus should be similar to that within reclaimed surface mine spoil, particularly to have a partial pressure of carbon dioxide sufficient to facilitate the dissolution of carbonate minerals. To ensure a representative and realistic gas mixture in kinetic tests for mine drainage prediction, it may be necessary to have the kinetic test apparatus fitted with gas ports to enable the constant or intermittent introduction of a controlled gas mixture into the apparatus (i.e. for carbon dioxide enrichment). For example, a mixture of 10% oxygen, 10% carbon dioxide and 80% nitrogen in a compressed gas cylinder would supply adequate and representative amounts of oxygen for pyrite oxidation and carbon dioxide for carbonate mineral dissolution.

8. Iron-oxidizing bacteria must be present and relatively abundant within the kinetic test apparatus, if the test conditions and results are expected to be representative of pyrite oxidation potential in the mine environment, because abiotic pyrite oxidation rates are 6 orders of magnitude less than bacterially catalyzed pyrite oxidation rates, and because the iron-oxidizing bacteria will be ubiquitous in the mine environment, unless conditions of high pH or very high temperature adversely affect their survival. It may be necessary to inoculate the rock sample with *Thiobacillus* bacteria at the commencement of the kinetic test, and maintain temperature conditions between 20°C and 40°C during the test to provide optimum conditions for a healthy bacteria population.

9. The ideal kinetic test for the prediction of mine drainage quality will be: (a) practical to construct and operate, (b) of reasonable time and cost requirements to encourage widespread acceptance and use, (c) representative of the physical, chemical and biological conditions of the mine environment (i.e., in conformance with the preceding 8 principles), and (d) readily interpretable due to the capability of producing the range of acidity, alkalinity, sulfate, and metals concentrations found in acidic and alkaline mine drainage. From the scientific and technical standpoint of accuracy, precision, and predictability, the number of leaching cycles and the total duration of the kinetic test must be of sufficient length to simulate mineral weathering and natural hydrologic conditions of the mine environment, and to guarantee acceptable reproducibility and repeatability of test results with the same rock samples and same kinetic test conditions. From the standpoint of economics and practicality, the number of leaching cycles and duration of the kinetic test should be short enough to be compatible with time and cost constraints of typical mine permitting. It may be necessary to employ interpretative tools (e.g. mathematical models) and interfaces between long-term laboratory research studies and short-term leachate production tests to satisfy all of these goals and correctly predict mine drainage quality in some relatively complex geochemical or hydrogeologic settings.

Development of Standard Kinetic Test Procedures for the Prediction of Mine Drainage Quality

The goal of developing standard kinetic test procedures for predicting mine drainage quality has been emphasized throughout this chapter. In the four years since the Third International Conference on Acidic Drainage in Pittsburgh in 1994, several significant steps have been taken toward consensus building on acid mine drainage research and development issues among Federal government regulatory and research agencies, state regulatory agencies, mining industry representatives, and university researchers. Recently the Acid Drainage Technology Initiative (ADTI) has been formed by a group of Federal agencies under the leadership of the U.S. Office of Surface Mining (OSM), the National Mining Association, the Interstate Mining Compact Commission, and the National Mine Land Reclamation Center. One of the two major working groups of this initiative is on prediction. It is hoped that this group may be able to develop a consensus on kinetic test procedures for the prediction of mine drainage quality as one of its primary goals. Two major advantages of developing standard kinetic procedures through this consensus building effort are that almost everyone, especially for mine permitting purposes, would be using the same test procedures (which facilitates data comparison and data base building) and that scientific and legal controversies between government and industry users of prediction techniques over interpretations of the test results and accuracy of the predictions would be substantially reduced.

Much can be learned from work completed in other industries on the development in application of standard kinetic test procedures. In the residual and hazardous waste industry, the Environmental Protection Agency, the state regulatory agencies, the industry and their consultants are consistently using the Toxicity Characteristic Leaching Procedure (TCLP) and the

Synthetic Precipitation Leaching Procedure (SPLP) and are building an acceptable data base from which scientific inferences, permitting decisions, and case-to-case comparisons can be made. In the nuclear waste industry, a significant amount of research was done on leaching processes leading to the development of ANS 16.1 (American Nuclear Society, 1984) and the MCC1 leach test (Pacific Northwest Laboratory, 1980). An example of the use of the MCC1 leach test on nuclear waste is described in Ebert and Bates (1992), while Zhao (1995) provides extensive data on leach testing of flyash and fluidized bed combustor (FBC)ash cements using the MCC1 test. The work of John K. Bates and associates at Argonne National Laboratory on nuclear waste glass also provides relevant information on surface area/leachate volume ratios (Aines et al., 1986; Ebert and Bates, 1992; Feng and Bates, 1993; Feng et al., 1994), which were discussed in the water handling section of this chapter. A summary description of the MCC1 test, ANS 16.1 and numerous other leaching methods is presented in Sorini (1997).

The Toxicity Characteristic Leaching Procedure (TCLP) is designed to simulate the leaching a waste will undergo if disposed of in a sanitary landfill, and is found as Method 1311 in the EPA manual entitled Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846. The Synthetic Precipitation Leaching Procedure (SPLP) is Method 1312 and it is designed to determine the mobility of both organic and inorganic analytes present in samples of soils, wastes, and waste waters. While both of these standard test methods are now well founded in the waste industry, it appears that neither of these methods is appropriate for the prediction of mine drainage quality, based in part, on studies by Franklin and Zahl (1988) and Boyle and Smith (1994). It would be desirable to develop a standard Mine Drainage Leaching Procedure (MDLP) for use by the mining industry and its consultants, state regulatory agencies, and Federal regulatory and research agencies, with the support and approval of the EPA, OSM, IMCC, and the NMA.

It would be unrealistic to expect that the development of a MDLP test would instantly be accepted and used by all mine drainage researchers and research users in the United States and elsewhere, and that long-standing kinetic test research programs at universities and Federal research centers would all abandon their efforts in favor of the new MDLP. That is not our expectation. After the development of a MDLP test, there would probably always be some specific research purpose that would require a kinetic test apparatus of greater sophistication, or a greater test duration than the MDLP. Those specific research purposes may be largely unaffected by the development of a MDLP test or suite of test methods. The real beauty of a standard MDLP for the prediction of mine drainage quality would be that it would be required or recommended as the preferred method where needed, as part of mining permit applications by the state and Federal regulatory agencies. Finally, it would facilitate a meaningful comparison of kinetic test results from rock type to rock type, mine site to mine site, state to state, and nation to nation in order to make sound permitting decisions, prevent mine drainage pollution problems which financially cripple mining companies, and build effective data bases for future use by all stakeholders.

Relationships Among Kinetic Tests, Static Tests, and Other Methods of Predicting Mine Drainage Quality

Kinetic tests alone are not the answer to the prediction of mine drainage quality. They should be used in combination with static tests and other predictive techniques including evaluation of background water quality, mine drainage quality produced at nearby mine sites or mines in similar lithologic settings, and detailed stratigraphic analyses. Kinetic tests will usually be more expensive and more time consuming than static tests; therefore the kinetic tests should be used selectively when needed because the static tests are inconclusive or require augmentation.

It may be appropriate to use a phased approach to the prediction of mine drainage quality for a proposed mine site, wherein all rock samples to be evaluated are initially subjected to relatively simple static tests, such as neutralization potential (NP) and total sulfur content; whereupon these indicators or surrogate measures of potential alkalinity and potential acidity of all strata to be affected are used to determine which of these rock samples should be subjected to kinetic tests for a more realistic simulation of mine drainage quality. The B.C. Research Initial Test and B.C. Research Confirmation Test described in Bruynesten and Hackl (1984) are an example of this type of approach, where the initial static test is followed by the kinetic test if the sample is initially found to be a potential acid producer. Another example is the Knoxville, Tennessee OSMRE Field Office guidelines on kinetic testing described in Maddox (1988), wherein experience proved that the net acid base account by itself on some samples, was not a reliable predictor of acid mine drainage generation, and

further kinetic testing of these samples was recommended.

A conceptual method of implementing a phased static and kinetic testing protocol for mine drainage quality prediction would be to construct a 3 x 3 matrix (9 cells) where on one axis three classes of percent sulfur values represent low, medium and high potential acidity, and on the other axis, three classes of neutralization potential values represent low, medium and high potential alkalinity. Based upon these static test results, each rock sample from an overburden analysis would be classified in one of these nine cells. By operational rules it could be determined which of these nine classes demonstrate that the static test results are sufficient for mine drainage quality prediction purposes, which of the nine classes demonstrate that kinetic tests are needed for a further simulation of mine drainage quality, and which of these nine classes would require some other type of predictive analysis.

Regardless of whether kinetic tests are used alone or in combination with other methods of predicting mine drainage quality, hopefully this chapter has presented a foundation and sufficient reasons why practical, efficient, reliable and interpretable standard kinetic test methods should be developed for use by the mining industry and regulatory agencies in the prediction of mine drainage quality.

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APPENDIX A

Chronology of the Development of Kinetic Tests for Mine Drainage: 1949 - 1994

Early History

One of the earliest workers in the field of coal mine drainage was S. A. Braley (1949, 1960) from the Mellon Institute of Industrial Research in Pittsburgh, Pennsylvania. Braley (1949) described experiments in which glass columns were filled with crushed coal samples, distilled water was added and aeration of the sample and influence of bacteria on AMD production were evaluated. Braley (1960) developed a test to estimate the oxidation of pyrite wherein 100 g of weathered crushed sample were placed in a 400 ml. beaker and submerged with 250 ml. of distilled water for 24 hours; then drained, filtered, diluted and analyzed for pH, acidity, calcium and sulfate. The residue was then returned to the beaker, flooded with 250 ml. of distilled water, and covered with a watch glass for repeated iterations of the test.

As coal surface mining in Appalachia flourished from World War II into the 1950's and 1960's, state and federal agencies and universities in the Appalachian states became increasingly more involved in acid mine drainage research when AMD impacts on surface waters and groundwaters increased in these areas. The Pennsylvania Sanitary Water Board (1952, 1958), Temple and Koehler (1954) in West Virginia, and Moulton (1957) and Brant and Moulton (1960) in Ohio, produced reports and manuals on the control, treatment, and prevention of AMD from bituminous coal mines in these states.

The U. S. Bureau of Mines (e.g. Lorenz and Tarpley, 1963), the U. S. Geological Survey (Biesecker and George, 1966), and the Appalachian Regional Commission (1969, a federal and state agency consortium) were working on the documentation of the magnitude of the AMD problem in Appalachia at that time, and were conducting research on the production, prevention, and abatement of AMD. Some of the publications referenced above, and related studies by some of the researchers, such as Hanna and Brant (1962), Lorenz and Tarpley (1963), and Emrich (1966) contain significant information on kinetic test developments and applications.

Hanna and Brant (1962, p. 483) describe leaching studies, in which "several basic laboratory apparatuses were designed and tested for the purpose of acid gen-

eration in order to simulate acid production in nature, but under controlled laboratory conditions." They describe the acid generator apparatus that was developed and used in their research, (shown on Figure 7.7), as follows:

> "The generator consists of a sample cell, a diffusion unit to supply saturated water vapor, a separatory funnel used for flushing, and a receiver. It is anticipated that this basic cell with modifications will make it possible to continue studies on various phases of the work, such as relationships between acid produced and particle size or reactive area exposed; the effects of bacteria on the acid production process; the effects of applications of various inhibitors to the sample; and many other factors which must be investigated in order to more thoroughly understand the acid formation phenomena."(p. 484)

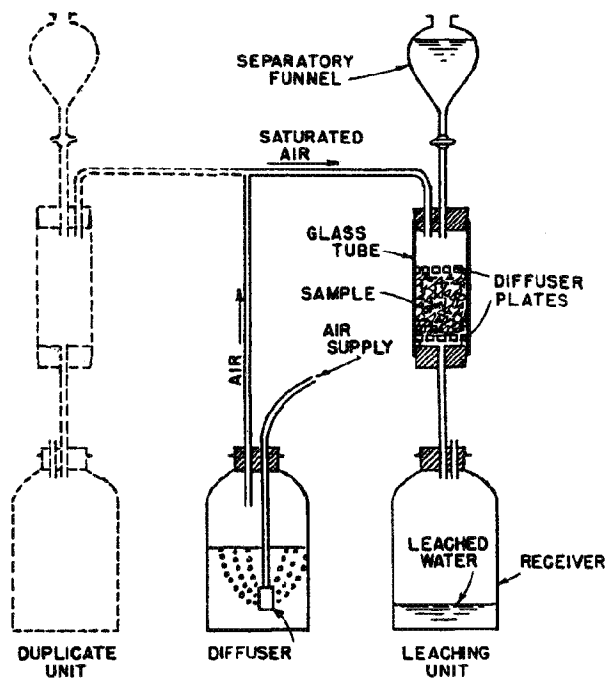

Figure 7.7 Acid generator apparatus (humidity cell) (from Hanna & Brant, 1962).

Hanna and Brant (1962) conducted comparative leaching studies on various particle sizes of coal, shales and sandstones from high walls and spoil piles. Because the samples were continuously exposed to water vapor between daily flushing episodes that removed accumulated weathering products, this type of kinetic test apparatus became generically called a humidity cell.

In studies at the U. S. Bureau of Mines in Pittsburgh, Lorenz and Tarpley (1963) used a laboratory apparatus called the Warburg constant-volume respirometer to evaluate pyrite oxidation. This apparatus, shown on Figure 7.8, was attached to a shaker arranged so that the sample in the reaction flask was immersed in a constant-temperature water bath, and that the liquid in the reaction flask was saturated with air. Lorenz and Tarpley (1963) evaluated the effect of iron oxidizing bacteria, the presence of calcite, and ferrous/ferric sulfate solutions on the pyrite oxidation in these laboratory studies. They also conducted X-ray diffraction, emission spectrography, and microscopic analyses of the pyrite samples. Hanna and Brant (1962) also used the Warburg Respirometer method on selected samples to measure the oxidation of pyritic materials, and to provide comparison to their leaching studies described above.

Emrich (1966) presents a survey of scientific literature and associated test methods for estimating the oxidation or acid potential of acid-forming material in coal seams and associated rocks (p. V-7). That technical bulletin is contained in the publication entitled "Mine Drainage Manual" by the Pennsylvania Department of Environmental Resources (1973), which is a precursor to this book. In fact, Emrich (1966) states, "The Pennsylvania Sanitary Water Board now requires that the quality and quantity of drainage from a proposed operation be estimated" (p. V-6). Emrich (1966) recognized that the beaker test described above from Braley (1960) has serious limitations for evaluating acid mine drainage potential including that: "During the test, the sample is continually submerged in distilled water and there is, at best, only an extremely limited opportunity for future oxidation of the acid-forming material." (p. V-8). Emrich (1966) also gave credit to the glass leaching column method of Braley (1949) in that: "This method very closely simulates conditions that occur in nature when coal is mined except for the periodic wetting, drying and oxidizing of the sample." (p. V-8). Emrich (1966) also describes a "European method" of Glover and Kenyon (1962) of evaluating the chemical character of drainage from coal stockpiles, using drain-tile leaching columns (12 in (0.305 m) diameter x 3 ft' (0.914 m) length) shown on Figure 7.9, constructed outdoors to utilize actual precipitation. Additional information on this kinetic test and European mine drainage control procedures is reported in Lyon and Maneval (1966). Finally, a kinetic test method is presented that was developed by

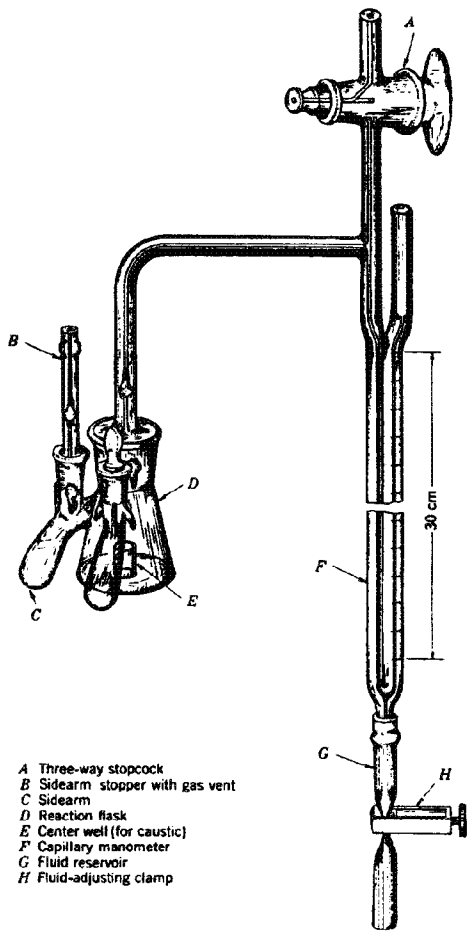

Figure 7.8 Warburg Respirometer (from Lorenz & Tarpley, 1963).

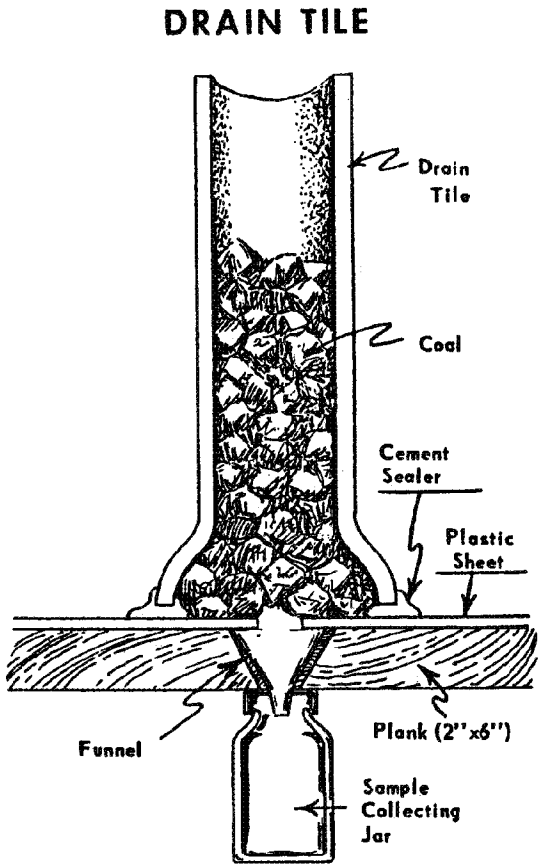

Figure 7.9 Field (drain-tile) leaching column (from Emrich, 1966).

Emrich (1966) and others at the Pennsylvania Department of Health, in which a Soxhlet Extractor (Figure 7.10), is used in a laboratory setting to accelerate the weathering process through repeated iterations or "passes" where the rock samples are aerated, heated, humidified, and flushed with distilled water.

The Pennsylvania State University has made significant contributions to the field of coal mine drainage research for many years. Some of the early work is summarized in Dutcher et al. (1966, 1967) and Parizek and Tarr (1972); while more recent summaries are found in Lovell (1983) and Hornberger et al. (1990). A long line of research reports involving kinetic test developments, refinements and applications in coal mine drainage research from the Department of Geosciences at Penn State commenced with the publications by Caruccio and Parizek (1967, 1968) and Caruccio (1967).

Caruccio and Parizek (1967, 1968) developed a humidity cell apparatus, similar in principle to that of Hanna and Brant (1962). The "simulated weathering" test method of Caruccio and Parizek (1967) emphasizes the continuous exposure of the rock sample to humid air piped into the sample container, and the regular flushing of accumulated weathering products with distilled water at intervals of 7 days. The paper by Caruccio and Parizek (1968) appeared in the Second Symposium on Coal Mine Drainage Research in Pittsburgh. Numerous other papers on kinetic test developments, including Singer and Stumm (1968), appeared in the symposium series, which originated in Pittsburgh under sponsorship by Bituminous Coal Research and the Mellon Institute.

Later, at the University of South Carolina, Dr. Frank T. Caruccio continued to conduct simulated weathering tests with the humidity cell apparatus(shown on Figure 7.2) on coal and overburden samples from the Appalachian Region, as reported in

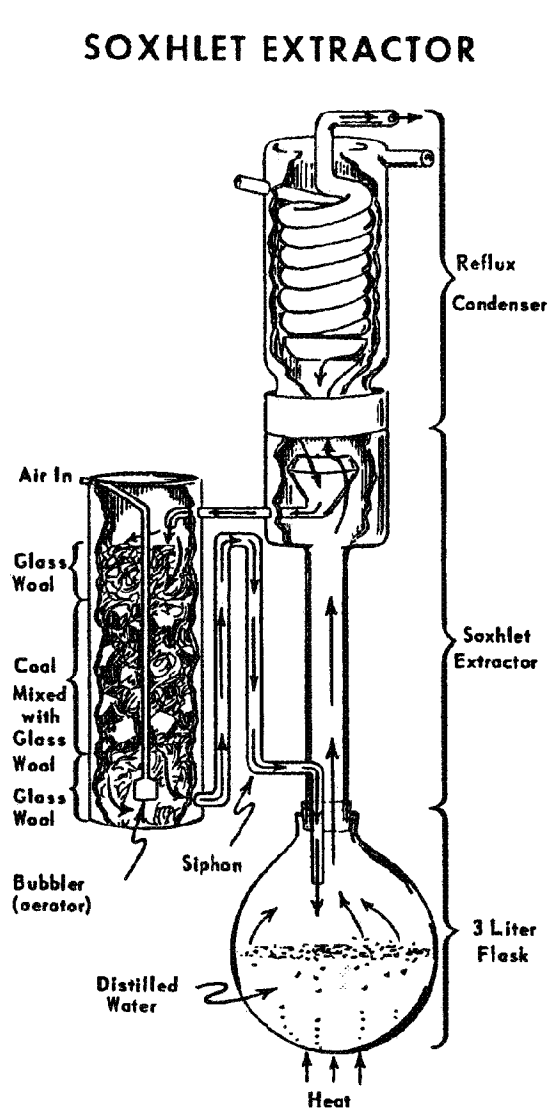

Figure 7.10 Soxhlet extractor (from Emrich, 1966).

Caruccio and Ferm (1974), Caruccio and Geidel (1978, 1980, 1981a, 1981b), and Caruccio et al. (1976, 1977, 1981). Dr. Frank Caruccio, Dr. Gwen Geidel and associates have been leaders in kinetic test developments and applications, some of which will be referred to later in this section (Caruccio and Geidel, 1986a; Bradham and Caruccio, 1990).

At West Virginia University, Dr. Richard M. Smith and associates, principally soil scientists, were conducting AMD research funded by the U. S. Environmental Protection Agency, including the development and use of static and kinetic tests for predicting mine drainage quality, as described in Grube et al. (1971), Smith et al. (1974), Smith et al. (1976), and Sobek et al. (1978). Laboratory weathering studies are described by Smith et al. (1974) in a section entitled, "Simulated Chemical Weathering With Intense Aeration." In this study, humidity cell type containers, 4 in (10.16 cm) x 12 in (30.48 cm) x 6 in (15.24 cm) plastic boxes, were utilized, and rock chip samples placed in the boxes were "inoculated with acid mine water from a deep mine to provide the essential microorganisms for reduced sulfur and iron oxidation" (p. 200). Moist air was passed through the plastic boxes for 3 1/2 days, followed by dry air for 3 days, and 1/2 day to leach the boxes and analyze the leachate; hence completing a 7-day cycle.

Regulatory Induced Developments

The Federal Surface Mining Conservation and Reclamation Act was enacted in 1977 and required that permit applicants determine the Probable Hydrologic Consequences of proposed mining activities, including the chemical analyses of the coal and overburden strata for AMD potential. Pennsylvania obtained primacy under SMCRA in 1982 and the Pennsylvania mining regulations, 25 PA Code Chapters 86 through 90, were promulgated to meet requirements in the federal and state laws. The federal and state regulations requiring the chemical testing of coal, overburden, and underclay samples as part of the surface mining permit application created a major demand for the development, use, and interpretation of kinetic and static tests to predict mine drainage quality by the regulatory agencies, mining industry consultants, and commercial laboratories. This demand forced a search of available laboratory methods used in AMD research and other sciences that might be used to obtain accurate and precise results, and also initiated the adaptation of some test methods from a university research study environment to the routine sample production environment of commercial laboratories.

The ASTM water shake extraction procedure (ASTM, D3987, 1978, 1983) initially appeared to be attractive to some regulatory agency personnel and some commercial laboratories because the test procedure was published and disseminated by the ASTM, the laboratory apparatus was in use in commercial labs, and the procedure and analytical results on residual waste and hazardous waste samples had received some degree of acceptance by regulatory agencies and the waste industry consultants. However, the procedure flooded the sample with a fluid to sample ratio of 4:1, and the 48-hour shaking cycle in sealed containers did little to promote oxidation of the sample. Conse-

quently, the diluted leachate usually had relatively low concentrations of acidity, sulfate, iron, manganese, and aluminum, even for rock samples with significant AMD potential. Most researchers ultimately concluded that the ASTM water shake extraction procedure was not principally designed nor intended for use in the analysis of overburden, coal, or coal refuse for AMD potential; and the procedure soon faded from use by most mining regulatory agencies, mining consultants, and commercial laboratories conducting mine drainage analyses.

Some commercial laboratories, such as Sturm Environmental Services in West Virginia, and West Penn Analytical Labs in Brookville, Pennsylvania, developed their own procedures or modified existing procedures for kinetic testing of overburden samples. The Sturm Environmental Services procedure is described in Sturey et al. (1982).

In an attempt to provide guidance to regulatory agencies, the mining industry, their consultants, and commercial laboratories, the EPA published "Field and Laboratory Methods for the Analysis of Overburden and Minesoils", by Sobek et al. (1978), which was rapidly and widely disseminated throughout the research user community. This manual had a primary focus on static test procedures, principally acid-base accounting, but also featured kinetic test procedures including simulated weathering tests.

In 1979, the PA DER distributed informal guidance to the mining industry on available overburden analysis methods, (static and kinetic), and was accepting analyses performed by acid-base accounting (Sobek et al. 1978), humidity cell methods (Caruccio et al. 1976, 1977) and the ASTM water shake extraction procedure (ASTM, D3987, 1978, 1983). As the data base of completed overburden analysis studies in DER permit files began to grow, results of various static and kinetic test methods on surface mine sites in the same vicinity and lithologic setting could be compared. Problems with test methods and data interpretation became evident. For example, in Big Sandy Creek watershed in Fayette County, Pennsylvania, Dr. Frank Caruccio and his associates conducted humidity cell tests as part of overburden analysis studies on 13 proposed surface mine sites, under contract to DER and in cooperation with mining industry permit applicants. On several of these sites where humidity cell tests found significant AMD potential, surface mining permit applications were denied. On three of these sites, the original permit applicant or a new applicant filed new permit applications including acid-base accounting data, which under literal interpretation, indicated a "net excess of neutralizers." In one case, where the new permit was issued based upon the acid-base accounting data, serious AMD discharges developed, and three miles of the Stony Fork tributary of the Big Sandy Creek watershed were degraded from the AMD pollution. On one of the other sites where the new permit application was denied (i.e. Boyle Land and Fuel Company), extensive litigation resulted over the accuracy of the various static and kinetic test methods used in the overburden analysis studies. Some of the geologic and mine drainage quality data for this watershed are explained by Brady et al. (1988).

The scientific and legal controversies surrounding the various static and kinetic overburden analysis methods in use at that time prompted state and federal regulatory and research agencies and other researchers to conduct comparisons of test results and to attempt to determine whether any of the available overburden analysis methods produced accurate and precise pre-mining predictions of post-mining water quality. In 1982, U.S. Bureau of Mines, under the direction of Dr. Robert L. P. Kleinmann at the Pittsburgh Research Center, commenced a large research project to evaluate the effectiveness of various overburden analysis methods at a range of surface mine sites throughout the bituminous coal fields of the eastern United States. The USBM funded the consulting firm, Engineers International, as the contractor of the project and its subcontractor Sturm Environmental Services conducted the laboratory analyses. A team of researchers from Engineers International, including A. A. Sobek, evaluated overburden samples from mine sites in Pennsylvania, West Virginia, Maryland, Kentucky, and Illinois, using static and kinetic test methods. USBM researchers conducted additional data analyses following completion of the contract. Results of the research were ultimately published in USBM Information Circular 9183 in 1988 in papers by Erickson and Hedin (1988) and Hedin and Erickson (1988). These works and additional studies on the comparison of various kinetic and static overburden analysis methods, will be discussed further at a later point in this chronology. Meanwhile, additional kinetic test developments were occurring throughout the United States and Canada.

The Middle Years - Penn State University

From the 1970s through the 1980s, researchers at the Pennsylvania State University were continuing to use kinetic test methods in a series of research projects

oriented toward evaluating the AMD potential of stratigraphic units in the bituminous coal fields of western Pennsylvania. These studies are related to the overburden characterization and kinetic test work commenced by Caruccio and Parizek (1967), and include reports by Hornberger, Parizek and Williams (1981), Waters (1981), Williams, Rose, Parizek and Waters (1982), Rose, Williams and Parizek (1983), Cathles (1982), Cathles and Breen (1983), Williams, Rose, Waters, and Morrison (1985), Hornberger (1985), and Morrison (1988).

Hornberger, Parizek and Williams (1981) conducted leaching tests on coal and overburden analyses in 1977, which are described briefly in Hornberger et al. (1981) and in greater detail in Hornberger (1985). They constructed simple leaching columns from 1/2 gal (1.89 l) plastic containers, as shown in Figure 7.11, which combined some features of humidity cells and leaching columns. The lower half of the leaching column was kept saturated, which provided a constant source of water and humidity within the container to facilitate the chemical reactions and promoted survival of the bacteria. Weekly leaching episodes produced two types of effluent from the columns: (a) "1-week" contact leachate drained from the bottom of the column, and (b) "1-hour" contact leachate which flushed accumulated weathering products from the upper half of the column.

Williams et al. (1982) used the same leaching columns, and essentially the same leaching procedure as Hornberger et al. (1981) but filled the lower portion of the column with glass beads, in order to place most of the rock sample in humid, but unsaturated conditions. Morrison (1988) and Williams et al. (1985) also used the same laboratory leaching vessels shown in Figure 7.11, but "slightly modified" the methodology of these kinetic tests.

Dr. Larry Cathles came to Pennsylvania State University in 1978, bringing with him a wealth of leaching experiences from the metal mining industry, especially Kennecott Copper Corporation, including studies by Cathles and Apps (1975), Cathles et al. (1977), Murr et al. (1977), Cathles (1979), Cathles and Murr (1980) and Cathles and Schlitt (1980). These studies involve a variety of leaching experiments including small-scale laboratory leaching columns, large-scale (i.e., 40 ft (12.19 m) high x 10 ft (3.05 m) diameter) column leaching experiments and the development of mathematical models to simulate the leaching process. At

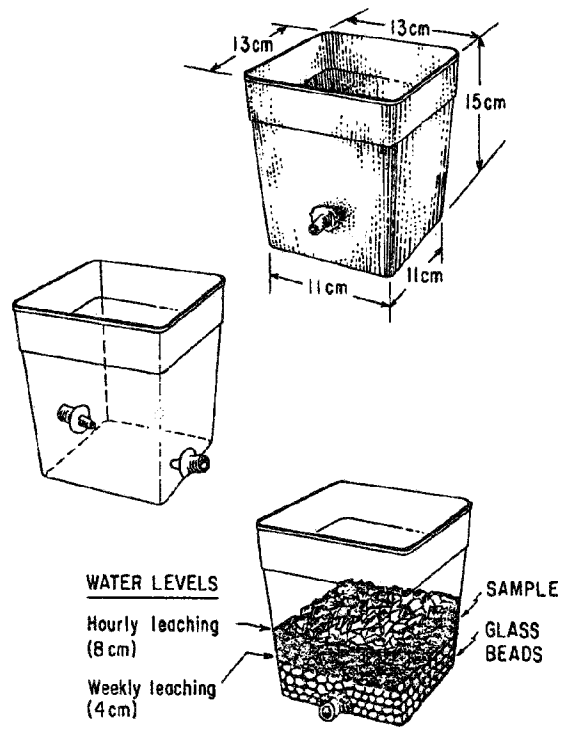

Figure 7.11 Simple leaching column (from Williams et al. 1982).

Penn State, Cathles and Breen (1983) studied the removal of pyrite from coal by heap leaching processes and utilized a constant temperature leaching column, shown in Figure 7.12, to conduct laboratory leaching experiments.

The Middle Years - West Virginia University and Related Work

While much of the effort to predict mine drainage quality in West Virginia during 1970s and 1980s was focused on the acid-base accounting method (i.e. static test), a significant interest in kinetic test developments was shown by the work of Renton and Stiller at West Virginia University and others associated with the West Virginia Department of Natural Resources, the West Virginia Surface Mine Drainage Task Force, and the West Virginia Acid Mine Drainage Technical Advisory Committee (AMDTAC). Accelerated weathering methods employing Soxhlet reactors in a laboratory setting were utilized by Renton, Hidalgo and Streib (1973), and Renton et al. (1984, 1985). Field-scale leaching column procedures were also developed as described by Stiller (1983) and Renton et al. (1984, 1985). In these field leaching tests, 35-gal (132.5 l) plastic barrels, fitted with plastic distribution plates,

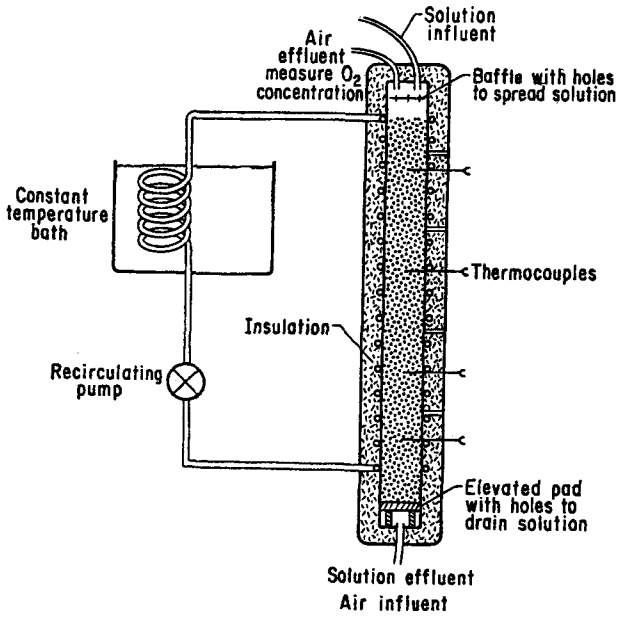

Figure 7.12 Constant temperature leaching column (from Cathles & Breen, 1983).

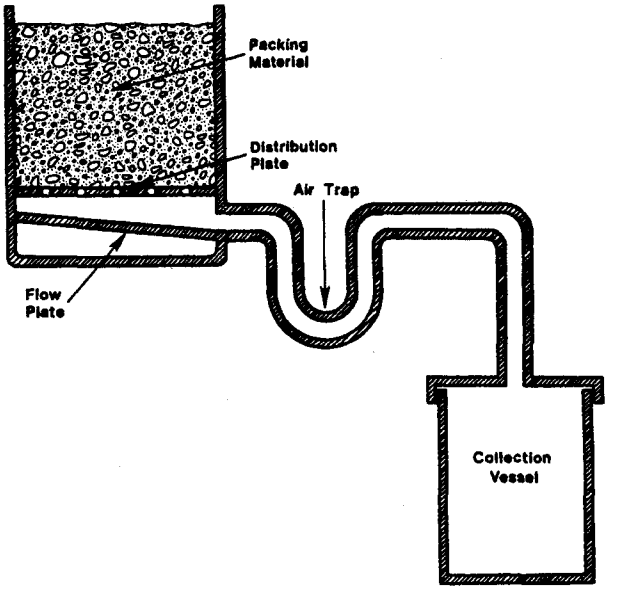

Figure 7.13 Field leaching barrel fitted with distribution and flow plates, and leachate collection vessel. (from Renton et al., 1984).

flow plates and leachate collection vessels, as shown in Figure 7.13 from Renton et al. (1984), were entirely filled with 300 lbs (136.1 kg) of coal preparation plant wastes, and leached by actual precipitation events to simulate normal weathering conditions. The primary objective of the study described by Stiller (1983) was to test the effectiveness of various ameliorants (i.e. agricultural lime, sodium lauryl sulfate, and apatite rock), in abating or preventing AMD production.

Dr. Frank T. Caruccio and Dr. Gwendelyn Geidel of the University of South Carolina and Dr. Robert L. P. Kleinmann from the U.S. Bureau of Mines in Pittsburgh were official members of the West Virginia Acid Mine Drainage Technical Advisory Committee (AMDTAC), a consortium of West Virginia DNR staff, West Virginia coal industry technical representatives, and AMD researchers from universities and government agencies, including Dr. Jack Renton and Dr. Al Stiller from West Virginia University. AMDTAC provided an excellent format and opportunity for the DNR, mining industry and researchers to interact and cooperate in projects on AMD prediction and abatement, including the development and practical application of kinetic tests at surface mine sites. Examples of these cooperative research projects on West Virginia surface mines are reported in Caruccio et al. (1984), Caruccio and Geidel (1983, DNR grant R-83-063), Renton et al. (1988), and Caruccio and Geidel (1986b, 1989). Kinetic test methods employed in these AMDTAC studies included humidity cells, Soxhlet reactors, and field-scale leaching columns or barrels.

During the same time period, related work on the use of Soxhlet reactors in the weathering of overburden and coal refuse samples was being conducted by researchers at Argonne National Labs and elsewhere, including Sobek et al. (1982) and Sullivan and Sobek (1982). Sobek et al. (1982) describe modifications to the Soxhlet reactor developed by them and Singleton and Lavkulich (1978), which were designed to improve simulated weathering studies and duplicate field conditions. Davies (1979, 1980) also discusses improving the efficiency and optimizing the performance of Soxhlet reactors. Sobek et al. (1982) credit Pedro (1961) as the first researcher to use the Soxhlet reactor in rock weathering studies, with further work reported in Henin and Pedro (1965). The study by Sullivan and Sobek (1982) contains a comparison of the leachate characteristics of Soxhlet reactors and humidity cells. Additional kinetic test research utilizing Soxhlet reactors to test pyritic coal waste is found in Sullivan et al. (1986).

Kinetic Test Developments in Central and Western U. S. and Canada

In other areas of the United States, outside of the Appalachian Coal Mining Region, kinetic test methods were being developed and evaluated including the studies by Infanger and Hood (1980), Hood and Oertel (1984) and Hood (1984) in Illinois, and Dolhopf

(1984) and Harvey and Dolhopf (1986) in Montana. In the Illinois studies, leaching columns were used. Infanger and Hood (1980) constructed leaching columns from 2 in (5.08 cm) PVC pipe in 7-ft (2.13 m) lengths, and filled the columns with three, 2-ft (0.61 m) thick layers of different overburden lithologies, which were subjected to fifteen leaching cycles of 1-, 2- or 3-week duration, between the introduction of one liter of influent water and collection of the effluent sample. Hood and Oertel (1984) and Hood (1984) constructed leaching columns using glass tubes 122 cm long by 3.5 cm inside diameter, shown in Figure 7.14, wherein distilled water was introduced into the columns from the bottom upward in order to avoid air locks, and a 1-week total cycle time was selected, using a 2-day rock-water contact time. Hood (1984) describes one set of leaching experiments in which "air was not permitted to enter the column" in order to simulate conditions below the water table; and a second set of experiments where the columns were open at the top to simulate conditions above the groundwater table.

Harvey and Dolhopf (1986) developed a "computerized automated rapid weathering apparatus" (CARWA), shown in Figure 7.15, which consists of three humidity-cell type "weathering chambers or compartments" with extensive mechanical and electrical supporting equipment. In describing the operation of the CARWA, Harvey and Dolhopf (1986, p. 14) state:

> "A bacteria inoculated... 200 gram minesoil sample (<2mm fraction) was placed into each of three acrylic weathering compartments. An automated weathering cycle began by spraying 200 ml of distilled/deionized water into each compartment. The minesoil solution was mechanically agitated for one hour, and then the water was extracted, under a vacuum suction, into a holding column. The minesoil was aerated for 30 minutes by an overhead fan to encourage oxygenation and partial drying. The extracted water was discharged into a beaker positioned on an automatic turntable, and the next cycle began... The computer control automatically conducted six weathering cycles of approximately 2.5 hours each on the samples. The extracts were monitored for volume, pH and titratable acidity."

In Canada, particularly British Columbia, research on static and kinetic test developments to evaluate AMD potential was ongoing during the 1970s and

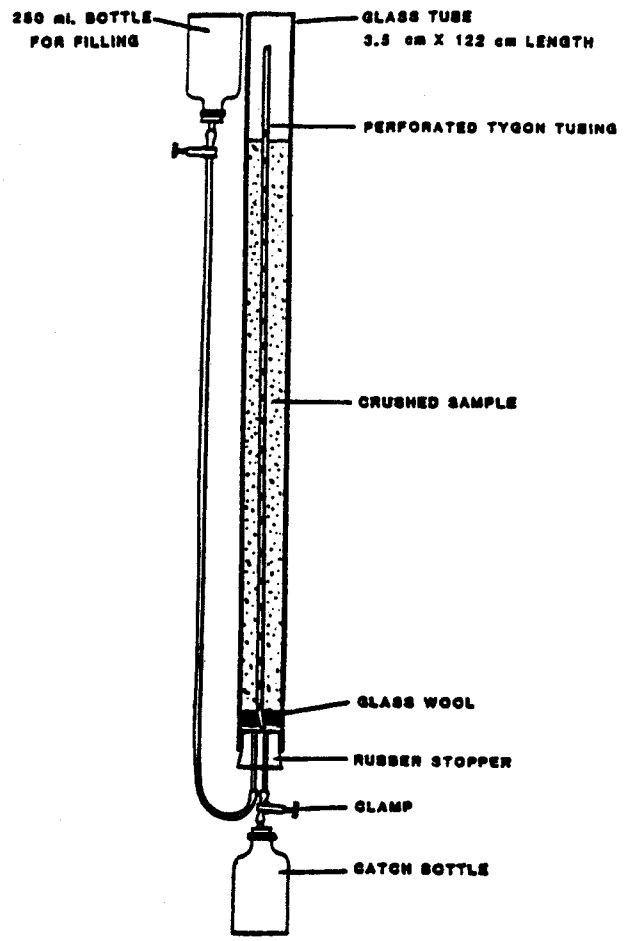

Figure 7.14 Leaching column with influent water entry at bottom.

1980s, including Bruynesten and Duncan (1979), Bruynesten and Hackl (1984), Ferguson (1985) and Ferguson and Mehling (1986), which paralleled similar efforts in the United States described previously in this section. The British Columbia research is primarily oriented toward metal mines and associated mine tailings. A static test, named the B. C. Research Initial Test and described in Bruynesten and Hackl (1984), is similar in procedure and interpretation to the acid-base accounting procedure described in Smith et al. (1974) and Sobek et al. (1978). If the B. C. Research Initial Test indicates the sample to be a potential acid producer, the static test is typically followed by a kinetic test named the B. C. Research Confirmation Test as described in Bruynesten and Hackl (1984), wherein the rock sample is placed in a 250-ml Erlenmeyer Flask with 70 ml of nutrient media and Thiobacillus bacteria culture. The flask is maintained in a carbon dioxide enriched atmosphere at a temperature of 35°C and placed on a gyratory shaker to monitor pH changes

(see also Ferguson 1985, Ferguson and Mehling 1986, and Ferguson and Erickson 1986). Additional Canadian kinetic test developments and field applications, including the use of shake flasks and lysimeters, are discussed in Duncan (1975), Ritcey and Silver (1981), Davidige (1984), Halbert et al. (1983), Wilkes (1985) and Ferguson and Erickson (1988).

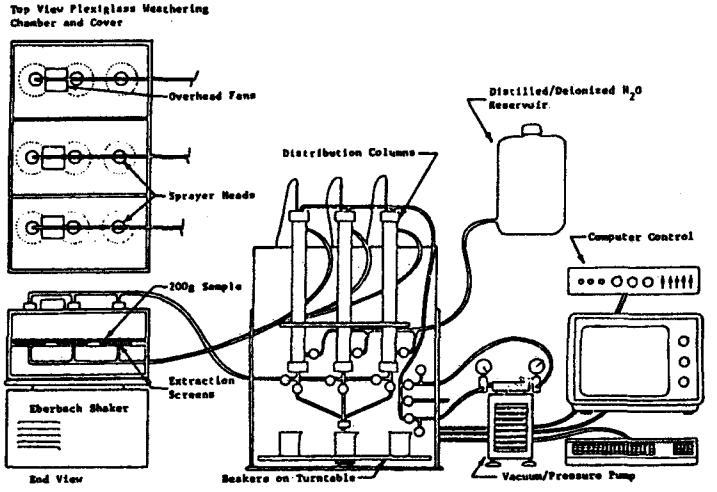

Figure 7.15 Diagram of the computerized automated rapid weathering apparatus (CARWA) prototype (from Harvey & Dolhopf, 1986).

Comparison of Test Methods 1985 to 1994

This chronology demonstrates that by the mid-1980's a wide variety of kinetic and static tests to predict AMD had been developed and used throughout the United States and Canada. Attention then focused on studies to evaluate and compare the various test methods to determine which provided the best prediction of AMD potential, and whether any method produced accurate and precise pre-mining predictions of post-mining water quality. Some of the literature cited earlier, including Hanna and Brant (1962) and Sullivan and Sobek (1982), contain comparisons of two kinetic test methods. The scientific and legal controversy surrounding various static and kinetic overburden analysis methods of concern to government research and regulatory agencies, and the genuine scientific curiosity to advance the process of AMD prediction led to a number of rigorous studies to either compare a wide variety of test methods or to evaluate overburden analysis test results over a wide geographic area or differing lithological units. Caruccio and Geidel (1986 a) conducted an excellent study to compare the results of humidity cells (with 200 g. of <4 mm. sample), Soxhlet reactors (with <125 micron particle size), leaching columns (9 cm. diameter, 30 cm. height, with sample of unspecified particle size), the B. C. Research Initial Test, the B. C. Research Confirmation Test, and acid-base accounting, in order "to determine which one most closely approximates the observed field conditions" (p. 147). Plastic tubs (approximately 0.5 m x 0.5 m x 0.3 m deep) and plastic barrels were installed in the field in order to weather samples with actual precipitation under natural climatic conditions for two years, for control purposes to compare to the laboratory results (similar to the field methods described by Renton et al. 1984, 1985). The advantages and disadvantages of all of these overburden analytical methods, plus the beaker leachate test (as described by Sobek et al. 1978) were listed by Caruccio and Geidel (1986 a, Table I, p. 149), who concluded that "All things considered, the column tests more clearly approximate the observed field results than the other analytical tests" (p. 153). They also concluded that the effluent acidity was markedly higher for finer particle size.

Erickson and Hedin (1988) evaluated overburden analysis data from 32 surface mine sites in Pennsylvania, West Virginia, Maryland, Illinois, and Kentucky where overburden samples and post-mining water quality samples were collected by Engineers International under USBM Contract No. J0328037. Acid-base accounting analyses and simulated weathering tests using humidity cells (with 300 g of <2 mm particles, leached weekly with 300 ml of water) were correlated with the actual mine drainage analyses from these mine sites. Concerning the kinetic test data, the only significant correlation found was between the sulfates in the simulated weathering test and sulfates in the actual mine drainage. However, the correlation coefficient of $r = 0.4059$ when squared, yields a coefficient of determination, $r^2 = 0.1648$, which indicates that sulfate in the test leachate explains only 16.5% of the variation in the sulfate data for the mine drainage. Erickson and Hedin (1988) concluded that :

> "The results of this study confirmed that the overburden analysis methods tested do not adequately predict post-mining drainage quality when used alone. This result is not surprising, as overburden analytical data is only one component of the pre-mining site assessment. Mine operators and regulatory authorities utilize other data and past experience in judging the environmental suitability of a proposed mine... The weathering procedure used in this study failed to yield an accurate prediction of water quality and failed to delineate boundaries for drainage of differing acid/alkaline character. The correla-

tion between sulfate produced during simulated weathering and sulfate concentrations observed in the field suggested that pyrite oxidation can be mimicked in the laboratory. Alkalinity-generating processes were not mimicked by this method. Limited data from laboratory weathering showed at least a potential for better simulation of neutralization processes when the overburden strata were composited into a single sample prior to weathering."

The authors also point out that no leachate sample from the kinetic tests exceeded 100 mg/L net alkalinity, while field samples of post-mining drainage had net alkalinity in the range of 100 to 620 mg/L. The low PCO_2 of the laboratory tests is suggested as a cause by Erickson and Hedin (1988). In a companion study, Hedin and Erickson (1988) evaluated the relationships between the initial geochemistry and leachate chemistry of overburden samples from the same 32 mine sites, using the humidity cell apparatus in simulated weathering tests to provide the leachate chemistry. Concerning, "the problem of predicting drainage chemistry on a mine level", Hedin and Erickson (1988, p. 28) state:

"Are the errors calculated and discussed in this paper responsible for predictive failures? We think not. The error of our relationships is about 25%, which is not great enough to account for the large differences between expected and actual drainage chemistry observed in our study... More likely, the failure of the methods lies in conservative assumptions and design features that are inappropriate... In our weathering tests, we produced conditions that maximized pyritic oxidation and minimized alkalinity. Both of these problems can be justified when one wishes to make conservative judgments. However, if accurate predictions are the goal, the assumptions and methodologies must be thoroughly reevaluated."

Comparisons of static and kinetic AMD prediction techniques in use in Canada and the United States were also presented in tabular and graphic format and discussed in Ferguson (1985), Ferguson and Mehling (1986), Ferguson and Erickson (1986, 1987, 1988), and Lapakko (1993). Additional comparative overburden analyses reports are found in Bradham and Caruccio (1990) and Caruccio et al. (1993).

A Plethora of Variations on a Theme

In addition to the papers by Erickson and Hedin (1988) and Hedin and Erickson (1988), the Mine Drainage and Surface Mine Reclamation Conference held in Pittsburgh in 1988 (and published as USBM Information Circular 9183), featured other papers on kinetic test developments and applications including Doepker (1988), Renton et al. (1988), Backes et al. (1988), Bennett et al. (1988), Watzlaf (1988), Hammack et al. (1988), Stahl and Parizek (1988), Lapakko (1988), Sullivan and Yelton (1988), Franklin and Zahl (1988), and Ammons and Shelton (1988). In these studies a variety of kinetic test procedures were employed involving leaching columns, humidity cells and other weathering chambers, Soxhlet reactors, field-scale barrels, and lysimeters, most of which have already been described herein. One new development was the evaluation by Franklin and Zahl (1988) of EPA's Toxicity Characteristics Leach Procedure (TCLP), "to determine what, if any, applicability the test has in evaluating mine wastes" (p. 205). After using the standard TCLP method and developing modified TCLP tests, Franklin and Zahl (1988, p. 205) concluded that: "Based on these results and other similar research at SRC, it appears that better laboratory assessment methods could be developed that more appropriately aid in the simulation or prediction of contamination from mine wastes."

Doepker (1988) constructed leaching columns from 2 ft (0.61 m) and 4 ft (1.22 m) lengths of 3 in (7.62 cm) inside diameter PVC pipe "equipped with cemented couplings and bushings in which perforated Nalgene plates had been installed" (p. 211) ..."A series of ten similarly constructed 1½" (3.81 cm) ID PVC columns were used to examine the effects of sample depth and column surface-to-volume ratios" (p. 211). Additional kinetic test research at the USBM Spokane Research Center, including a series of at least four leaching column studies, is reported in Doepker and O'Conner (1991a, 1991b) and Doepker (1991a, 1991b, 1994). Experimental methods utilized in Doepker (1994) "included leaching columns, perforated baskets, and Buchner funnels, coupled with humidity and controlled atmosphere chambers" (p. 55). A kinetic technique for carbonate species is in Roberts et al. (1984).

In 1988, the Knoxville, Tennessee Field Office of OSMRE released an outline of an acceptable procedure for conducting leaching tests as described in Maddox (1988). This leaching procedure or simulated

weathering test is designed to augment acid-base accounting results because:

> "It is likely that some permit applicants will not recognize the overburden conditions that may result in a deficiency requiring a leach test on overburden samples that have been defined as nonacidic by the net acid-base account (NAB)... based on OSMRE, Division of Tennessee Permitting's experience, it has become obvious that, in Tennessee at least, the NAB by itself is not a reliable predictor of acid mine drainage (AMD) generation... Therefore, whenever there is no "fizz" but the analysis shows a potential acidity of 5 or more, an NAB indicating nonacidic strata is suspect and may require a leach test... So, even though the NAB indicates an excess of neutralization capacity, the reaction kinetics actually occurring under natural weathering conditions may still result in acid production. The acid-forming process is quite efficient because the acidic products of pyrite oxidation are highly soluble in water and are readily mobilized."

In this Tennessee OSMRE procedure, an advantage of using a leaching column is noted, but other appropriate apparatus may be used, and the test method includes some features of humidity cell methods.

At the 1990 Mining and Reclamation Conference in Charleston, West Virginia, Bradham and Caruccio (1990) presented the results of a comparative analytical study of Canadian metal mines tailings using acid-base accounting, humidity cells, leaching columns (Hood-Oertel type), and Soxhlet reactors. In contrast to the comparative study by Caruccio and Geidel (1986a), wherein leaching columns were found to be the most accurate predictive test, Bradham and Caruccio (1990) found that the humidity cells were the most accurate predictor, and the leaching columns were the least accurate. According to Bradham and Caruccio (1990, p. 19):

> "The fine-grained nature of the tailings afforded high specific retention of fluid, creating airlocks within the columns that skewed the results. When the leachate quality predicted and obtained by the various tests was compared to the actual drainage quality emanating from the sites from which the samples were collected, the least accurate were the column tests, next were the acid/base accounting projections, then the soxhlets, with the weathering cell tests being most accurate."

The 1990 Charleston conference proceedings contain other papers using kinetic tests including Halverson and Gentry (1990), Hart et al. (1990), Morrison et al. (1990a, 1990b), and Hammack and Watzlaf (1990). In the study by Halverson and Gentry (1990), the leaching column method of Doepker (1988) was used to conduct weekly leaching episodes with simulated precipitation for fifty weeks. Morrison et al. (1990b) used the leaching column method described in Hornberger et al. (1981), Waters (1981), Williams et al. (1982, 1985), Hornberger (1985), and Morrison (1988). In Hammack and Watzlaf (1990), small leaching columns (i.e. 40 cm length x 2.54 cm ID) and large leaching columns (i.e. 1.92 m length x 0.25 m diameter) were used to evaluate pyrite oxidation rates. Hart et al. (1990) used the Soxhlet extraction procedures previously described in Renton et al. (1973, 1984, 1985, 1988).

Watzlaf (1992) used "small leaching columns" to evaluate pyrite oxidation of coal waste samples under saturated and unsaturated conditions. These 5.1 cm diameter x 46 cm length columns were larger than the small leaching columns, but smaller than the large leaching columns used by Hammack and Watzlaf (1992). Four different leaching scenarios (i.e. combinations of saturated and unsaturated conditions with distilled water or recycled AMD influents) were evaluated by Watzlaf (1992), who concluded that saturated conditions can significantly reduce the rate of pyrite oxidation.

Filipek et al. (1991) developed and evaluated a kinetic test method named the "shake flask/humidity cell test" in order to predict the chemistry of drainage from exploration tunnels in a massive sulfide deposit in Maine. The method modified and combined some kinetic test features of shake flask tests and humidity cell tests because, "water discharging from the tunnel is expected to react with the associated rocks in a manner somewhere between the two extremes tested by the shake flask and humidity cell tests." Filipek et al. (1991) also evaluated the effect of test-water chemistry on the results of the kinetic tests using a "simulated acid-rain" influent water, and the effect of the rock:water ratio on leachability.

Lapakko and Antonson (1994) conducted a laboratory study of the oxidation of sulfide minerals associated with copper and nickel deposits in the Duluth Complex in northwestern Minnesota , "to examine the

quality of drainage generated by potential Duluth Complex mining wastes" (p. 593). To conduct these kinetic tests, they used a reactor apparatus shown in Figure 7.16 (from Lapakko 1994a, p. 272), which was also used in studies by Lapakko (1988) and Lapakko (1990). This apparatus and kinetic test procedure is essentially a humidity cell method, because humidity and temperature conditions are controlled and monitored between weekly flushing episodes. Lapakko and Antonson (1994) reported on leachate data from 150 weeks of leaching experiment duration, as Lapakko (1988) considered kinetic test performance for 70 weeks duration, and Lapakko (1990) demonstrated that some samples require at least 50 to 80 weeks of laboratory accelerated weathering before NP is deleted and actual acid production occurs.

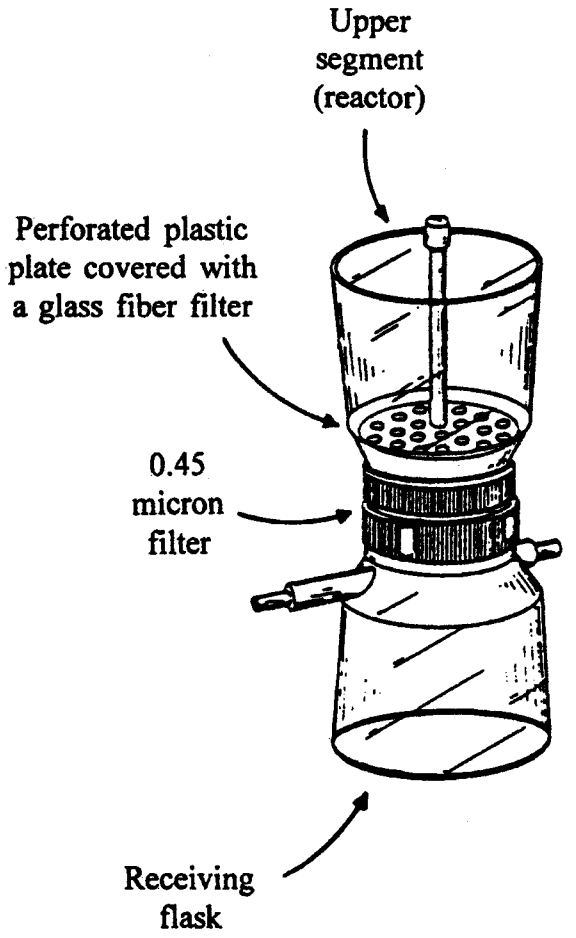

Figure 7.16 Reactor apparatus (from Lapakko, 1994a).

White and Jeffers (1994), from the Salt Lake City Research Center of USBM, conducted humidity cell tests as part of an effort to develop a "geochemical predictive model for acid mine drainage (AMD) from waste rock associated with metal mining" (p. 608). They used a humidity cell array described as follows:

> "...comprised of sixteen individual cylindrical cells, each 20.32 cm long, with an inside diameter (I.D.) of 10.16 cm. Waste-rock charges for each cell are comprised of 1,000 g of sample crushed to 100 % passing 1/4 inch. The test protocol is comprised of weekly leach cycles that include 3 days of dry air and 3 days of wet air pumped up through the sample, followed by a drip-trickle leach with 500 ml of de-ionized water on day 7. Duration of the leach is approximately 2 hours. Bureau tests are continued beyond the 20-week duration currently used in commercial practice; the rationale is to evaluate calculated rates of NP depletion and subsequent acid production from samples whose effluents may appear benign at the end of 20 weeks of testing". (p. 612)

In the study by White and Jeffers (1994), the humidity cell test results for 51 weeks of leaching cycles were reported and sulfate release rates after 21 weeks and 51 weeks were compared. From combined static and kinetic test results it was predicted that some samples may initially have neutral to alkaline leachates, but because their acid-producing potentials were greater than their neutralization potentials in acid-base accounting tests, AMD should develop after 110 through 130 weeks of laboratory accelerated weathering. According to White and Jeffers (1994, p. 628):

> "The ultimate goal of this modelling approach is to enable the mine operator to use short-term laboratory static- and kinetic-test data along with field measurements to make long-term predictions about rates of AP and NP depletion and consequent acid-generation behavior."

This chronology concludes with the publication of the proceedings of the International Land Reclamation and Mine Drainage Conference and Third International Conference on the Abatement of Acidic Drainage held in Pittsburgh, PA in 1994. The proceedings were published in four volumes (USBM Special Publication No. SP-06A-94 through SP-06D-94) and total 1648 pages. A wide array of mine drainage and mine reclamation subjects were presented in a total of 186 papers, of which at least 45 include kinetic test developments, evaluations, and applications. Of these papers, at least 21 involve the use of leaching columns including the work of Moran and Hutt (1994b), St-Arnaud (1994), Davé and Vivyurka (1994), Rich and Hutchinson (1994), Day (1994), Evangelou (1994), Aachib et al. (1994), Kuyucak and St-Germain (1994a, 1994b),

Rose and Daub (1994), and Stromberg et al. (1994). Of the five kinetic test papers involving the use of humidity cells, Pool and Balderrama (1994) from the USBM Reno Research Center, provided an excellent evaluation of humidity cell parameters; while additional humidity cell testing is described in Moran and Hutt (1994a), White et al. (1994), and Domvile et al. (1994). Two papers incorporate the use of Soxhlet reactors (Adams et al. 1994 and Rich and Hutchinson 1994), in combination with other test procedures. At least six test kinetic test papers involve the use of a field scale apparatus such as a barrel, test pile, or leach pad, including studies by Ferguson and Robertson (1994), Donovan and Ziemkiewicz (1994), Moran and Hutt (1994b), Lapakko (1994b), and Ziemkiewicz and Meek (1994). Thirteen additional papers contain some type of kinetic testing involving a wide variety of apparatus and procedures including beakers (Miller et al. 1994) reactor vessels (Lapakko 1994a, Kuyucak and St-Germain 1994a and 1994b, and Wildeman et al. 1994), shake flasks or batch flasks (St-Arnaud 1994, Kuyucak and St-Germain 1994a), bubbler tanks (Adams et al. (1994), Buchner funnels and leaching racks (Gentry et al. (1994), the Ontario Regulatory Extraction Procedure (Rao et al. 1994), the Sequential Extraction Analysis Procedure (Prairie and McKee 1994, Hakansson et al. 1994), and the TCLP (Boyle and Smith 1994).

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Chapter 8

INFLUENCE OF GEOLOGY ON POSTMINING WATER QUALITY: NORTHERN APPALACHIAN BASIN

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Summary

Mining accelerates the weathering of coal overburden. The weathering products of two minerals groups, iron sulfides and calcareous carbonates, dominate the chemical characteristics of postmining water. These minerals need only be present in an abundance of a few percent or less to be significant. By comparison the other 95% or so of overburden minerals play a minor role. The most important factor as to whether or not a site will produce alkaline drainage is the presence or absence of calcareous minerals. Pyrite, although necessary for acid formation, is of secondary importance, because if sufficient carbonates are present postmining water will be alkaline.

The coal-bearing rocks in Pennsylvania are from the Pennsylvanian and Permian? Periods of geologic time. The rocks of the Bituminous Coal Field of western Pennsylvania are divided, from oldest to youngest, into the Pottsville, Allegheny, Conemaugh, Monongahela, and Dunkard Groups. The majority of mineable coal occur in the Allegheny and Monongahela Groups. Several lithologic trends can be observed in this sequence of rocks. The clay/shale content increases upward from a low of about 25% in the Pottsville Group to highs of 70 to 80% in the Dunkard Group. In general there is a inverse relationship with sandstone, with sandstone increasing from ~20% or less in the higher Groups to a high of 50% in the Pottsville. The percentage of calcareous rocks increases upward. The Pottsville Group has less than 1% calcareous rock. The lower Allegheny is less calcareous (6%) than the upper Allegheny Group (14%). Rocks of the Casselman Formation in the Conemaugh Group and higher are greater than 50% calcareous. The percentage of sandstone that is calcareous generally reflects the percentage of overall rock that is calcareous. The uppermost Dunkard Group rocks contain the least amount of siderite, whereas over 20% of the strata in the Allegheny Group and Glenshaw Formation contain siderite. Within the Allegheny and Pottsville Groups sideritic rocks are more abundant than calcareous rocks.

The important depositional environments, from a mine drainage standpoint, are the location of marine zones and distribution of calcareous rocks. The marine rocks are frequently associated with high-sulfur strata, but can also have calcareous zones. Brackish rocks tend to have high sulfur and lack calcareous minerals. Marginally brackish (paralic) rocks frequently have less sulfur than their marine and brackish counterparts. Truly freshwater sediments tend to have calcareous minerals and limestone.

The strata in the Anthracite Region are divided, from oldest to youngest, into the Pottsville and Llewellyn Formations. The Pottsville Formation is entirely of a nonmarine depositional environment. As in western Pennsylvania, the dominant lithology of the Pottsville is sandstone and conglomerate, although the Pottsville of the Anthracite Region contains significant pebble conglomerates. The Pottsville contains up to 14 coal beds, but most are not mineable. The Llewellyn Formation consists predominantly of sandstone, but also contains conglomerates, plus lesser amounts of finer-grained rocks and coals. There are up to 40 mineable coals in the Llewellyn, the thickest and most persistent occur in the lower part of the formation. The Llewellyn and Pottsville Formations are believed to be nonmarine with the exception of the Mill Creek marine zone in the Northern Field. In addition to this marine zone, other calcareous rocks have also been found in the Northern Field. Some of the water quality reflects this source of alkalinity. Although stratigraphic studies have not yet identified calcareous rocks in the Southern and Western Middle Fields, highly alkaline mine waters imply that calcareous rocks exist. The lack of alkaline drainage in the Eastern Middle Field suggests a dearth of calcareous strata in this anthracite field.

Pleistocene glaciation came as far south as the northwestern corner of Pennsylvania's bituminous coal field. Tills, where calcareous, can contribute significantly to the alkalinity of postmining water quality. Tills in the Northern Anthracite Field are not calcareous and do not contribute alkalinity to water.

Sulfur in sedimentary rocks occurs in three forms: sulfide (e.g., pyrite), sulfate, and organic. The oxidation of pyrite results in the formation of sulfuric acid and iron. This acid can dissolve other minerals, releasing other ions such as aluminum, manganese and magnesium. Sulfate minerals are typically weathering products of pyrite oxidation. Frequently these sulfate salts are essentially stored acidity and will produce acid when dissolved in water. Organic sulfur is generally assumed to produce little acid.

The most reactive carbonates in terms of their ability to neutralize acid are calcite and dolomite. The iron-carbonate, siderite, is a common mineral throughout the Pennsylvanian and Permian? strata of Pennsylvania, but it does not generate alkalinity. Calcite and dolomite not only neutralize acidity, but it appears that they can also contribute to the inhibition of acid production.

The presence or absence of calcareous minerals and pyrite is a function of several geologic processes. The paleodepositional environment and paleoclimate during the Pennsylvanian Period were important in determining the original mineralogic composition of strata. Paleoclimate influenced pyrite and carbonate concentrations for terrestrial rocks. For example, wet climates typically yielded less pyrite than dry climates and dry climates favored deposition of freshwater limestones. Rocks deposited in marine environments often have high sulfur and high neutralization potential. Brackish environments generally produce high sulfur with no calcareous minerals, although siderite can be present. High sulfur occurs in marine and brackish environments because of abundant sulfate ions in marine waters. This sulfate served as the source of pyritic sulfur. Marginally brackish environments are generally lower in sulfur and have little neutralization potential. Freshwater (terrestrial) deposits are often calcareous and frequently contain limestones. More recent geologic processes such as glaciation and surficial weathering have also influenced the mineralogy of coal overburden. Tills, if calcareous and of sufficient thickness, can contribute alkalinity to mine waters. Weathering by oxidation removes pyrite and by dissolution removes carbonates The relative depth of removal of these two mineral groups can be an important factor in determining the water quality potential of a mine site.

The geologic controls on coal overburden that have and are operating in Pennsylvania have resulted in overburden that can contain a wide range of concentrations of pyrite and calcareous minerals. Mine drainage quality reflects this variable mineralogy; water can be significantly alkaline to severely acidic.

Within Pennsylvania's Bituminous Coal Field, mine drainage problems differ by stratigraphic horizon and geographic region. Acid problems are more significant in the lower Allegheny Group than in higher strata. Regional variations are often due to paleodepositional environment. For example, lower Allegheny overburden deposited in marine, brackish-marine, to marginally-brackish environments, will differ in the amount of pyrite and amount and type of carbonates present. The highest alkalinities are associated with the thick freshwater limestone sequences of the Pittsburgh Formation (Monongahela Group) in the southwestern corner of Pennsylvania, the thick marine Vanport limestone of the lower Allegheny Group in the central to northwestern area of the bituminous region, and the freshwater limestones of the upper Allegheny Group in areas where these limestones and associated calcareous shales are abundant. In addition, significant alkalinity concentrations occur in the Conemaugh Group where marine limestones are present, and the lower Allegheny Group mines in northwestern Pennsylvania where the overburden includes calcareous tills.

The highest acidity concentrations are associated with overburden: (a) of the Clarion and lower Kittanning coals, particularly where black brackish shales and thick marine shales predominate in the overburden, (b) in the Pittsburgh Coal and Waynesburg Coals of the southwestern portion of the bituminous region, in areas where the carbonate strata are absent or lack appreciable thickness, and (c) of Allegheny Group coals where sandstone predominates. The wide rang of pH and the range in alkalinity and acidity concentrations for each stratigraphic group documents that some strata within each group has the potential to pr duce alkaline and acidic drainage.

Overall, mine water in the anthracite and bituminous regions has a bimodal distribution of pH. Wat is either acidic or circumneutral. This is because Pennsylvanian Period rocks, at least in western Penn sylvania, can have significant concentrations of pyrit and calcareous carbonates. Calcareous overburden

produces alkaline drainage and pyrite-rich and carbonate-poor overburden produces acidic drainage in the absence of appropriate pollution prevention techniques.

Regional-scale water quality variations are seen in the Anthracite Region. The most obvious being an absence of alkaline discharges in the Eastern Middle Field. The Eastern Middle Field also lacks severely acidic mine drainage. The Northern Field has proportionally more water with a pH above 5, than below 5. This is consistent with the finding of calcareous rocks in the Northern Field. The Western Middle and Southern Fields show a wide range of pH values. Combined data for all the anthracite fields display a bimodal distribution for pH similar to that for the Bituminous region.

An understanding of mine site geology is necessary for developing a representative drilling program, for providing information as to the acid or alkaline producing potential of strata, and for design of a groundwater monitoring program. Also, knowledge gained from these geologic factors can be used in developing site specific pollution prevention techniques such as material handling and calculation of alkaline addition rates. Geologic information is essential for determining the economic feasibility of a proposed mine site.

Introduction

Geologic factors play a major role in the kind of water quality produced by a surface coal mine. This chapter examines those geologic factors with respect to the northern Appalachian Basin. Surface mining accelerates weathering by exposing fresh rock surfaces which contain minerals not at equilibrium with the newly mined environment. The two most important groups of minerals, in terms of postmining water quality impacts, are carbonates and sulfides. Weathering of the carbonates produces alkalinity and weathering of sulfides produces acidity. Other major ions can be calcium, sulfate, and iron. The weathering of other minerals also contributes to the composition of mine drainage, especially under low pH conditions. Some of these ions include manganese, magnesium and aluminum. The minerals available for weathering, and the resultant water quality, is to a large extent a function of geology. Some minerals were present at the time of deposition of the coal and enclosing sediments, while others are the result of more recent processes. More recent processes include near-surface weathering and effects from Pleistocene glaciation, such as deposition of till and glacial erosion.

Although acid mine drainage (AMD) is not unique to the northern Appalachians, the problem is more severe in this region than in any other coal producing region of the United States. Within Pennsylvania mine drainage problems differ by geographic region and stratigraphic horizon. Over the years some rules of thumb have been developed relating regional and stratigraphic geology to postmining water chemistry in Pennsylvania. An understanding of mine site geology is important in developing a representative drilling program, for providing information on the acid or alkaline producing potential of strata, and for design of a groundwater monitoring program. Also, knowledge gained from these geologic factors can be used in developing site-specific pollution prevention techniques, such as overburden handling and calculation of alkaline addition; in any case this geologic information is a necessary part of economic determinations.

All mine drainage prediction tools, and some of the prevention tools, in one way or another, require an understanding of the site's geology. For example, many of the factors pertaining to the proper interpretation of previous mining as a prediction tool (Chapter 9) are related to an understanding of geologic similarities and differences between mine sites. Premining groundwater quality (Chapter 10) is dependent on the mineralogy of the rocks through which the water flows. Strategies to obtain representative samples for acid-base accounting (Chapters 6 and 11) and kinetic tests (Chapter 7) require an understanding of lateral and vertical facies changes of rock units and an understanding of the depth of weathering. Special handling (Chapter 14) requires a knowledge of the site stratigraphy and alkaline addition (Chapter 13) requires a knowledge of the relative amounts of pyrite and carbonates.

Pennsylvania During the Pennsylvanian Period

Pennsylvania during the Pennsylvanian Period was part of the "supercontinent" called Pangea. The equator was just north of present-day Pennsylvania (Edmunds, et al.,1998) (Figure 8.1), and the climate was tropical (Cecil et al., 1985). A mountain range existed in present-day New Jersey and southeastern Pennsylvania, which was the result of the converging African and North American continental plates and collisions of micro-continents with the North American plate (Faill, 1997b). A further consequence of the convergence and collisions was the formation of an ever deepening

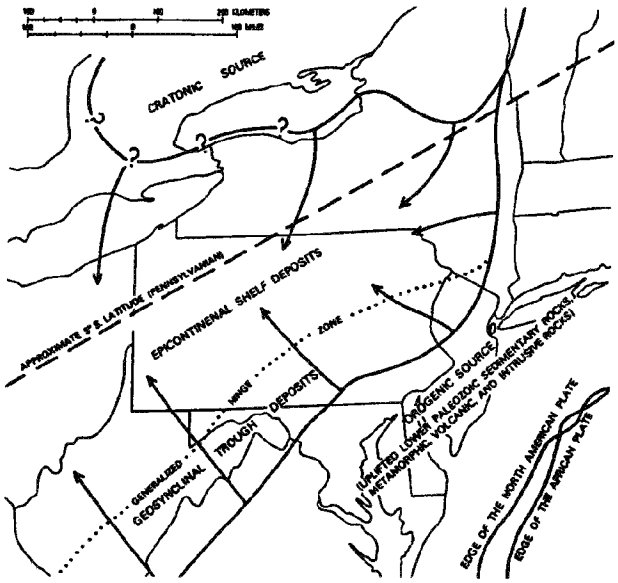


Figure 8.1 Generalized paleogeographic map of the Pennsylvanian depositional basin and source areas. Modified from Edmunds, et al. (1979).

foreland basin. This foreland basin is preserved as the present Appalachian basin. Sediments, eroded from mountains to the east and highlands to the north, were deposited in the basin (Figure 8.1) and became the coal and associated rocks of the coal fields of Pennsylvania (Figure 8.2).

Cyclicity in Pennsylvanian Period strata is a common phenomena in the United States (Cecil and Edgar, 1994). This cyclical pattern has been termed a "cyclothem" (Wanless, 1931). The "ideal" cyclothem is illustrated in Figure 8.3. The "ideal" cyclothem is a rare phenomena in Pennsylvania. Despite this, an overall cyclicity seems to be present. For example, in the Allegheny Group, the major coals are typically separated by ~50 ft (15 m) of sediments. The stratigraphic sequences associated with some of the Conemaugh marine invasions (e.g., Brush Creek and Ames) are most similar to the "ideal" cyclothem.

Figure 8.2 (Figure is in pocket at back of book). Generalized stratigraphic section of the bituminous coal field of western Pennsylvania showing stratigraphic nomenclature, positions of principal coals, marine zones, and major freshwater limestones. Also shown are distributions of rock types and carbonates that can influence mine drainage quality.

There appear to have been two major controls on regional cyclicity. One of these was basin subsidence due to collision between the North American and African plates. A second factor was climatic controls on sea level. Although, during the Pennsylvanian, the area of present day eastern North America was located near the equator and had a tropical climate, the southern polar regions of Pangea were experiencing widespread glaciation (Crowell, 1978; Veevers and Powell, 1987). Waxing and waning of continental glaciers resulted in episodic sea level changes, similar in amplitude to those during the Quaternary (~100 m; Heckle, 1995). Klein and Willard (1989) evaluated the relative impacts from these two mechanisms on the Pennsylvanian Period coal basins of the United States. They attribute the control of cyclothems in the Western Interior Basin to repeated transgressions and regressions of a mid-continent sea. These changes in sea level were caused by glaciation. Klein and Willard conclude, based on the more clastic nature of Appalachian sediments and the deeper basin warping, that the Appalachian Basin was affected most by tectonic controls. They also invoke a combination of transgressive-regressive cycles and tectonism as controls on cyclicity in the Illinois basin.

Two more factors have been proposed to explain the distribution of coals and intervening sediments. These are the "deltaic" model of Ferm (1970, 1974) and Donaldson (1969, 1974, and 1979) and the "climatic" model of Cecil et al. (1985) and Donaldson et al. (1985). The deltaic model accounts for rapid facies changes that occur over very short horizontal distances. These rapid changes are due to repetitive channel switching, as in the modern Mississippi delta. The climatic model explains the marked vertical stratigraphic, sedimentological, and mineralogic variations from the beginning to end of Pennsylvanian sedimentation, throughout the Appalachian Basin, and explains chemical and physical changes in coals through time. For example the red beds found in the Conemaugh Group are attributed to dry conditions. The widespread freshwater lake deposits of the upper Allegheny and Monongahela Groups are also indicative of dry conditions (Cecil et al., 1985). Skema and Lentz (1994) contend that deposition during the Pennsylvanian, within the region of present-day Pennsylvania, was complex. They conclude that multiple factors were at work. For example, Cecil et al.'s climatic model explains the widespread development of redbeds and freshwater limestones, and the glacial-eustatic model is consistent with widespread marine deposits in the lower Allegheny Group and Glenshaw Formation. The discontinuous nature of non-marine beds and abrupt facies changes imply more localized control, which Skema and Lentz (1994) attribute to "deposition

Table 8.1 Tabulation of stratigraphic horizons that were evaluated for construction of Figure 8.2. X indicates complete section was represented in the drill core; * indicates a portion of the section was represented.

Core No.	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10	C11	C12	C13
Dunkard	X	X							*				
Monongahela	X	X							X				
Conemaugh	X	X	X	X	*	X		*	X				
Allegheny	X	X	X	X	X	X	X	X		X	*	X	X
Pottsville	X	X	X			X	X	X		X	X		X

on a fluvially prograding coastal plain" (p. 33). This process along with compactional subsidence explains much of the abrupt lateral stratigraphic changes observed in coal overburden. In summary, sedimentation in the northern Appalachians was complex and controlled by both basin-wide and local factors.

Pennsylvanian and Permian(?) Stratigraphy of Western Pennsylvania

A generalized stratigraphic column of the Pennsylvanian and Permian(?) units of western Pennsylvania is depicted on Figure 8.2. Shown are the groups and formations, principal coals, marine zones, and major freshwater limestones. Additionally, lithologic information that is important to mine drainage quality is portrayed.

The lithologic descriptions of Figure 8.2 are based on an examination of 13 core logs in the files of the Pennsylvania Geologic Survey. Figure 8.4 shows the locations of the cores and Table 8.1 shows the formations that occurred within each core. The core logging was very detailed, with stratigraphic units as thin as 0.05 ft (1.5 cm) identified. For the purposes of this study, lithology was simplified to clay, shale, siltstone, sandstone, limestone, coal, and boney coal. Particular attention was paid to units that were calcareous and

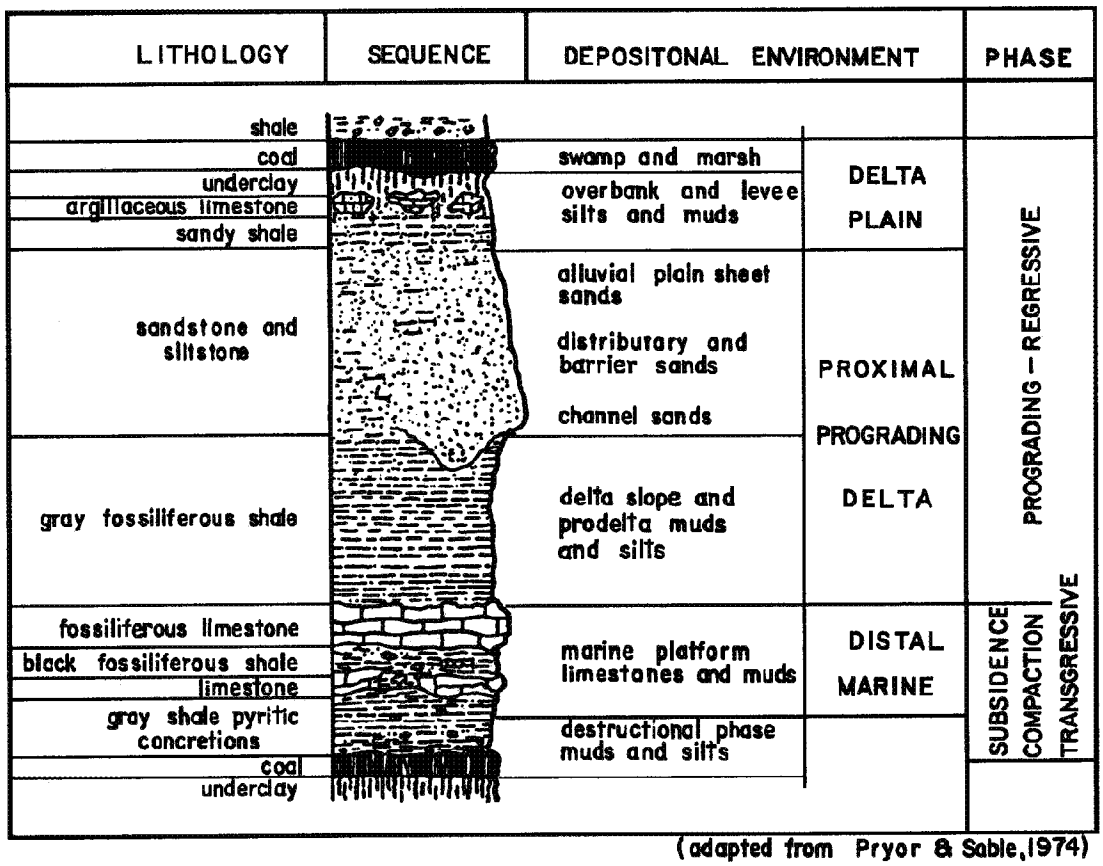


Figure 8.3 "Ideal cyclothem." Modified from Pryor and Sable (1974)

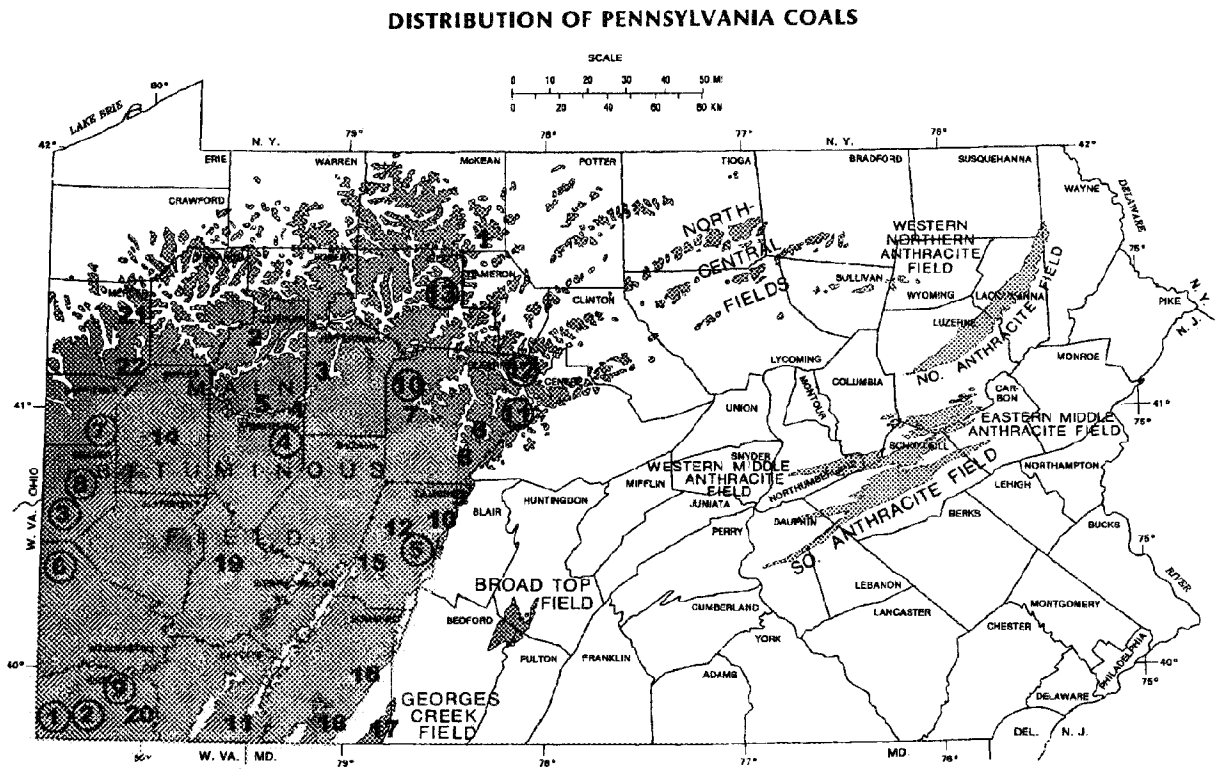


Figure 8.4 Map showing the locations of cores used in construction of Figure 8.2 (circled) and sites of overburden drill holes used in the figures displaying overburden chemistry (not circled) throughout this chapter. Site numbers correspond to those shown in figures of overburden chemistry.

siderite. Percentages of select lithology and calcareous and siderite attributes are depicted by group or formation. In some instances, such as the Allegheny Group and Waynesburg Formation, these have been subdivided to provide more detail because of known differences in stratigraphy within the group/formation. The histograms should be viewed as semi-quantitative.

In addition to the core holes, overburden analysis drill holes with percent sulfur and neutralization potential (NP) were obtained from the permit files of the Department of Environmental Protection's District Mining Offices. Percent sulfur furnishes an indirect estimate of pyrite content and neutralization potential furnishes an indirect estimate of calcareous carbonates (e.g., the minerals calcite and dolomite). NP in some instances may also reflect siderite. Pyrite and calcareous carbonates are the minerals that have the greatest influence on mine drainage quality. Examples are provided for all the major coals and some of the minor coals mined in Pennsylvania. The figures depicting stratigraphic logs show only total percent sulfur values greater than 0.25 percent, and neutralization potential (NP) values greater than 15 parts per thousand (ppt) $CaCO_3$. This has been done for clarity of the figures and because lower values typically have minimal influence on water quality. A key to these logs is shown in Figure 8.5

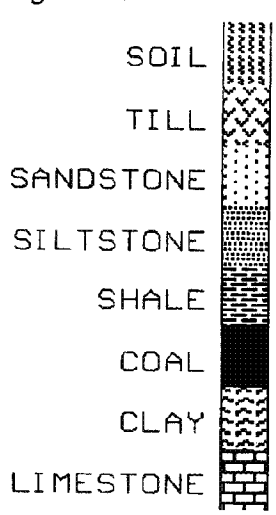


Figure 8.5 Key to drill logs depicted in this chapter, showing lithologic symbols. Figures also show sulfur values greater than 0.25 percent sulfur (on left) and neutralization potentials above 15 ppt $CaCO_3$ (on right).

Glass et al. (1977) dedicated their report to George Hall Ashley (1866-1951) a former State Geologist of Pennsylvania and "life-long combatant with the perplexing rocks of southeastern Clearfield County." They point out that their work is built upon his foundation and that "(t)he geology was not as difficult as you thought, Dr. Ashley - it was worse!" The stratigraphy of the Pennsylvanian of Pennsylvania is not as simple as is often assumed. For most of the past 150 years stratigraphic correlations were made using the coal seams. The group-level boundaries are based on coal seams. The Allegheny Group, for example, was designed to contain all the mineable coals within that section of the Pennsylvanian, and the Pittsburgh coal defines the base of the Monongahela Group. Many coal seams are not continuous over large areas, some are only local. A good example is the Brookville coal, which marks the base of the Allegheny Group. This coal can only be precisely defined in the area where it was first described. Readers of this chapter will hopefully get some feel for the fact that the real world is not simple. Recent work by the Pennsylvania Geologic Survey has relied on laterally persistent units such as marine zones for correlation. This has proven to be much more reliable. As will be shown, many of these marine zones are quite extensive.

Whether to refer to the Pottsville and Allegheny as formations or groups is still in dispute and is not consistent in the literature. We have, for the most part, used the term "group." Resolution of which is the proper designation must be left to others. For a broader discussion of the Pennsylvanian stratigraphy, consult Edmunds et al. (1998). The quotes below from Edmunds et al. have had metric conversions added.

Pottsville Group

The Pottsville Group is variable in thickness. It is dominated by sandstone, and the coals are discontinuous. Because of the discontinuous nature of these coals, and the fact that they are often split with numerous partings, mining is not common in the Pottsville Group. The principal coal that is mined is the Mercer. This is actually a coal zone rather than a single coal. The Mercer clay, below the Mercer coal, has also been mined in some areas.

Edmunds et al. (1998) discuss the Pottsville of western Pennsylvania in terms of strata below the Mercer coal and above the Mercer coal.

> "The Pottsville Formation in western Pennsylvania ranges from 20 ft (6 m) to at least 250 ft (75 m) in thickness. Its basal contact is apparently everywhere disconformable and from south to north overlies increasingly older Mississippian and possibly uppermost Devonian rocks....The base of the Brookville coal marks the upper boundary of the Pottsville Formation" (Edmunds, et al., 1998, pp. 150-151).

> "In some places, the Pottsville is particularly thin, mainly because of depositional overlap... (which) is believed to reflect trends in the topographic relief of the pre-Pottsville erosion surface" (Edmunds, et al., 1998, p. 152).

V. Skema (Geologist, PA Geol. Survey, 1997, personal communication) has observed a complete absence of Pottsville rocks on areas of pre-Pottsville topographic highs in portions of Clinton County.

Edmunds, et al. (1998) state that

> "In Pennsylvania, the pre-Mercer Pottsville is entirely nonmarine. Its thickness varies from 0 to as much as 175 ft (53 m).... The upper part of the Pottsville Group, commencing with the lowest Mercer coal or its underclay, is a very complex highly variable sequence between 20 (6 m) and approximately 80 feet (24 m) thick.... (I)n Mercer and adjacent counties, it contains two marine limestones. Shales containing marine or brackish-water fauna occur widely, if irregularly, throughout western Pennsylvania" (p. 153).

Figure 8.6 shows examples of Mercer coal overburden from Clarion and McKean Counties, PA. The Clarion County drill holes (DH 201-1, 201-2, and 201-3) are from the same mine site and all within a hundred or so acres (~40 ha). These holes illustrate the lateral and vertical variation of the Mercer coal zone. For example in hole DH 201-3 there are three coals, in DH 201-1 the zone is represented by six coals. The lateral correlation of any single coal can not be assured from drill hole to drill hole. The acid-base accounting data shows no significant calcareous strata (i.e., no NP > 30 ppt $CaCO_3$), but there are frequent high sulfur (sulfur > 0.5%) strata. As with the coals, the high sulfur rock units are not laterally continuous and they vary greatly in thickness. Discontinuous units, such as those shown in Figure 8.6 create problems for coal reserve studies because it is difficult to determine the lateral extent or thickness of a particular coal. Similarly, this geologic complexity makes overburden sampling very difficult.

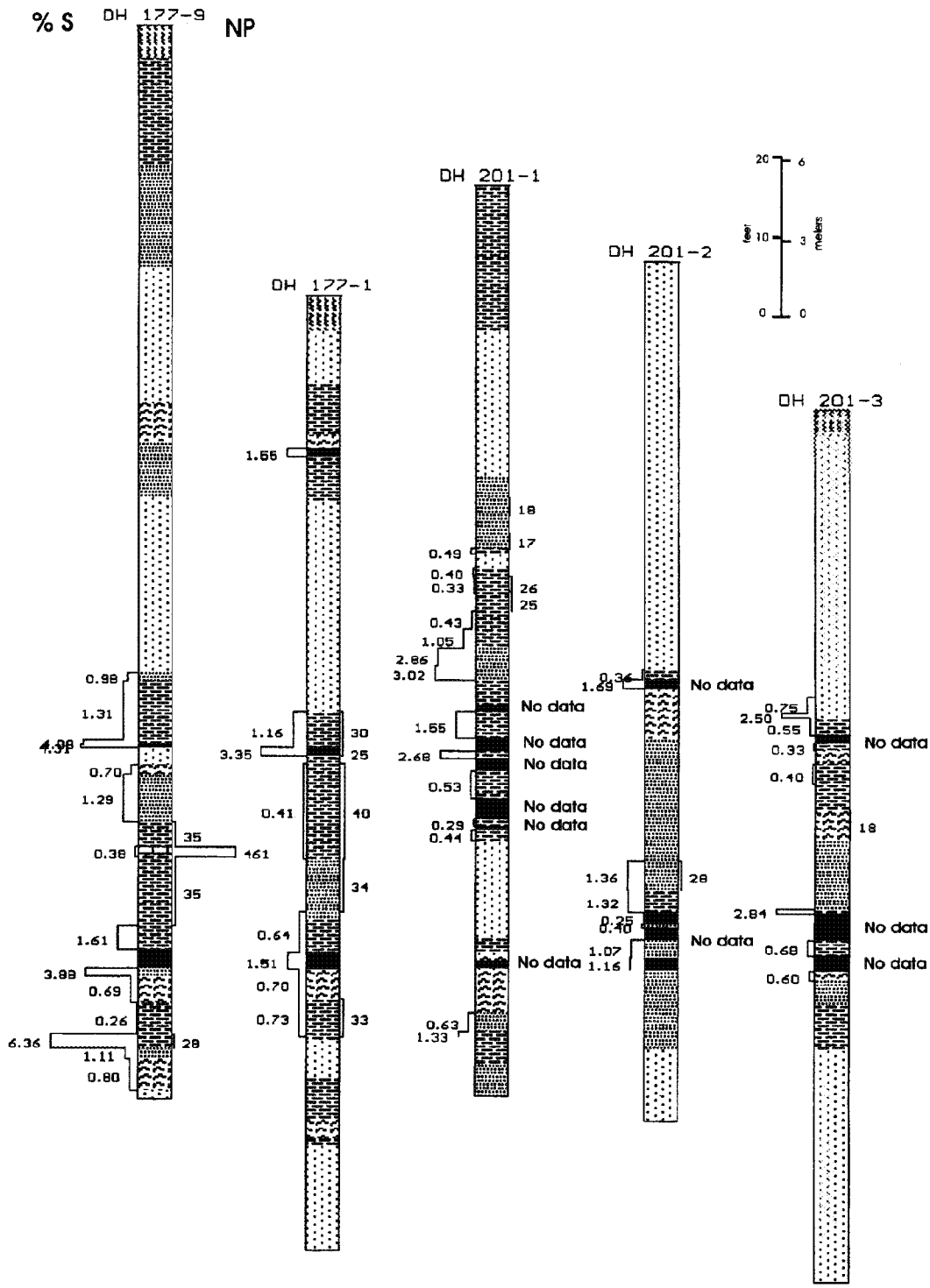


Figure 8.6 Overburden analyses of the Mercer coal zone. Location 1: DH 177-9 and DH177-1, Norwich Township, McKean County, and Location 2: DH 201-1, -2, and -3, Elk Township, Clarion County. Site locations shown on Figure 8.4.

A thorough understanding of mine site geology is necessary to insure that representative samples are selected. Complex stratigraphy can also make mine drainage prevention plans, such as special handling and alkaline addition, hard to design and implement.

Drill hole DH 177-9, from McKean County (Figure 8.6) contains one of the Mercer marine zones. This zone has a NP of 461 ppt $CaCO_3$. The two McKean County holes show more lateral continuity of the coals than did the Clarion County site. The marine zone, however, occurs in only the one hole. It is unknown whether the NPs from 30 to 40 ppt $CaCO_3$ equivalent are calcareous minerals or siderite.

Figure 8.2 shows the unconformable nature of the Pottsville Group. The Pottsville is dominated by sandstone, and is marked by a near absence of calcareous strata. Siderite occurs in about 13% of the strata. This lack of calcareous strata probably accounts for acid mine drainage problems that are often associated with mining of Pottsville coals and underclays.

Table 8.2 (Located in pocket at back of book). Postmining water quality of Pennsylvania Bituminous Coal Region by stratigraphic interval.

Typical examples of mine drainage quality of Pottsville Group coals and most other coal-bearing stratigraphic sections of the bituminous coal region of western Pennsylvania are shown in Table 8.2 (located in pocket at back of book). The water quality data contained in Table 8.2 were obtained from the surface mine permit files of the Department of Environmental Protection's District Mining Offices. Whenever possible, the water quality data were obtained from the same permit files as the overburden analysis data shown on the drill logs in the figures contained in this chapter. This enables a direct comparison of the percent sulfur and NP data used to predict mine drainage quality, with the actual water quality monitored at the mine site. In some cases where during-mining and postmining water quality data were lacking for a site, the water quality data were obtained from nearby sites on the same coal seams. The relationships between the stratigraphic data described in this section and the mine drainage data contained in Table 8.2 and related tables are more fully described later in this chapter.

Allegheny Group

The Allegheny Group is one of two groups within the Pennsylvanian that contains the majority of economically mineable coals. For the purpose of discussion, the Allegheny has been divided into the upper and the lower Allegheny. The lower Allegheny extends from the base of the Brookville coal to the base of the Johnstown limestone (or upper Kittanning coal where the limestone is absent). The upper Allegheny extends from the base of the Johnstown limestone to the top of the upper Freeport coal. This division is made because "marine units occur only below the upper Kittanning underclay"... "and, with minor exceptions, nonmarine limestones occur only at or above that unit" (Edmunds, et al., 1998, p. 154). This distinction of "marine" and "nonmarine" is to a large extent based on the work of Williams (1960). Williams defined four faunal groups, inferred as "fresh-water", "restricted marine or near-shore marine", and two marine groups, one having a more diverse fauna than the other. Williams also relied on the geochemical investigations of Degens et al. (1957, 1958) in defining his depositional environments.

Williams (1960) interpreted the rocks in the Allegheny Group above the upper Kittanning coal (and including the Johnstown limestone below the coal) to be freshwater. This interpretation was based on fossil Esterids (now referred to as conchostracans or "clam shrimps"). Conchostracans are found above the upper Kittanning, lower Freeport, and upper Freeport coals (e.g., Williams, 1960; Edmunds, 1968). New analysis and interpretations of the ecology of conchostracans during the Pennsylvanian Period support a marginally-brackish environment. Thus, conchostracan-bearing sediments are not completely devoid of marine influence and therefore some marine sulfate would be available for reduction to sulfide sulfur (and pyrite). This is consistent with the sulfur content of the upper Kittanning and Freeport coals and roof rocks. The assignment of conchostracans as an indicator of freshwater depositional environments was debated at the time Williams wrote his paper, and is acknowledged by Williams. A detailed discussion of this topic is found at the end of this chapter in the Appendix.

Although conchostracan-bearing sediments apparently had some marine influence, it was less than that of brackish or truly marine sediments and this is often reflected in the lesser amount of sulfur and the thinner sequences of high-sulfur strata associated with conchostracan-bearing rocks. Marginal-brackish facies would be exposed to saline influences for less time during transgressive-regressive cycles than marine or brackish sequences; thus the thinner zone of high sulfur rock.

According to Edmunds et al. (1998) the Allegheny Group:

"was specifically defined to include all of the economically significant coals present in that part of the Pennsylvanian sequence. The thickness of the formation is between 270 (82 m) and 330 feet (100 m) in Pennsylvania, and there is no obvious regional trend. The Allegheny Formation is a complex, repeating succession of coal, limestone, and clastics, ranging from claystone or underclay to coarse sandstone....No individual bed or lithosome is universally persistent, but some coals, marine shales, and limestones seem to be fairly continuous over thousands of square miles (thousands of square kilometers). The group is fairly uniform in its lithologic diversity... The Allegheny Formation contains six major coal zones. The coal in each zone may exist as a single, more-or-less continuous sheet, as a group of closely related individual lenses, or as a multiple-bed complex in which the various beds can be separated by tens of feet or merge into a single thick coal" (pp. 153-154).

Because the Allegheny Group is extensively surface mined, and some portions of and areas within this formation have created acid mine drainage, the Department has an extensive database of acid-base accounting data for the Allegheny Group. For the purposes of simplifying discussion, the overburden above the upper Freeport, although part of the Glenshaw Formation of the Conemaugh Group, is included in the discussions as part of the upper Allegheny Group.

Lower Allegheny -The base of the lower Allegheny is defined as the base of the Brookville coal. This is not a useful working definition because the Brookville coal is not always present so that the base of the Allegheny may be difficult or impossible to define. What is often called the Brookville is probably often correlative with a lower Clarion coal. Thus, the base of the lowest Clarion coal often substitutes as a working definition. The Clarion and Brookville coals are not differentiated in this discussion.

Marine units occur over large areas and at several stratigraphic horizons within the lower Allegheny Group. The paleoenvironment of the marine zones can vary regionally and vertically. A good example of this is the Vanport horizon which occurs above the Clarion coal. The marine limestone facies covers an area of at least hundreds of square miles (km^2) and is over 20 ft (6 m) thick in the center of the basin. A maximum thickness of over 40 ft (12 m) has been recorded for a small area in northeastern Lawrence County. Core logs in the files of the PaGS were examined to determine the extent of the Vanport zone south of the area mapped by Williams and Keith (1963). The presence of the Vanport marine horizon cannot be confirmed for the southwestern corner of the state because sandstone typically occupies this horizon. This sandstone may indicate non-deposition of limestone and the presence of distributary channels that emptied into the Vanport sea. Alternatively, but less likely, the sandstone may occupy channels that cut through and removed the limestone.

Clarion Coal Overburden and the Vanport Limestone - Where present, the Vanport can be a nearly pure limestone. Figure 8.7 shows the Vanport limestone in drill hole DH 23-6. Site locations for the drill logs with overburden chemistry are shown in Figure 8.4. The Vanport in DH 23-6 has a NP of 999 ppt $CaCO_3$. The Vanport in DH-4 in Figure 8.39 (presented in the section on glacial sediments) is greater than 920 ppt $CaCO_3$. The rocks below the Vanport are high sulfur (up to 4.1 % in DH 23-6 and up to 5.2% in DH-4). The high sulfur strata are 10 to 30 ft (3 to 10 m) thick. These high sulfur units are associated with NPs that are typically less than 35, but as high as 73 ppt $CaCO_3$. These low NPs may be due to siderite. These two logs represent, from the coal to the limestone, a transgressive sequence. The lower shale units have marginal marine (brackish) or shallow marine fossils and the limestone represents maximum transgression in Appendix for description of faunal facies). In drill hole DH 23-6 the high sulfur strata are associated with marine fossils. The strata for a drill hole in Black Lick Township, Indiana County (logged by Al Glover and Vic Skema, Pennsylvania Geological Survey) nicely show this transgressive sequence from brackish to marine conditions. Glover found *Lingula* and *Dunbarella* fossils immediately above the Clarion coal. These are indicative of brackish waters and represent the earliest portion of the marine transgression. Above this is a sandier zone that is bioturbated with siderite-filled burrows, typical of marine or brackish environments. Marine fossils and siderite concretions occur near the top of this unit. The next unit upward contains marine brachiopods, some of which are pyritized. This unit is overlain by the Vanport limestone which contains crinoids, an indicator of deeper, less muddy and consistently saline marine water.

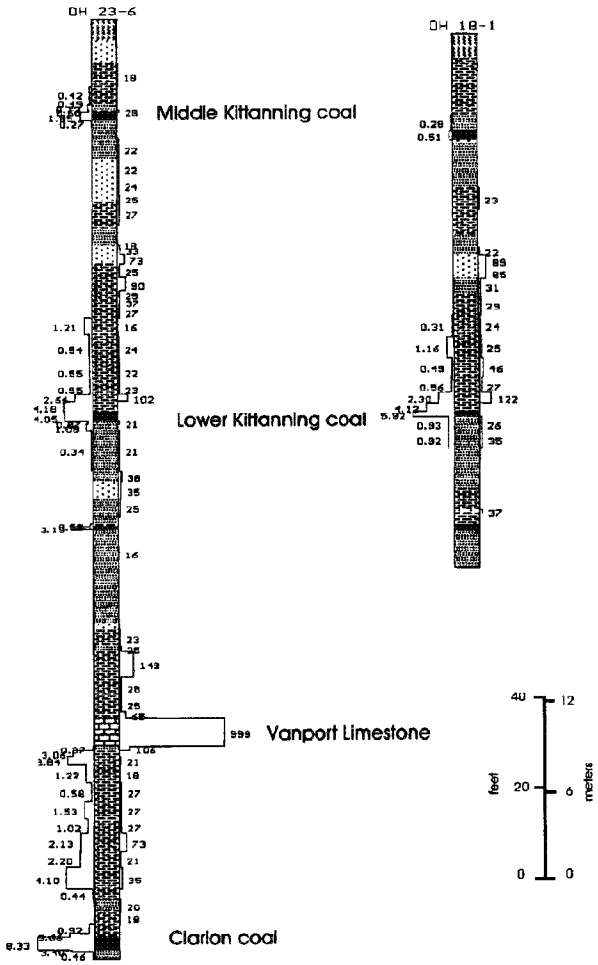


Figure 8.7 Stratigraphy at Location 3, Porter Township, Clarion County. Interval is from the Clarion coal through middle Kittanning overburden. The overburden above all three coals is marine.

The Vanport horizon, which occurs above the Clarion coal, is often laterally (and vertically) transitional from marine to brackish conditions. Figure 8.8 and Figure 8.9 show regional changes in thickness of the Vanport limestone and the location of other contemporaneous facies in a portion of western Pennsylvania. In Butler County, where the Vanport is thick and in close proximity to the coal (Figure 8.9), mining of the Clarion coal will result in alkaline drainage. Where the Vanport-equivalent facies are brackish shale and the shale lacks calcareous minerals, such as in Clearfield County, the mine water is typically acidic. Figure 8.10 shows the distribution of pH for Clarion coal mine drainage from areas with and without the Vanport limestone. Median pH for areas without the limestone is 3.6 and with limestone is 5.0. Many of the mines were probably "pre-Act" and unreclaimed, and thus may be producing poorer quality water than would be produced by modern mining methods.

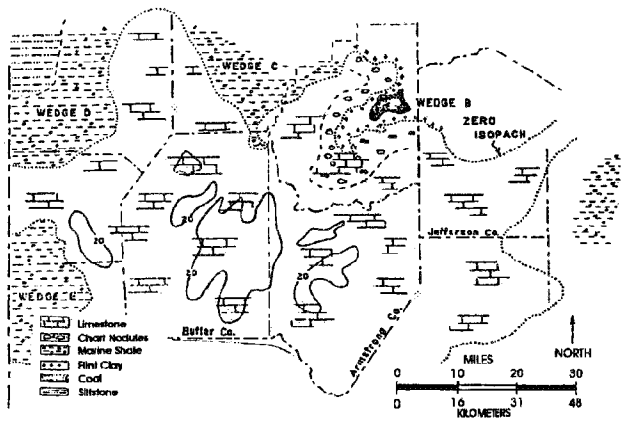


Figure 8.8 Generalized isopach map of the Vanport limestone and lateral facies for a portion of western Pennsylvania. Figure from Bergenback (1964).

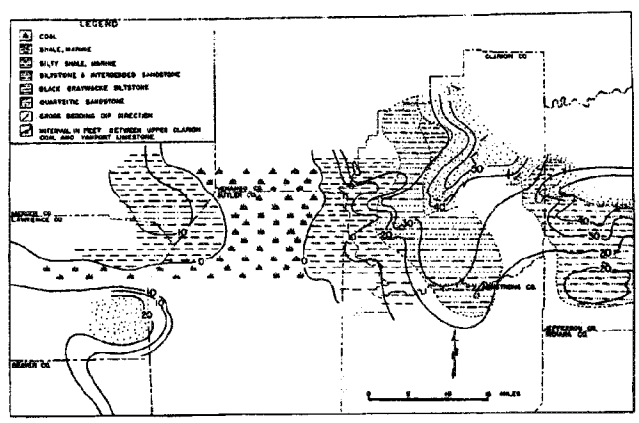


Figure 8.9 Isopach map showing the thickness of rock between the Vanport limestone and the upper Clarion coal, and the rock types/facies occurring directly below the limestone. The Vanport rests directly on the coal in northern Butler and southern Venango counties. Figure from Williams et al. (1964).

Lower Kittanning to Middle Kittanning Interval - Williams (1960) and Williams and Keith (1963) determined, using fossils, that the lower Kittanning (LK) was overlain by rocks deposited under marine, brackish (marginal marine) and freshwater depositional environments. The marine and brackish rocks are formally referred to as the Columbiana shale. They published maps showing the distribution of LK paleoenviron-

ments. A revised map is presented in Figure 8.11. This map was derived from more recent published and unpublished studies by the Pennsylvania Geologic Survey (PaGS), and discussions with PaGS geologists (in particular, V. Skema and J. Shaulis), and BMR studies. The locations of LK drill holes discussed below are shown on this map. The faunal facies used to construct Figure 8.11 are discussed in the Appendix. The drill holes provide examples of sulfur and neutralization potential for coal and overburden deposited under different depositional environments.

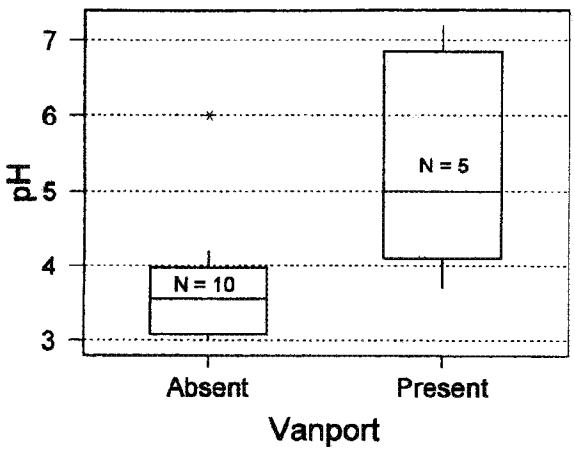


Figure 8.10 Boxplots of pH of surface mine water from mines on the Clarion coal in areas where the Vanport limestone is present and in areas where it is absent. Lower boundary of the box represents the 25th percentile, the upper boundary represents the 75th percentile. The line between the two is the median. "Whiskers" indicate the range of data. Data are from Williams et al. (1982).

Figure 8.7 shows overburden of marine origin. Drill cores DH 23-6 and DH 18-1 contain marine brachiopods (e.g., *Mesolobus*) in the black carbonaceous shale overlying the lower Kittanning coal. The carbonate minerals siderite, dolomite and calcite were all identified within this zone at this site (Cravotta et al., 1994). High sulfur, identified as pyrite by Cravotta et al., is associated with the brachiopod-bearing rocks. The drill cuttings analyzed by Cravotta et al. did not encounter the highest NP zone located a few feet above the lower Kittanning coal. This zone with NP's over 100 ppt $CaCO_3$ is probably calcite or dolomite. The alkaline postmining water quality confirms that calcareous minerals are present.

The lower Kittanning overburden is also marine in northeastern Armstrong County and southern Jefferson County (Figure 8.12). The drill logs show 30 or more feet (10+ m) of rock with over 0.5 % sulfur (2.37 % maximum). They also show NP's in the range of 15 to 40 ppt $CaCO_3$. X-ray diffraction analyses indicate that calcite is the only carbonate present (R. Smith, PaGS, personal communication, 1996). The water associated with lower Kittanning mines in this area is alkaline despite the high sulfur overburden.

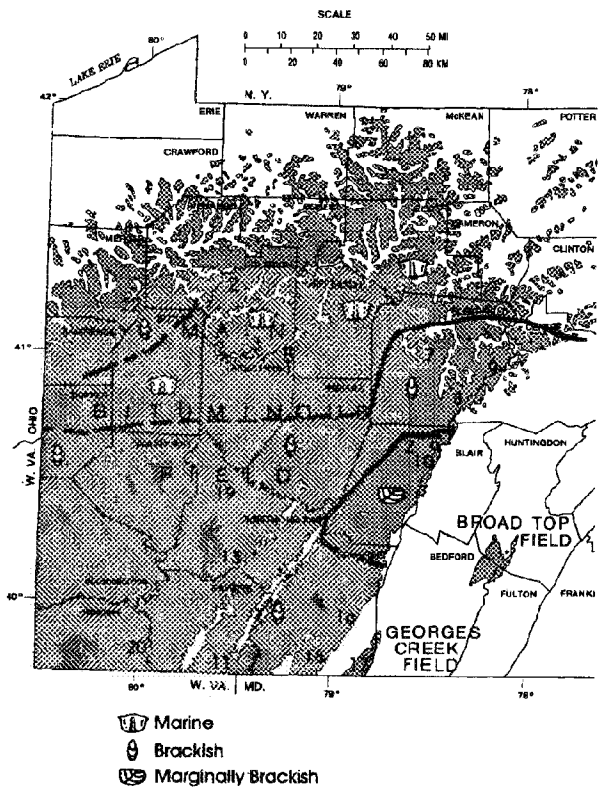


Figure 8.11 Tentative paleodepositional environment map for the rock above the lower Kittanning coal. Dashed line indicates uncertainty as to the actual location of the boundary between depositional environments; solid lines indicates that good paleontological control was available and boundary location is better known. Numbers identify locations of sites discussed in text and shown in figures. Fossil symbols are used to identify the area of a depositional environment and do not necessarily indicate that fossils occur at the location of the symbol. Sources used in the construction of this map: drill logs and site locations shown on Figure 8.4 and Table 8.1, Glass (1972), Edmunds (1968), Edmunds and Berg (1971), Berg and Glover (1976), Glover and Bragonier (1978), Williams and Keith (1960), personal observations by K. Brady, and insights gained from conversations with V. Skema, J. Shaulis and C. Dodge, all with the PaGS.

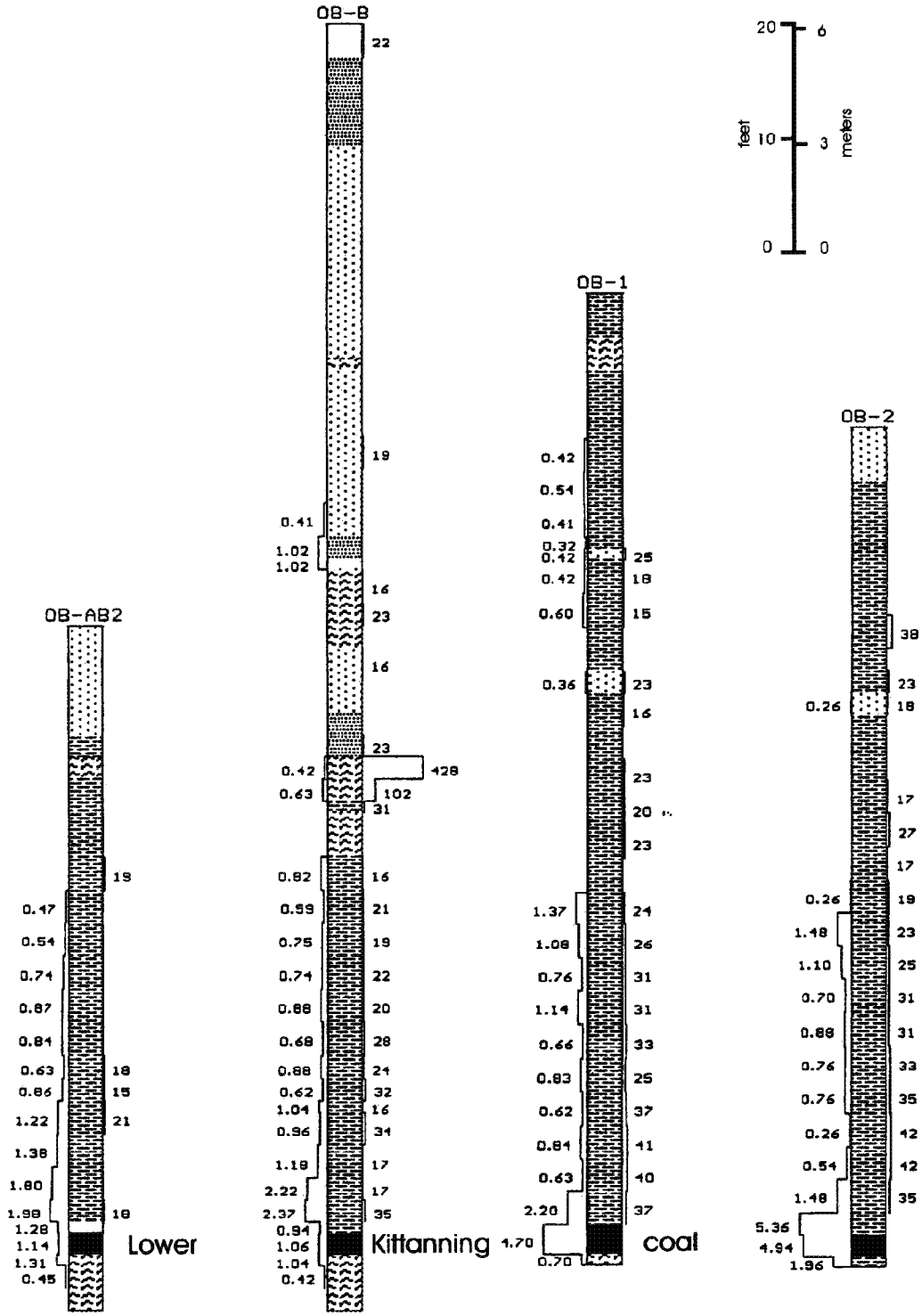


Figure 8.12 Drill logs showing lower Kittanning overburden chemistry where the roof rock was deposited in a marine environment. Drill logs OB-AB2 and OB-B are from Site 4 in Rose Township, Jefferson County. Drill logs OB-1 and OB-2 are from Site 5 in Redbank Township, Armstrong County.

Figure 8.13 and Figure 8.14 show sulfur and NP for the lower Kittanning in Clearfield County where the overburden was deposited in a brackish depositional environment. Typically the shale above the coal is high in sulfur. Guber (1972) found that the high sulfur rocks often contain the brachiopod *Lingula*. Guber's findings are discussed in more detail in a later part of this chapter. *Lingula*, as discussed in Williams (1960), is indicative of brackish environments. Geologic reports for the areas of the drill holes shown in Figure 8.13 and Figure 8.14 describe brackish fossils above the lower Kittanning coal (Glen Richey Quadrangle, Edmunds, 1968; Luthersburg Quadrangle, Edmunds and Burg, 1971; Ramey Quadrangle, Glass, et al., 1977). The high sulfur zones shown in Figure 8.13 near the middle of the shale above the LK coal in holes OB-1 (0.92 % S), OB-4 (4.4 % S) and near the top of the shale unit in A-8 (1.15 % S) contain *Lingula*. The NP that is present is probably due to siderite, the exception being the base of the sandstone and immediately adjacent shale in A-8, which is likely calcareous. LK mines in the brackish areas of Clearfield County are notorious for producing acid mine drainage.

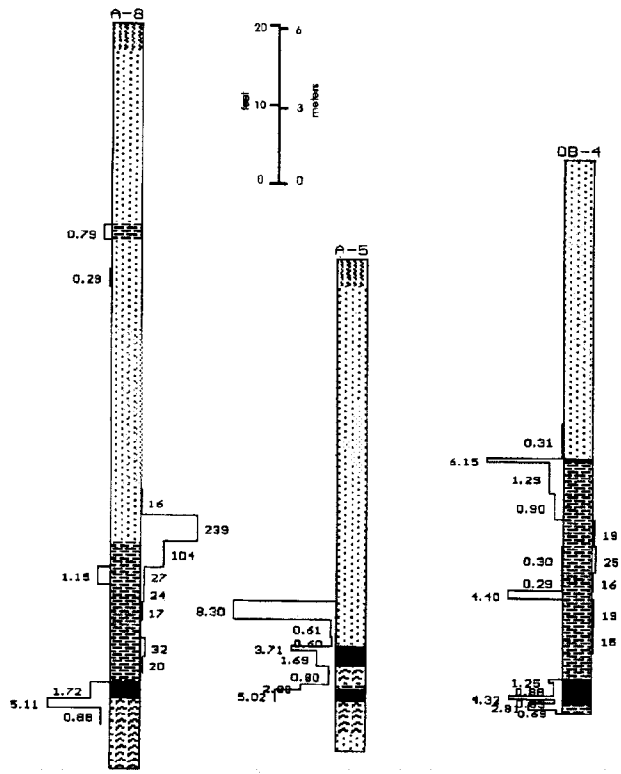


Figure 8.13 Drill logs showing lower Kittanning overburden chemistry where the roof rock was deposited in a brackish environment. All examples are from Clearfield County. Logs are from the Kauffman site in Boggs Township. The sandstone occurs in place of the shale units to varying degrees. The sandstone is of a fluvial origin.

Williams (1960) shows a small portion of the LK roof rock in northeastern Cambria County as having been deposited in what he defined as a freshwater depositional environment, based on the presence of conchostracans. Recent investigations by J. Shaulis and V. Skema (personal communication, 1997) have confirmed the presence of conchostracans in extreme northern Somerset County. Fossil fauna however are rare (Figure 8.11). LK overburden chemistry in this region does appear to be different from the other areas discussed above (Figure 8.15). Sulfur is seldom above 0.5 percent. The small amount of NP (between 15 and 36) may be siderite because the postmining water is not alkaline. Mines from these areas tend to produce mild acid mine drainage, with pH ~4 and acidity ~100 mg/L.

Middle Kittanning to Johnstown Limestone Interval - The middle Kittanning (MK) coal is overlain by marine or brackish sediments over most of Pennsylvania's bituminous coal field. The exception is an area around Cambria County where the MK overburden has conchostracans or no fossil fauna. The marine zone is formally referred to as the Washingtonville Shale. Figure 8.16 is a map of paleodepositional environments for the rocks overlying the middle Kittanning coal. The northern portion of this map is from Williams (1960) and the southern portion is derived from drill hole data made available by the PaGS and PaGS publications. This MK horizon, in a PaGS drill hole in northwestern Washington County, is represented by a coquina limestone. This was probably the deepest part of the MK "basin" in what is now Pennsylvania. Faunal facies used to construct this map are discussed in the Appendix.

The "MK" is a coal zone in many areas rather than a distinct coal seam. Over much of Clearfield County there are typically two to four "splits" of the MK. For example, in the Hazen, Reynoldsville, Falls Creek, and DuBois quadrangles the MK consists of a "middle Kittanning" that is typically two feet (0.7 m) thick and up to 42 inches thick (1.1 m) (Glover and Bragonier, 1978). This is the MK coal that is mined locally. This however is not the coal that the marine zone overlies. The marine zone overlies a "middle Kittanning rider" coal and the marine zone is about 30 ft (10 m) above

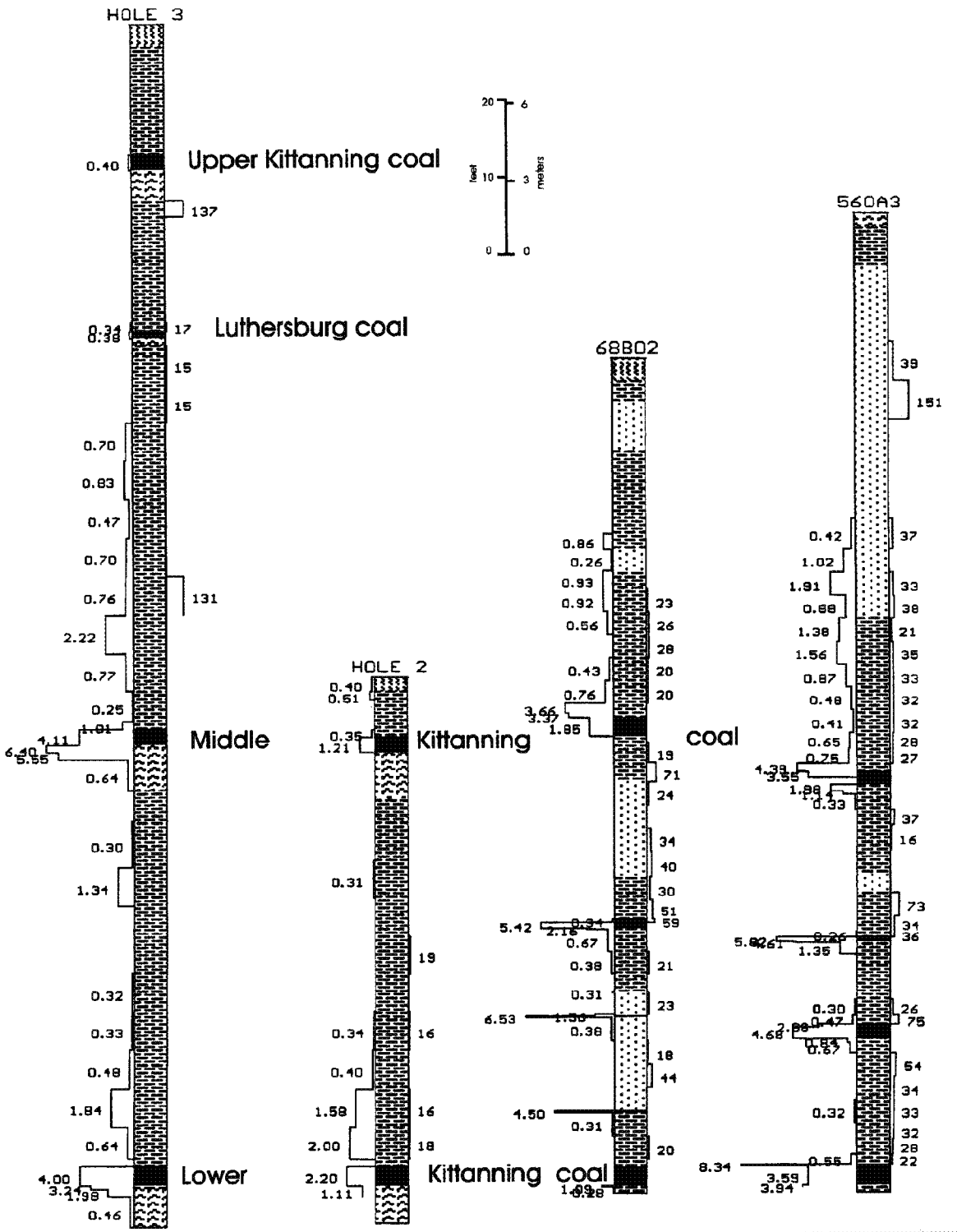


Figure 8.14 Lower Kittanning overburden deposited under brackish conditions. Hole 3 and Hole 2 are from Union Township, Clearfield County (Location 7, Figure 8.4). Logs 68BO2 and 56OA3 are from Bigler Township, Clearfield County (Location 8). The middle Kittanning overburden is also brackish.

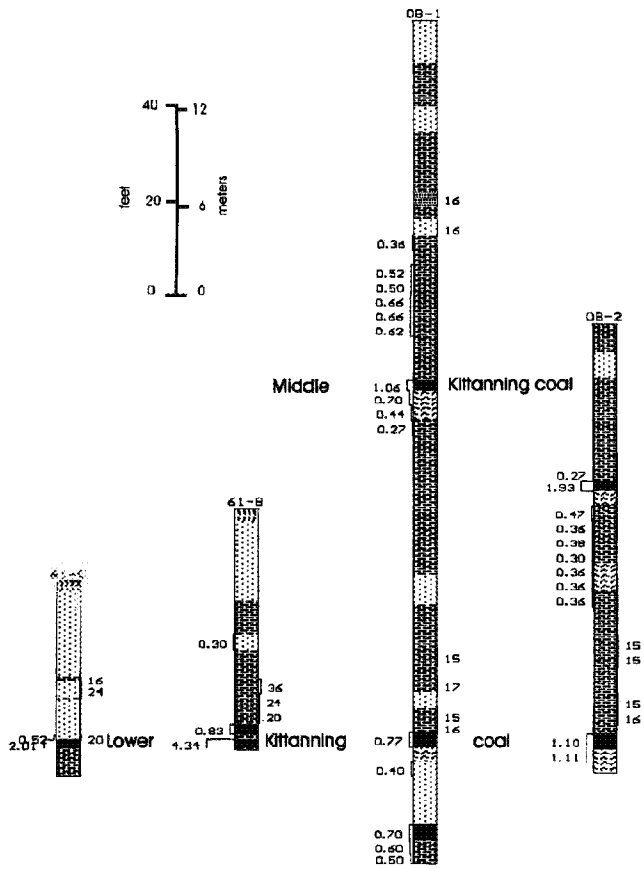


Figure 8.15 Drill logs depicting lower Kittanning overburden in the area of Cambria County that Williams and Keith (1963) indicated finding conchostracans. Holes 61-C and 61-B are in Reade Township, Cambria County (Site 9) and holes OB-1 and OB-2 are in Dean Township, Clearfield County (Site 10).

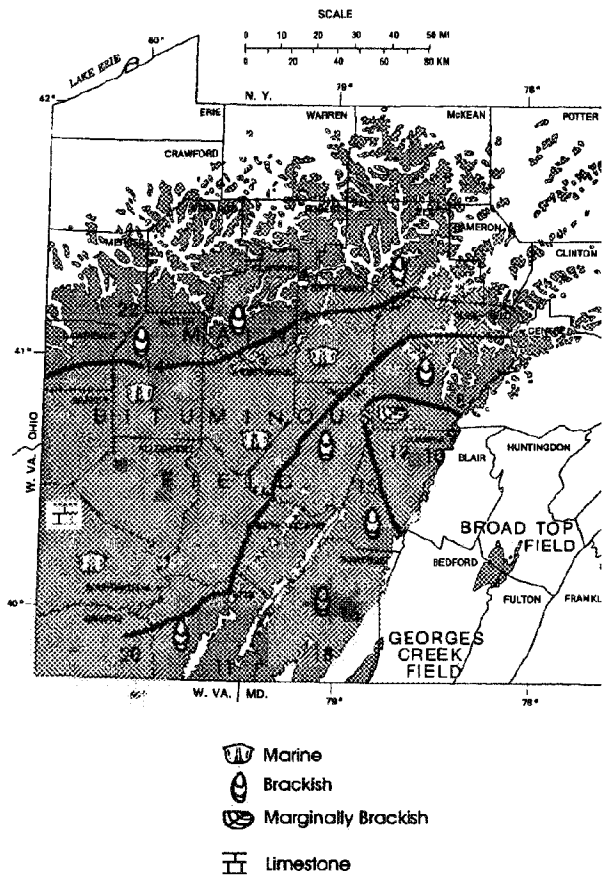


Figure 8.16 Tentative paleodepositional environment map for the rock above the middle Kittanning coal. Good paleontological control was available for construction of this map. Fossil symbols are used to identify the area of a depositional environment and do not necessarily indicate that fossils occur at the location of the symbol. The northernmost line showing the division between brackish and marine environments is essentially that of Williams and Keith (1963). Work for this chapter agreed with the location of this boundary. Other sources used for the construction of this map were drill logs and site locations shown on Figure 8.4 and Table 8.1, Glass (1972), Edmunds (1968), Edmunds and Berg (1971), Berg and Glover (1976), Glover and Bragonier (1978), Williams and Keith (1960), personal observations by Keith Brady, and insights gained from conversations with V. Skema, J. Shaulis and C. Dodge, all with the PaGS.

the "middle Kittanning" that is mined. This raises the likely prospect that the "middle Kittanning" seam being mined in one area may be a different split than that being mined in another area.

Holes showing the results of NP and percent sulfur above the MK coal (Figure 8.7, and Figure 8.14) were drilled in areas that are marine or brackish environments (Figure 8.16). The MK at Area 5, in the area of marine deposition, occurs beneath shallow cover which is probably weathered and therefore not very revealing for determining depositional controls on overburden mineralogy. Locations 7 and 8 (Figure 8.14; and see Figure 8.4 map for site locations) occur in the area of brackish overburden. The three holes with significant overburden (Hole 3, 68B02, and 560A3) have 30 to 40 ft (10 to 12 m) of high sulfur overburden overlying the coal. X-ray diffraction analyses reveal that the carbonate present over the MK at Location 7 is siderite. It is uncertain whether the zone with a NP of 131 is siderite or a calcareous carbonate. X-ray diffraction showed strata from other holes with NP as high as 75 contained siderite and no detectable calcite. The high sulfur and abundance of siderite for brackish overbur-

den is similar to that observed above the LK. The zone with an NP of 151 in the sandstone of drill log 560A3 is probably calcareous.

Figure 8.15 shows the MK in the area of the Figure 8.16 map where the MK is overlain by conchostracan-bearing shales. The highest sulfur in the overburden in drill log OB-1 is only 0.66 percent. This low sulfur is consistent with sulfur values from the conchostracan-bearing depositional environment for the LK coal. Further work needs to be done to establish relationships between concentrations of sulfur and carbonate minerals and depositional environment.

Upper Allegheny - The base of the upper Allegheny, as defined for this chapter, is the bottom of the Johnstown limestone. It is realized that this "limestone" is often transitional with the sediments below and does not occur everywhere, although it is remarkably persistent over much of the Bituminous Region and can be a good stratigraphic marker bed. Where the Johnstown limestone does not occur the base of the upper Kittanning coal substitutes as the base of the upper Allegheny. The reason for this stratigraphic break in the Allegheny is that this sequence includes nearly all the freshwater limestone units in the Allegheny Group. Fauna in the freshwater limestones is generally dominated by ostracods, *spirorbis,* and fish remains. This fauna is completely different from the fossils found in upper Allegheny coal-roof rock. Typically the only fossil fauna found in the rock above the coals in the upper Allegheny are conchostracans. The separate depositional environments of the roof-rock and the freshwater limestones is evidenced not only by the different faunas, but also by position and composition. The freshwater limestones are usually found below the coals, whereas the conchostracan-bearing rocks are above the coals. The "limestones" are highly calcareous and lack carbonaceous material, whereas the roof-rocks may not be calcareous at all and are often black due to abundant carbonaceous matter. It would appear that during the time of deposition of the upper Allegheny, coal deposition was followed by a marginally brackish transgression. Eventually truly freshwater sediments were deposited, including the freshwater limestones.

The Johnstown limestone is shown in Figure 8.17 and Figure 8.18. The Johnstown limestone has NP greater than 900 ppt $CaCO_3$ in LH-3 and 700 or greater in the other two drill holes in Figure 8.18. The high NP values are in the range of those of the marine Vanport limestone for "purity." Sometimes the Johnstown horizon is not a true limestone, but a calcareous claystone or shale (e.g., the zone just below the upper Kittanning coal in OB-9, Figure 8.17). Hole #101 in Figure 8.19 does not show a calcareous zone below the UK. This may simply be because the Johnstown limestone occurs below the bottom of this drill hole. The drill logs in Figure 8.20 are from an area where the Johnstown limestone does not occur. The limestone does occur, however, about a mile (1.6 km) west of these drill holes.

The interval between the UK coal and the lower Freeport (LF) coal often includes a calcareous zone beneath the LF coal. Where this zone is a limestone, it is referred to as the lower Freeport limestone. The interval between the LF and upper Freeport (UF) is similar to that of the underlying UK-LF interval. A widespread limestone or calcareous shale/claystone unit also lies beneath the UF coal. The rocks between the UK and LF, and LF and UF, as well as the overburden above the UF are portrayed in Figure 8.17, Figure 8.18, Figure 8.19, Figure 8.20, and Figure 8.21. The fauna of the Johnstown limestone, and LF and UF limestones are interpreted as freshwater in origin.

The lateral distribution of individual freshwater limestones in the Allegheny Group can be quite extensive, covering hundreds of square miles. The limestone is variable in thickness, and frequently there are areas where the limestone is absent. One freshwater limestone, the upper Freeport limestone, has been studied by Williams et al. (1968) and Weedman (1988). This limestone occurs between the lower and upper Freeport coals. Their findings illustrate the variability in thickness and distribution of an upper Allegheny limestone. Williams et al. (1968) looked at an area of approximately three 7.5 minute quadrangles in Clearfield County, and Weedman (1988) studied an area which covered slightly more than four 7.5 minute quadrangles in Indiana county. Observations by the authors confirm that this limestone is present, and persistent, between their two study areas. In Clearfield County, the thickness ranged from absent (where replaced by channel sandstone) to greater than 4 ft (1.2 m). Figure 8.22 shows the area studied by Weedman. The isopach map shows the variability in thickness that is typical of the upper Freeport limestone. Williams et al. (1968) indicate that the limestone in rare instances approached 100% calcium carbonate. Our experience is that these limestones are often "dirty" with a high component of clay and silt. At places this stratigraphic interval is represented by calcareous rocks with less than 50%

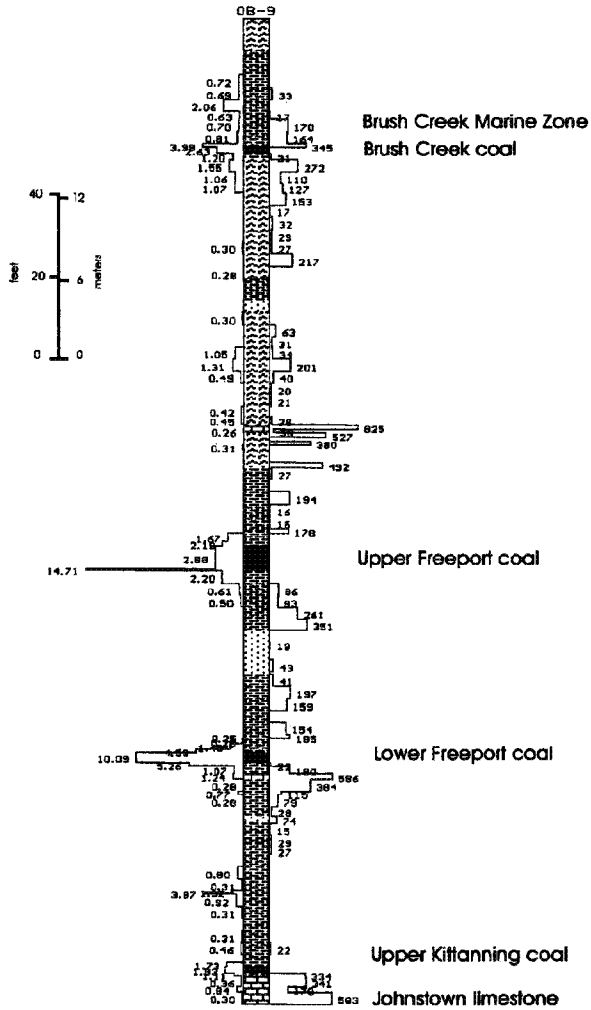


Figure 8.17 Overburden and chemistry of the interval from the Johnstown limestone to the Brush Creek marine zone. The overburden exhibits the calcareous nature of the upper Allegheny Group. High sulfur is typically restricted to the coal and immediately adjacent rock. This hole was drilled at Site 15 in Jackson Township, Cambria County.

calcium carbonate, and therefore by definition not a limestone, although they are often referred to as limestones on drillers' logs.

In addition to freshwater limestones, the upper Allegheny Group frequently contains an abundance of calcareous claystones, mudstones and siltstones. Figure 8.20 shows a stratigraphic section in Fayette County, between the upper Kittanning and lower Freeport coals. Much of this interval is calcareous (NP > 100; i.e., >10% $CaCO_3$), but only small portions could be classified as limestone (> 50% $CaCO_3$).

Conemaugh Group

The Conemaugh Group "is stratigraphically defined as the rocks lying between the upper Freeport coal horizon and the Pittsburgh coal. The thickness of this interval ranges from 520 feet (158 m) in western Washington County to 890 feet (270 m) in southern Somerset County. A gradual eastward thickening of the Conemaugh is apparent" (Edmunds et al., 1998, p. 154). The Conemaugh is subdivided into a lower formation called the Glenshaw, and an upper formation called the Casselman. The division is made at the top of the Ames marine limestone. Mineable coals are uncommon in the Conemaugh.

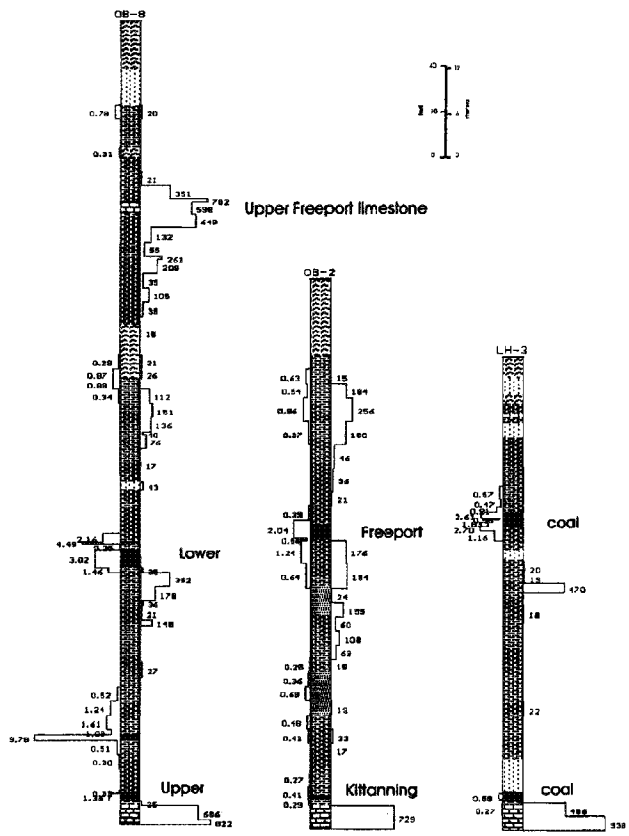


Figure 8.18 Upper Kittanning and lower Freeport overburden and chemistry for three drill logs at Site 15 in Jackson Township, Cambria County. The overburden exhibits the calcareous nature of the upper Allegheny Group. High sulfur is typically restricted to the coal and immediately adjacent rock.

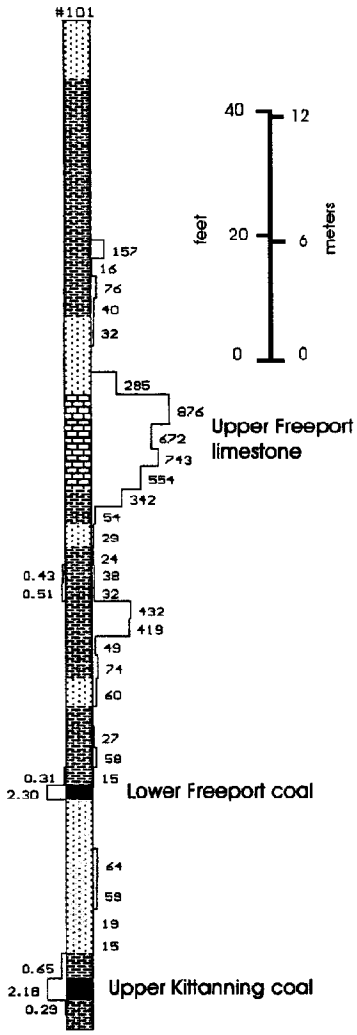


Figure 8.19 Upper Allegheny Group overburden and chemistry at Site 12 in West Carroll Township, Cambria County. Note the thick freshwater limestone with NP's over 300 ppt $CaCO_3$ above the lower Freeport coal.

Glenshaw Formation - The Glenshaw contains several widespread marine zones (see Figure 8.2). There are possibly as many as seven marine zones within the Glenshaw (Skema, personal communication, 1997). The Glenshaw is thickest in Somerset and southern Cambria counties, where it reaches 400 to 420 ft (122 to 128 m). It is thinnest near the Ohio border where it is about 280 ft (85 m) thick (Edmunds et al., 1998).

The Brush Creek limestone facies is present within most of its outcrop belt in western Pennsylvania. An area of more clastic shale and siltstone occupies the limestone horizon in Washington, southern Allegheny, northern Westmoreland, southern Indiana, and Cambria Counties (Skema et al., 1991). The Brush Creek coal, which occurs below the marine zone, is typically thin and not mined over much of western Pennsylvania. The coal is sometimes mineable in portions of the south-central and southeastern sections of the bituminous coal fields of Pennsylvania. Figure 8.23 shows Brush Creek overburden from Wharton Township, Fayette County and Figure 8.24 and Figure 8.17 show overburden from Jackson Township, Cambria County. The rock above the coal, in each area, has relatively high sulfur (> 0.5%) and relatively high NP (> 30 ppt $CaCO_3$). A true limestone is not present in any of these holes, the highest NP being 345 ppt $CaCO_3$ in OB-9 from Cambria County. Because the limestone or a calcareous facies is typically present where the Brush Creek coal is of mineable thickness, the drainage is generally alkaline.

Figure 8.25 shows overburden for the lower and upper Bakerstown coals. The Woods Run marine zone overlies the lower Bakerstown coal, although in Somerset County it is poorly developed and is represented by a brackish facies containing *Lingula* and *Dunbarella* (J. Shaulis, personal communication, 1997). Just below the upper Bakerstown coal a freshwater limestone sometimes occurs. This is evident in DH-12. The upper Bakerstown coal is commonly overlain by a black shale with abundant conchostracans in Somerset County (Shaulis, personal communication, 1997). This zone is the stratigraphic equivalent of the Noble marine zone, which is a restricted marine to brackish shale in some other portions of the bituminous field (Edmunds, et al., 1998).

The overburden above the lower Bakerstown coal is similar to lower Allegheny coal overburden with a brackish depositional environment. It is characterized by sulfur greater than 0.5 percent and NP generally 30 ppt $CaCO_3$ or less. The zones with higher NP, above the brackish zone, may be freshwater calcareous zones related to the freshwater limestone. Unfortunately it is hard to evaluate the overburden above the upper Bakerstown. The upper Bakerstown coal in Hole 11 F is only about 10 ft (3 m) below the surface. Holes DH-3 and DH-12 have sandstone and shale, respectively, above the coal. Both show some zones with elevated sulfur, but the sulfur in these drill holes is always less than 1.0 percent. NP is negligible. More comparisons need to be made, but this overburden looks similar to the lower Kittanning overburden in eastern Cambria County where conchostracans occur.

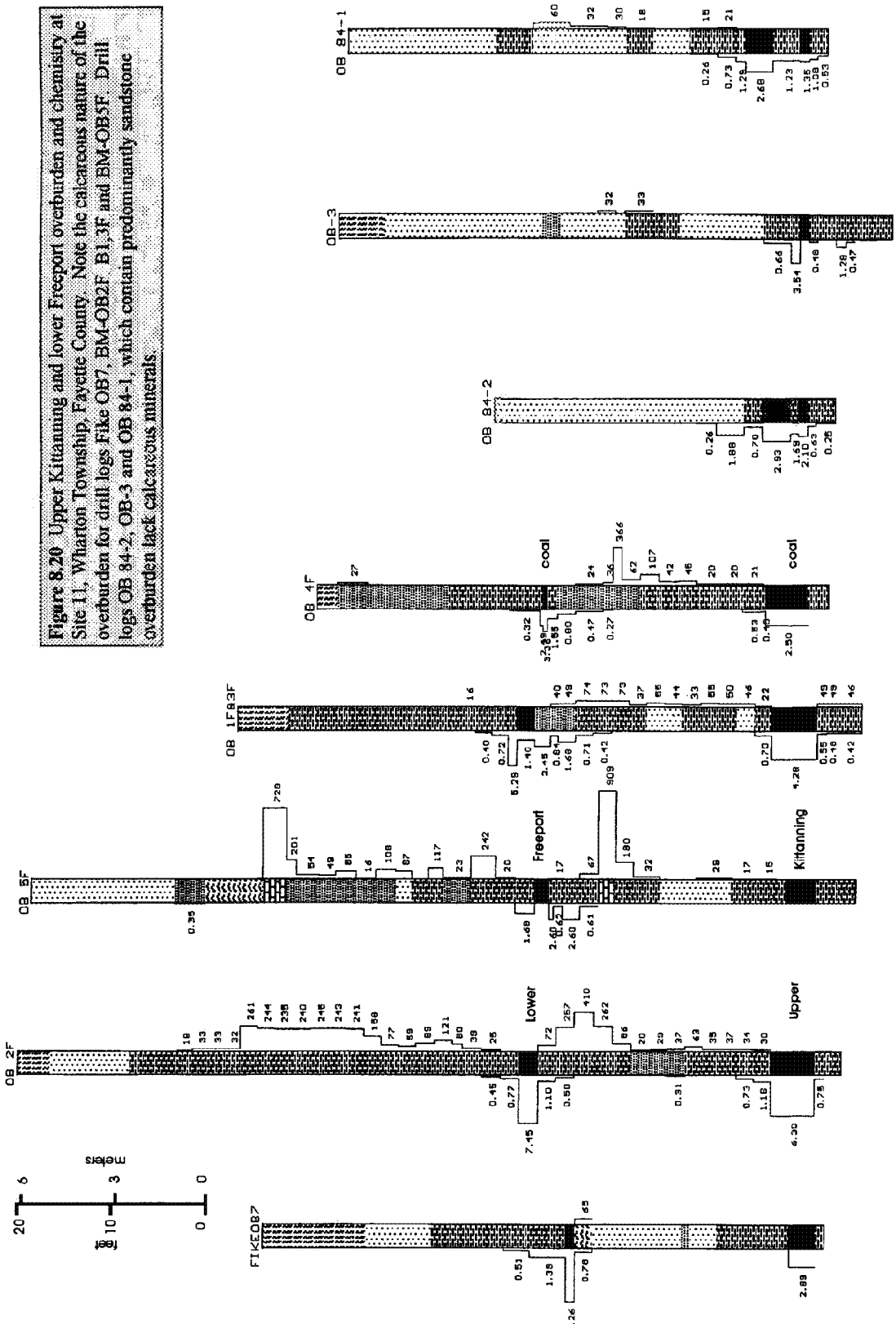


Figure 8.20 Upper Kittanning and lower Freeport overburden and chemistry at Site 11, Wharton Township, Fayette County. Note the calcareous nature of the overburden for drill logs Fike OB7, BM-OB2F B1,3F and BM-OB5F. Drill logs OB 84-2, OB-3 and OB 84-1, which contain predominantly sandstone overburden lack calcareous minerals.

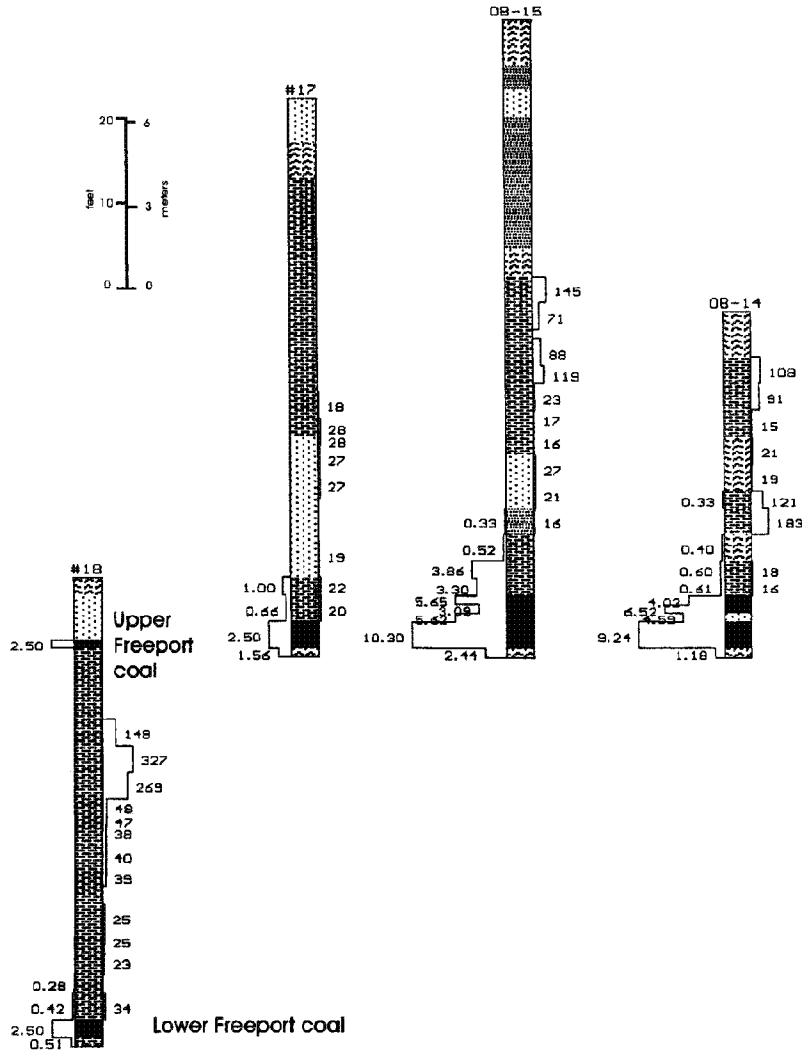


Figure 8.21 Lower and upper Freeport overburden and chemistry. Drill logs #17 and #18 are from Site 13 in Mt. Pleasant Township, Westmoreland County, and drill logs OB-15 and OB-14 are from site 14 in Clay Township, Butler County.

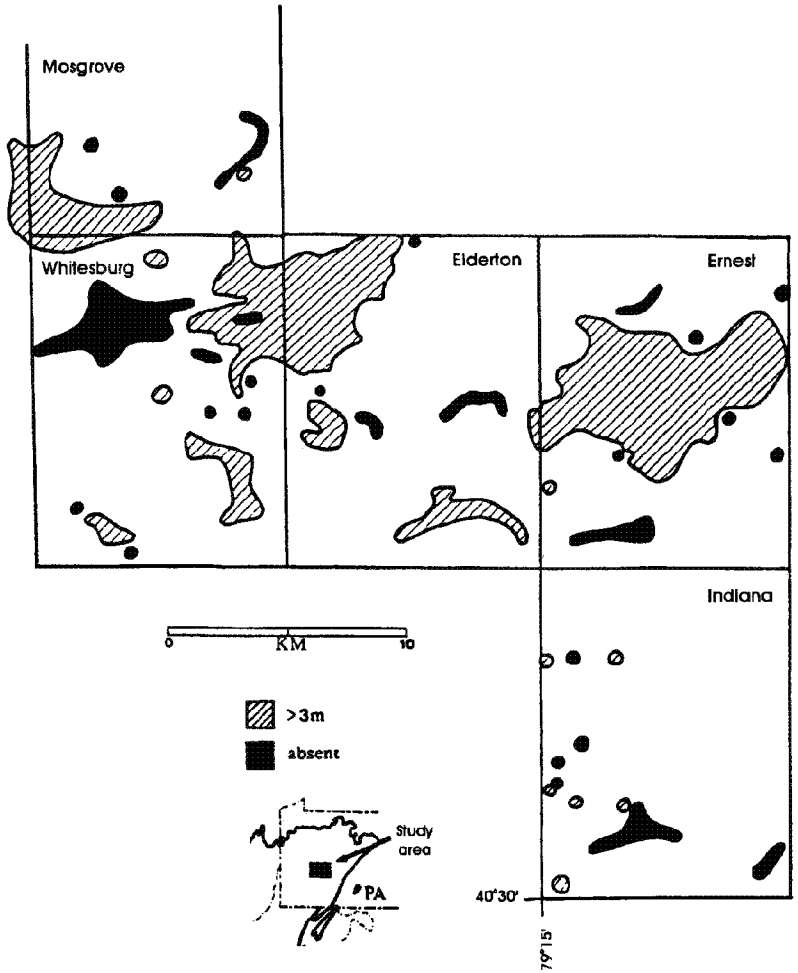


Figure 8.22 Isopach map of the limestone that occurs between the upper Freeport coal and the next lower coal. Areas of zero occurrence and greater than three meters are contoured. Areas with three meters or more of limestone were probably the deepest parts of the freshwater lake into which the limestone was deposited. Figure modified from Weedman (1989).

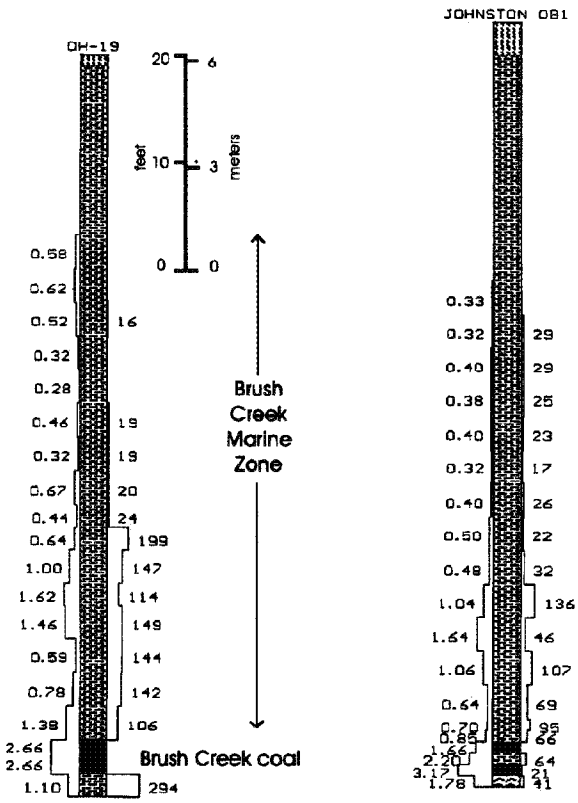


Figure 8.23 Brush Creek coal and overburden at Site 11 in Wharton Township, Fayette County. The overburden is of marine origin.

Casselman Formation - "The thickness of the Casselman Formation ranges from 230 feet (70 m) in the extreme western part of the Appalachian Plateaus province to 485 feet (148 m) in southern Somerset County" (Edmunds, et al., 1998, p. 156). With the exception of the marine shales above the Ames limestone, and the Skelly horizon, which occurs about 30 to 60 ft (9 to 18 m) above the Ames marine zone, the Casselman is made up of exclusively fresh water rocks. Redbeds, which are regionally discontinuous, are scattered throughout the Casselman in the western portion of Pennsylvania. "Eastward they become thinner and fewer in number. This trend continues into eastern Somerset and Cambria Counties, where large areas of the Casselman Formation are completely devoid of red beds. Conversely, coals are nearly absent or very thin in the west but increase in quantity eastward. In Somerset County, a few coals are thick enough to mine" (Edmunds, et al., 1998, p. 156).

Very little coal is mined in the Casselman Formation. Figure 8.25 shows overburden for the Wellersburg coal which is of mineable thickness only in the Wellersburg syncline of Somerset County (equivalent to the Georges Creek Field in Maryland). Although the overburden contains some strata with sulfur greater than 0.5 percent, the overburden is largely calcareous. Figure 8.26 displays chemical data for overburden above and below the Morantown coal, the uppermost coal in the Casselman. This coal is only mined in Somerset County. Shaulis (1993) feels the Morantown is actually a lower split of the Pittsburgh coal, which would place the coal in the Monongahela Group. One of the reasons cited for this stratigraphic placement is the presence of the freshwater limestone below the Morantown. This limestone occurs in OB-A in Figure 8.26 with an NP of 524. Whatever the stratigraphic position, the overburden in the two examples from Somerset County exhibits low sulfur and some neutralization capability. The Morantown, when it is present, is mined in conjunction with the Pittsburgh coal.

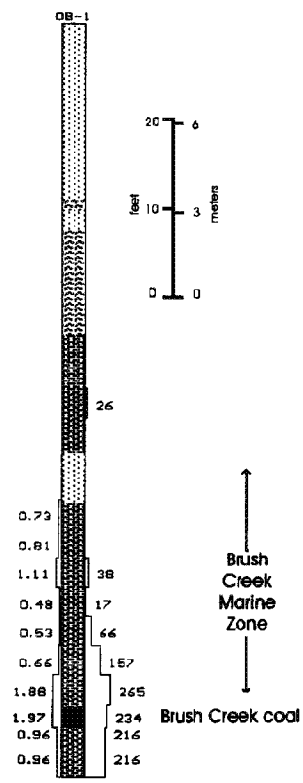


Figure 8.24 Brush Creek coal and overburden at Site 15 in Jackson Township, Cambria County. The overburden is of marine origin.

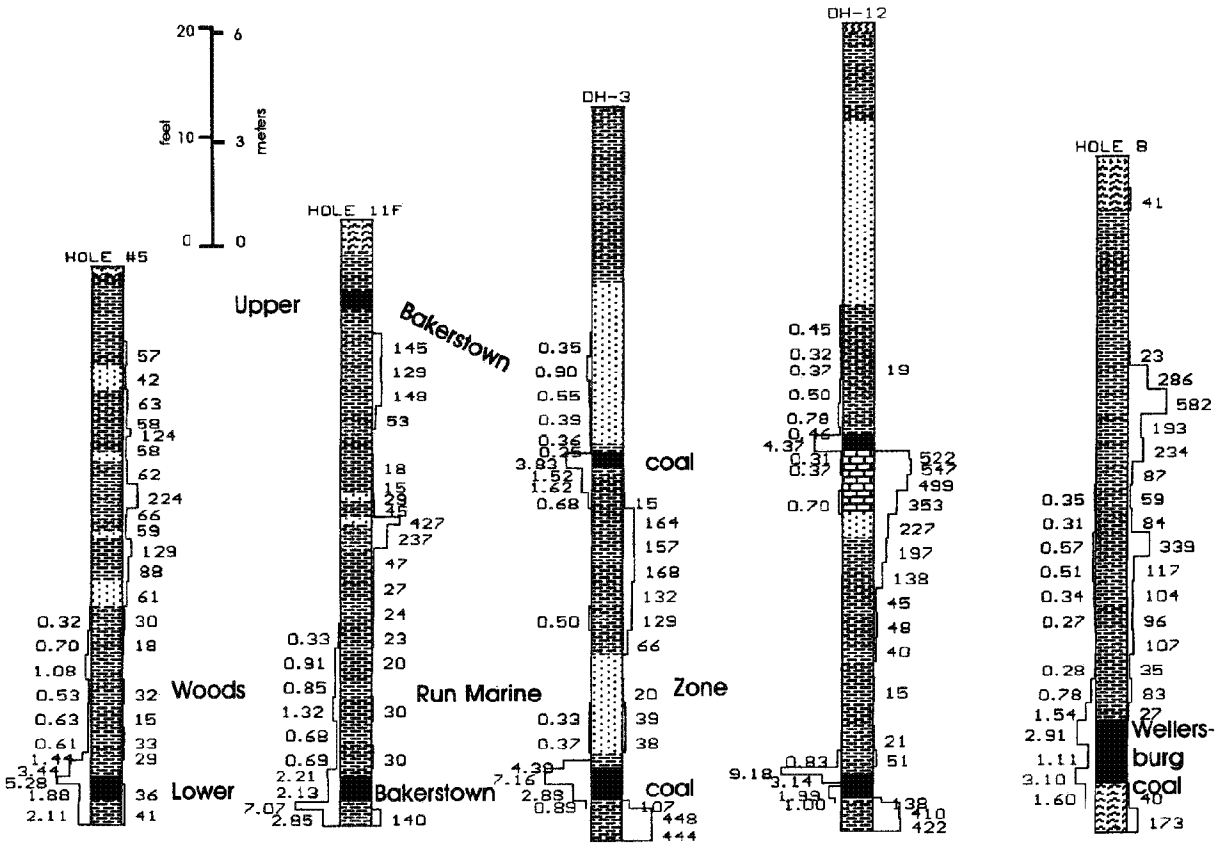


Figure 8.25 Upper and lower Bakerstown coals and Wellersburg coal overburden in Somerset County. Bakerstown coal Hole #5 and Hole 11F are at Site 16 in Brothersvalley Township, and DH-3 and DH-12 are at Site 17 is in Southampton Township. The Wellersburg coal Hole 8 is also from Site 17 in Southampton Township.

Monongahela Group

"The Monongahela Group extends from the base of the Pittsburgh coal to the base of the Waynesburg coal. It is divided into the Pittsburgh and Uniontown Formations at the base of the Uniontown coal. The group is about 270 to 400 feet (82 to 122 m) thick in Pennsylvania, increasing in thickness irregularly from the western edge of the state to western Fayette County....It is entirely nonmarine" (Edmunds, et al., 1998, p. 156).

The Monongahela Group is

"...dominated by limestones and dolomitic limestones, calcareous mudstones, shales, and thin-bedded siltstones and laminites... The only sandstone of significant thickness within the formation lies directly above the Pittsburgh coal complex. A major fluvial channel system, flowing north to northwest through what is now Greene and Washington Counties, deposited an elongate sandstone body up to 80 feet (24 m) thick and several miles (kms) wide" (Edmunds, et al., 1998, pp. 156-157).

This sandstone channel is shown in Figure 8.27. The mineable coals in the Monongahela Group are restricted to the lower portion of the group. The number of mine sites with overburden data for the Monongahela Group in the files of the Department of Environmental Protection are few in number. This is not because the Monongahela coals are rarely mined, it is because mining almost always produces alkaline drainage, and water quality from previous mining is used as the prediction tool.

Pittsburgh Formation - The lower half of the Pittsburgh Formation contains the majority of mineable coals in the Monongahela Group. The Pittsburgh coal,

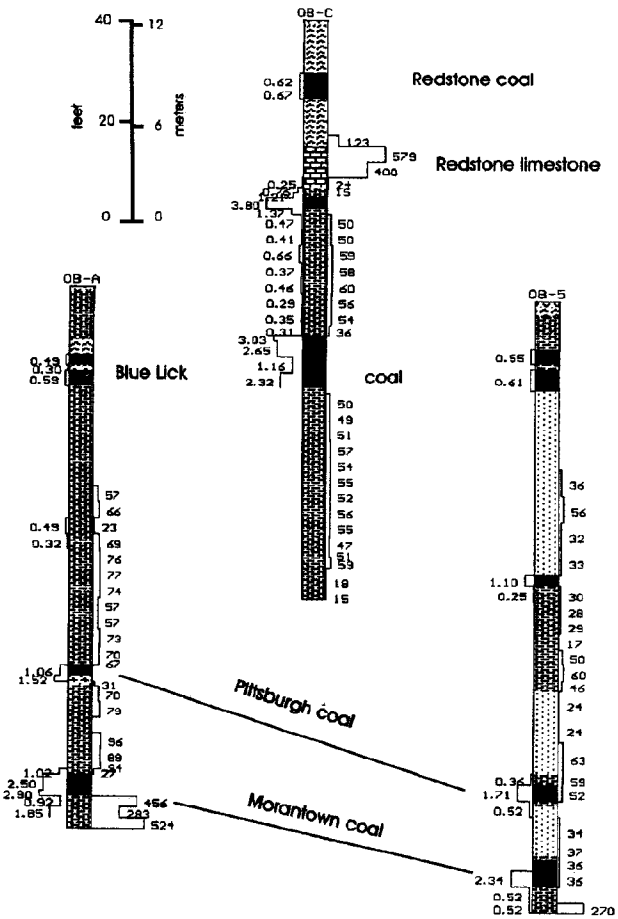


Figure 8.26 Overburden and chemistry of coal and rocks from the Morantown to the Redstone coals at Site 16 in Somerset County. This interval is considered to have been deposited entirely in a freshwater environment. Relationship to paleogeography at time of deposition of Pittsburgh overburden is shown on Figure 8.28.

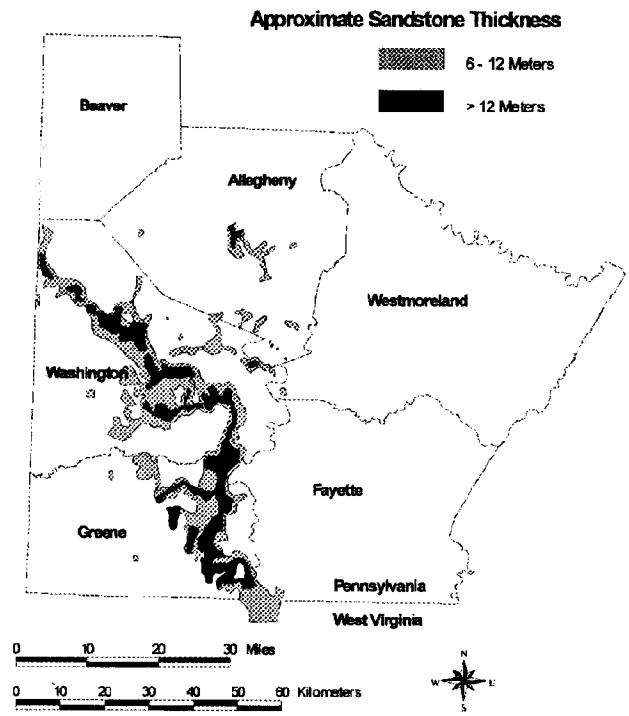


Figure 8.27 Location, geometry and isopach map of a sandstone channel above the Pittsburgh coal in Green and Washington Counties. Isopach map modified from Donaldson (1979).

which defines the base of the formation and group is unusually continuous, covering thousands of square miles (km^2) and is unusually thick (5 to 10 ft; 1.5 to 3 m) for a coal of western Pennsylvania. The other major coals are the Redstone and Sewickley. In Somerset County an additional coal, the Blue Lick, occurs between the Pittsburgh and Redstone coals. Shaulis (1993) believes the Blue Lick coal is a split of the Pittsburgh coal.

Pittsburgh Coal to Redstone Coal Interval - Pittsburgh coal overburden varies from sandstone to limestone to shale. Figure 8.28 is a reconstruction of paleodepositional environments during the time of deposition of the Pittsburgh coal overburden.

Sandstone was deposited in the distributary channel running through the southwestern corner of Pennsylvania. An isopach map of the thickness of this channel is shown in Figure 8.27. Limestone or shale was deposited in the lakes and on the mud flats. Some examples of the distribution of Pittsburgh Formation limestones in Greene County, PA and northern West Virginia, are illustrated by Figure 8.29, Figure 8.30, and Figure 8.33. Figure 8.29 is an isopach map of the Redstone limestone. Figure 8.30 is a cross-section of the Pittsburgh/Redstone interval. This cross-section is oriented east-west and approximately parallels the Pennsylvania-West Virginia border shown on Figure 8.29. The Redstone limestone is "patchy", which may simply be due to variable carbonate content of the lake-deposited sediments. The intervening shales may be a lateral, less calcareous, facies of the freshwater limestone. The drill logs shown in Figure 8.31 are from an area east of the major channel shown in Figure 8.27 (isopach map of Pittsburgh sandstone), but they show the nature of the Pittsburgh overburden when it is sandstone. It is characterized by some high sulfur strata, especially the shale portions of OB-2, and some calcareous zones within the sandstone (e.g., the zone in

OB-1 with a NP of 115 ppt, and the zone in OB-2 with a NP of 122 to 169 ppt). The overburden in Somerset County (Figure 8.26) is shale in holes OB-A and OB-C, and a mixture of sandstone and shale in OB-5. The overburden is slightly calcareous with NP's commonly in the range of 30 to 70 ppt. This is true whether the overburden is sandstone or shale. The overburden from the Somerset County sites is lower sulfur than that in Westmoreland County. Pittsburgh coal mines can produce acid and alkaline water (see Table 8.2).

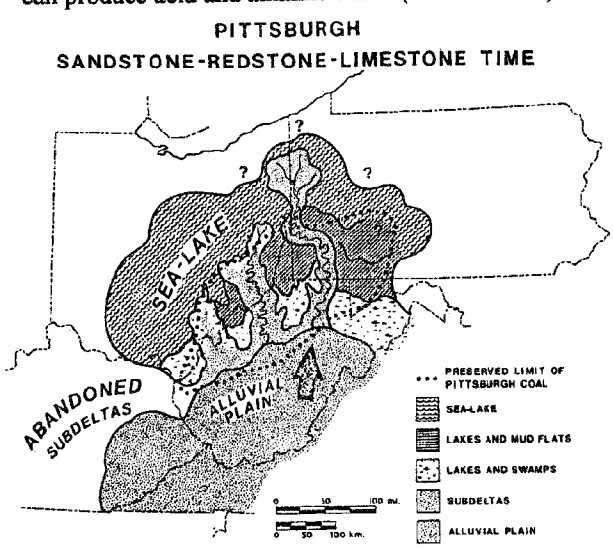


Figure 8.28 Paleogeographic reconstruction of the Pittsburgh sandstone and Redstone limestone time. The river in the southwestern corner of Pennsylvania is the sandstone channel shown in Figure 8.27. The Redstone limestone was deposited in freshwater lakes (see Figure 8.29). The shale overburden above the Pittsburgh coal shown in Figure 8.26 would have been deposited on "mudflats." From Donaldson and Shumaker (1979).

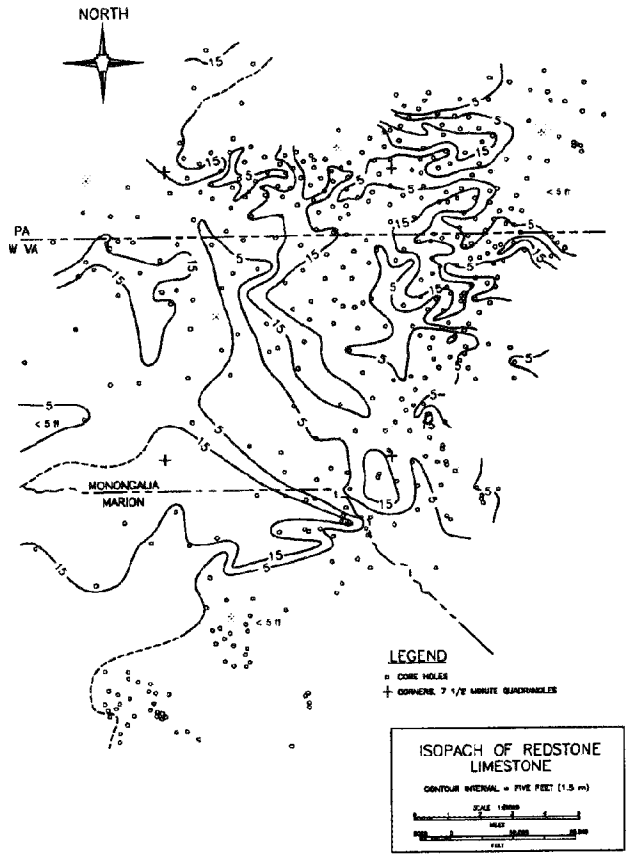


Figure 8.29 Isopach map of Redstone limestone in southern Pennsylvania and northern West Virginia. From Linger (1979).

Blue Lick Coal to Sewickley Coal Overburden - The Pittsburgh coal often has a rider coal positioned approximately 5 to 50 ft (1.5 to 16 m) above it. This rider coal is usually thin and not economically significant. However, in Somerset County the coal at this stratigraphic horizon, named the Blue Lick, attains mineable thickness. The Blue Lick coal is usually overlain by calcareous units and produces alkaline drainage. Blue Lick coal overburden NP values are shown in OB-C, Figure 8.26. OB-C shows only a small amount of strata with sulfur greater than 0.5 percent. There is a zone of calcareous rock, including limestone, above the Blue Lick rider coal.

The Redstone/Sewickley interval is shown in Figure 8.32. This zone contains strata with sulfur greater than 0.5 percent, however, abundant limestone and other calcareous rocks are present. Although limestone occurs above the Sewickley in OB-3, this log is not typical of overburden further west in Pennsylvania. To the west this interval is typically occupied by a very thick limestone, known as the Benwood. The Benwood is the thickest limestone in the Monongahela Group and can be 60 or 70 ft (18 to 21 m) thick. Figure 8.33 is a facies map showing the Benwood interval at 55 feet (16.8 m) above the Sewickly coal.

Pittsburgh Formation Limestones - Figure 8.33 illustrates the lateral persistence that many Monongahela lacustrine limestones exhibit. The lakes in which these laterally extensive limestones were deposited had to have been very large. For example the Benwood limestone above the Sewickley coal covers more than 4,000 square miles (10,000 km^2) (Berryhill, et al.,), and Eggleston (1993) notes that the Redstone limestone

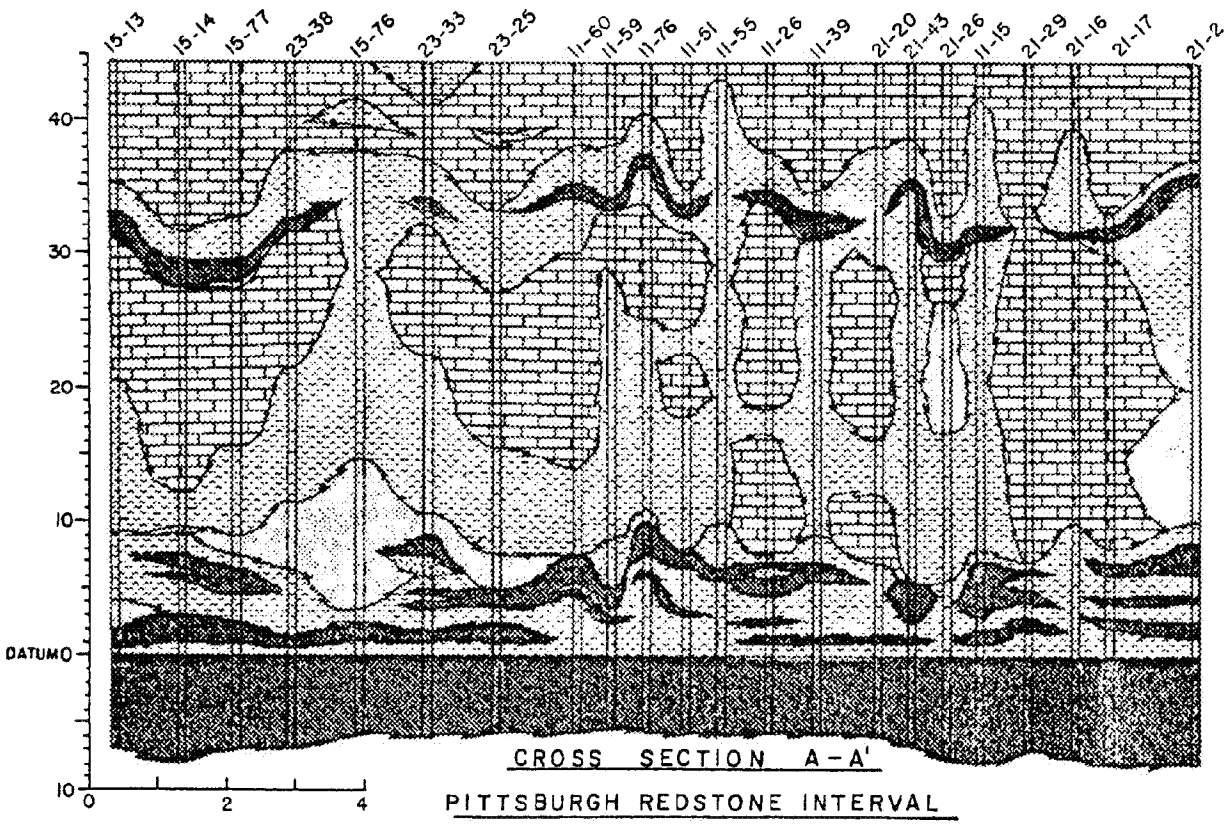


Figure 8.30 Cross-section of the Pittsburgh-Redstone coal interval oriented east-west near the Pennsylvania/West Virginia border shown on Figure 8.29. Vertical exaggeration is approximately 1000 times the horizontal. From Linger (1979)

extends from Somerset County, PA to as far south as Cabell County, WV, and as far west as Morgan County, OH. Figure 8.32 illustrates the NP for the Redstone and Fishpot limestones, and an unnamed limestone above the Sewickley coal. The highest NP for the Fishpot in OB-3 is 735 ppt.

Eggleston (1993) concludes that the Redstone limestone was deposited in a "very shallow lake that was subject to periodic subaerial exposure during drier periods." As evidence of drying she refers to desiccation breccia, root traces, and lack of original bedding. Evidence of shallow depositional conditions include rounded intraclasts, broken and nested shells, and bioturbated limestone. Berryhill et al. (1971) arrived at similar conclusions, using similar evidence, concerning the depositional environment of other limestones in the Monongahela and Dunkard Groups. Berryhill et al. suggest that the limestones were deposited in shallow lakes, where water depth "probably never exceeded a few feet" and that "(n)either fossil evidence nor physical properties of the rocks indicates any influence of marine conditions" (Berryhill et al., 1971, p. 34). In addition to the limestones, the sandstones and shales of the Monongahela Group are also often calcareous (Figure 8.2). The environmental interpretations of Eggleston (1993) are consistent with the paleoclimatic interpretations of Cecil et al. (1985) and Donaldson et al. (1985) for this stratigraphic interval.

Berryhill et al. (1971, p. 16) found that of 50 limestone samples from the Monongahela and Dunkard Groups, 34 were classified as limestone or magnesium limestone (< 10% dolomite, > 90% calcite), 13 were dolomitic limestone (10% to 50% dolomite, remainder being calcite) and three were calcitic dolomite (50% to 90% dolomite). The clay content is generally greater than 10%, thus the limestones are classified as marly. The ratio of calcium to magnesium varies both from bed to bed and also vertically and laterally within a single bed.

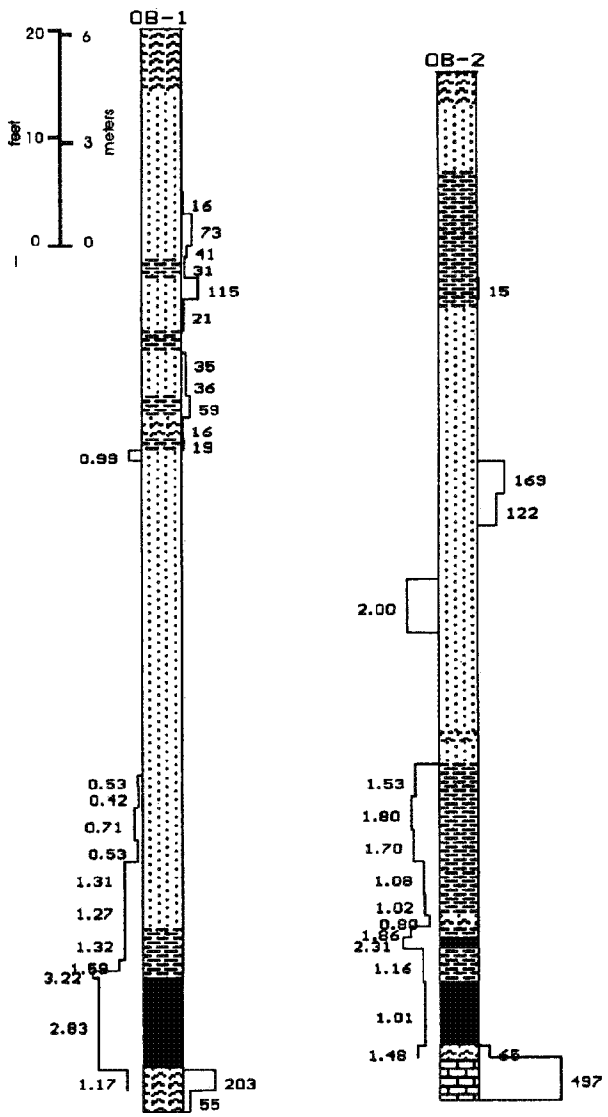


Figure 8.31 Logs and chemistry of Pittsburgh overburden at Site 19 in Salem Township, Westmoreland County. Relationship with paleogeography is shown on Figure 8.28.

Dunkard Group

The Dunkard Group is found only in the most southwestern corner of Pennsylvania in Greene and Washington Counties. It is made up of Waynesburg, Washington and Greene Formations (Berryhill et al., 1971). The Dunkard reaches a maximum thickness of about 1120 ft (340 m) in Greene County and the upper surface is the modern day erosional surface. The lower boundary of the Dunkard Group is defined as the base of the Waynesburg coal, which is the only coal routinely mined in the Dunkard.

The Dunkard is generally composed of fine-grained clastics which are frequently calcareous. Thick lacustrine limestones are especially prevalent in the Washington Formation. The only significant interval with sandstone is above the Waynesburg coal (Figure 8.2). This sandstone is often, but not always, calcareous. The Dunkard Group data represented in Figure 8.2 is all from Greene County. A comparison of this data with the study by Berryhill et al. (1971) for Washington County shows some differences in abundance of lithologies. For example Berryhill et al. show that 33% of the Group is limestone, whereas this study found only 6.2% limestone. This is probably largely attributable to a facies change between Washington and Greene Counties. Skema (personal communication, 1997) reports that the Upper Washington and Lower Washington Limestones, which are thick in Washington County are barely present in Greene County.

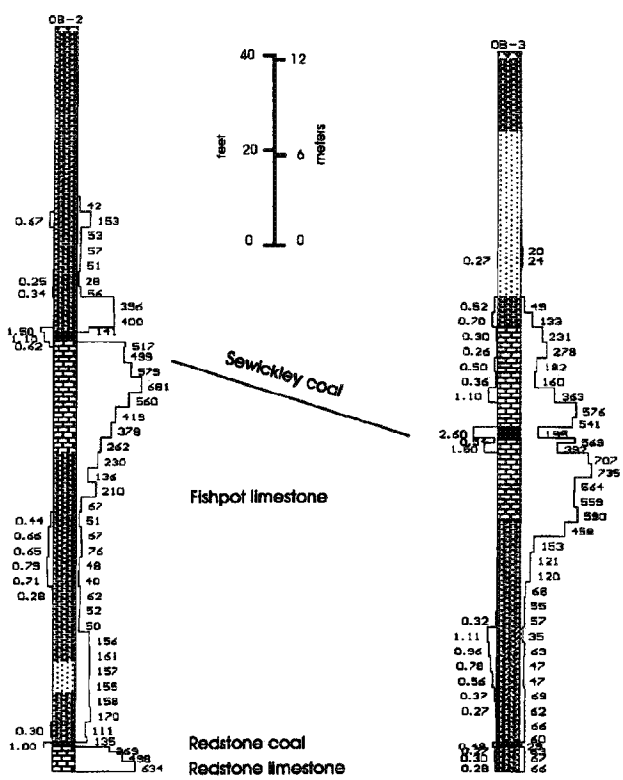


Figure 8.32 Overburden and chemistry of the Redstone and Sewickley interval at Site 18 in Elklick and Summit Townships, Somerset County. Note the presence of freshwater limestones and abundant calcareous shales.

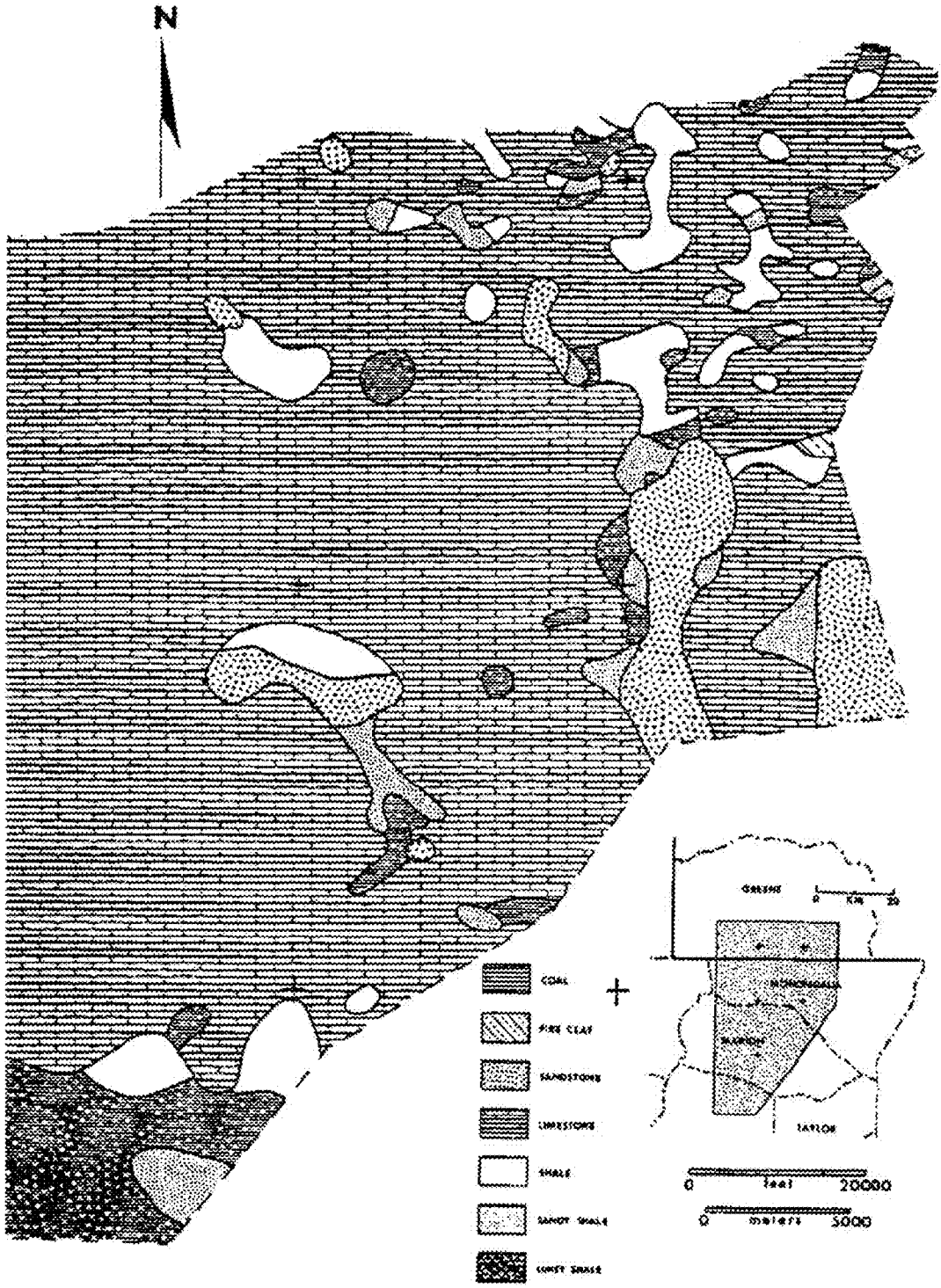


Figure 8.33 Facies map 55 ft (17 m) above the Sewickley coal (Benwood limestone horizon). At this interval the limestone is predominant. Although not indicated as such (with the exception of "limey shale"), the other facies are probably calcareous. The area shown is in northern West Virginia and southwestern Pennsylvania. From Linger (1979).

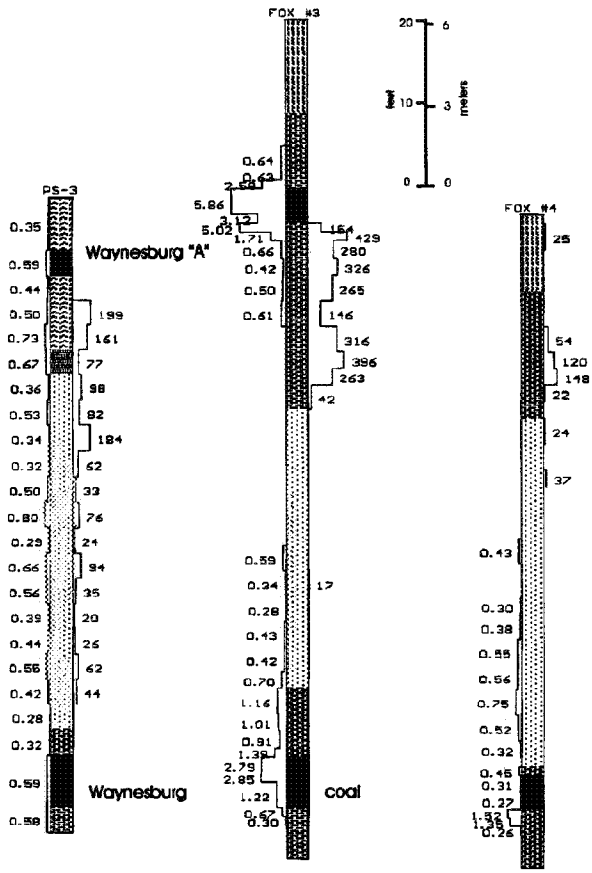


Figure 8.34 Overburden and chemistry of the Waynesburg and Waynesburg 'A' coals at Site 20 in Greene Township, Greene County. Note the variability in NPI within the sandstone.

As mentioned, the only coal routinely mined in the Dunkard is the Waynesburg. For purposes of this study the Waynesburg Formation has been divided into upper and lower members. This is because in recent years mining has generally been restricted to only the Waynesburg, thus not disturbing strata above the Waynesburg 'A' coal. Also, the Waynesburg overburden is lithologically different. As shown in Figure 8.2, much of the Waynesburg overburden is sandstone, and much of this sandstone is calcareous. The Waynesburg 'A' and its overburden are notorious for producing poor quality water. Figure 8.34 shows the Waynesburg coal overburden. The shale above the coal can be high sulfur as illustrated in drill hole Fox #3. The three drill logs in Figure 8.34 illustrate the variability in overburden chemistry for this unit. Of the three holes, the sandstone is only calcareous in PS-3. The finer-grained calcareous zones, near the tops of drill holes Fox #3 and Fox #4, would not be encountered unless more than 50 or 60 ft (15 or 20 m) of cover is mined. Where the sandstone is calcareous, mines produce alkaline drainage, where it is not calcareous mining results in acid mine drainage.

Pennsylvanian Stratigraphy of Pennsylvania's Anthracite Region

The stratigraphy of the anthracite region of eastern Pennsylvania has not been studied as extensively as that of Pennsylvania's bituminous coal region. Geologic and mining engineering work done in the anthracite region over the past 150 years, however, documents some significant stratigraphic differences between the anthracite and bituminous coal regions. The anthracite region is comprised of four coal fields as shown on Figure 8.4: The Northern Field, the Eastern Middle Field, the Western Middle Field, and the Southern Anthracite Field.

The four anthracite coal fields are located within the Valley and Ridge Physiographic Province and the orogenic activity in this province since the Pennsylvanian Period has resulted in: (a) the increase in rank of the coals due to metamorphism (as compared to time-equivalent coal beds in the Appalachian/Allegheny Plateau Province of the bituminous region), and (b) the preservation of the anthracite coal fields within synclinal basins which are essentially surrounded by sandstone/conglomerate ridges that are more resistant to erosion than the coal and associated finer-grained sedimentary rocks. A comprehensive description of the geologic history of the north-central Appalachians, is contained in Faill (1997a, 1997b, 1998a, 1998b). The most recent orogenic episode, the Alleghenian, commenced in the Early Permian (Faill, 1997b). Faill (1997a, p. 552) states that "(l)ate in the Allegheny orogeny, rock thrust northward over the Carboniferous rocks in the Anthracite region of northeastern Pennsylvania caused anthracitization of the underlying coals."

Much of the Southern and Western Middle Fields has been geologically mapped by Wood and associates (e.g., the Minersville Quadrangle, Wood, et al., 1968, and related cross sections). The maps depict the synclinoria and other complex geologic structures. The geologic structure and stratigraphy of the Southern Anthracite Field are described in Wood et al. (1969) and the depositional and structural history of the entire Anthracite Region are presented in Wood et al. (1986). The complexity of the geologic structure, resulting in nearly vertical beds of coal and other rocks in some areas of the anthracite fields, has impeded the acquisition

of stratigraphic data from routine exploration drilling. Detailed mine maps of the abandoned underground mines and cross-sections through vertical shafts and nearly horizontal tunnels have added to the understanding of the structure and stratigraphy of the anthracite coal fields, however most stratigraphic efforts have been directed toward coal seam delineation.

The Pennsylvanian age rocks of the anthracite region of Pennsylvania have been divided into two major formations, the Pottsville and the Llewellyn. Generalized columnar sections of the Pottsville and Llewellyn Formations are shown on Figure 8.35.

Pottsville Formation

The Pottsville Formation ranges in thickness from a maximum of approximately 1600 ft (490 m) in the Southern Field to less than 100 ft (30 m) in the Northern Field. The Tumbling Run and Schuylkill Members of the Formation are not present in the Northern Anthracite Field (Wood et al., 1969, 1986; Meckel, 1967, 1970; and Edmunds et al. 1979, 1998).

The Pottsville Formation contains up to 14 coal beds in some areas, but most are relatively discontinuous and only a few persist outside of the Southern Field (Edmunds et al. 1998). Figure 8.35 shows the mineable coals of the Pottsville Formation. The Lykens Valley Coal Numbers 4 through 7 are within the Tumbling Run Member; the Lykens Valley Coal Numbers 1 through 3 are within the Schuylkill Member; and the Scotty Steel and Little Buck Mountain Coals are within the Sharp Mountain Member of the Pottsville Formation (Figure 8.35). The base of the Buck Mountain Coal is considered the top of the Pottsville Formation in eastern Pennsylvania; however, the Buck Mountain coal is generally correlated with the lower Kittanning Coal within the lower Allegheny Group in western Pennsylvania (see Edmunds et al., 1998). The type section of the Pottsville Formation (located near Pottsville) is described by C.D. White (1900) and more recently by Wood et al. (1956) and Levine and Slingerland (1987).

The Pottsville Formation in eastern Pennsylvania is entirely of a nonmarine depositional environment (Edmunds et al., 1998). As in western Pennsylvania, the dominant lithology of the Pottsville Group is sandstone and conglomerate; but the Pottsville Formation of the Anthracite region contains significant pebble conglomerates derived from an orogenic source area to the southeast (Meckel, 1967, 1970; Edmunds et al. 1998; and Faill, 1997b). The Tumbling Run Member is composed of approximately 55% conglomerate and conglomeratic sandstone, about 30% fine- to coarse-grained sandstone, and about 15% shale and siltstone. Conglomerate and conglomeratic sandstone comprise about 50% of the Schuylkill Member, and the sandstone in the member ranges from very fine to very coarse, constituting approximately 30% of the member. The Sharp Mountain Member in most of the Southern Anthracite Field is composed of about 45% conglomerate, 25% conglomeratic sandstone, 15% sandstone, 5% siltstone, 9.5% shale, and 0.5% anthracite (Wood et al. 1969, 1986). The carbonate content of the rocks has not been determined.

Llewellyn Formation

The Llewellyn Formation is as much as 3500 feet (1050 m) thick. The maximum known thickness of the Pennsylvanian in Pennsylvania is approximately 4400 ft (1340 m) near the town of Llewellyn in Schuylkill County (Edmunds et al., 1998). The Llewellyn Formation contains up to 40 mineable coals (Edmunds et al., 1998), most of which are shown on Figure 8.35. The thickest and most persistent coals occur in the lower part of the Llewellyn Formation, particularly the Mammoth coal zone. The Mammoth coal zone typically contains 20 ft (6 m) of coal and thicknesses of 40 ft to 60 ft (12 to 18 m) are not unusual. A local thickness of greater than 125 ft (38 m) has been reported in the Western Middle Field. This was attributed to structural thickening in the trough of the syncline. The nomenclature and stratigraphy of the coal bearing rocks of the Llewellyn Formation in the Northern Anthracite Field are different than in the Southern and Middle Fields (Figure 8.35).

The dominant lithology of the Llewellyn Formation is sandstone, including conglomerate units, as in the Pottsville Formation. According to Edmunds et al. (1998, p. 159): "Lithologically, the Llewellyn is a complex, heterogeneous sequence of subgraywacke clastics, ranging from conglomerate to clay shale and containing numerous coal beds. Conglomerates and sandstones dominate". The Llewellyn Formation in the Southern and Middle Fields is believed to be entirely continental in depositional environment (i.e., lacking any marine beds). The Llewellyn Formation in the Northern Field, however, contains one known marine bed, the Mill Creek Limestone (Figure 8.35). I.C. White (1903) suggested that the Mill Creek was correlative with the Ames limestone of western Pennsylvania. This belief is generally held to the present. The

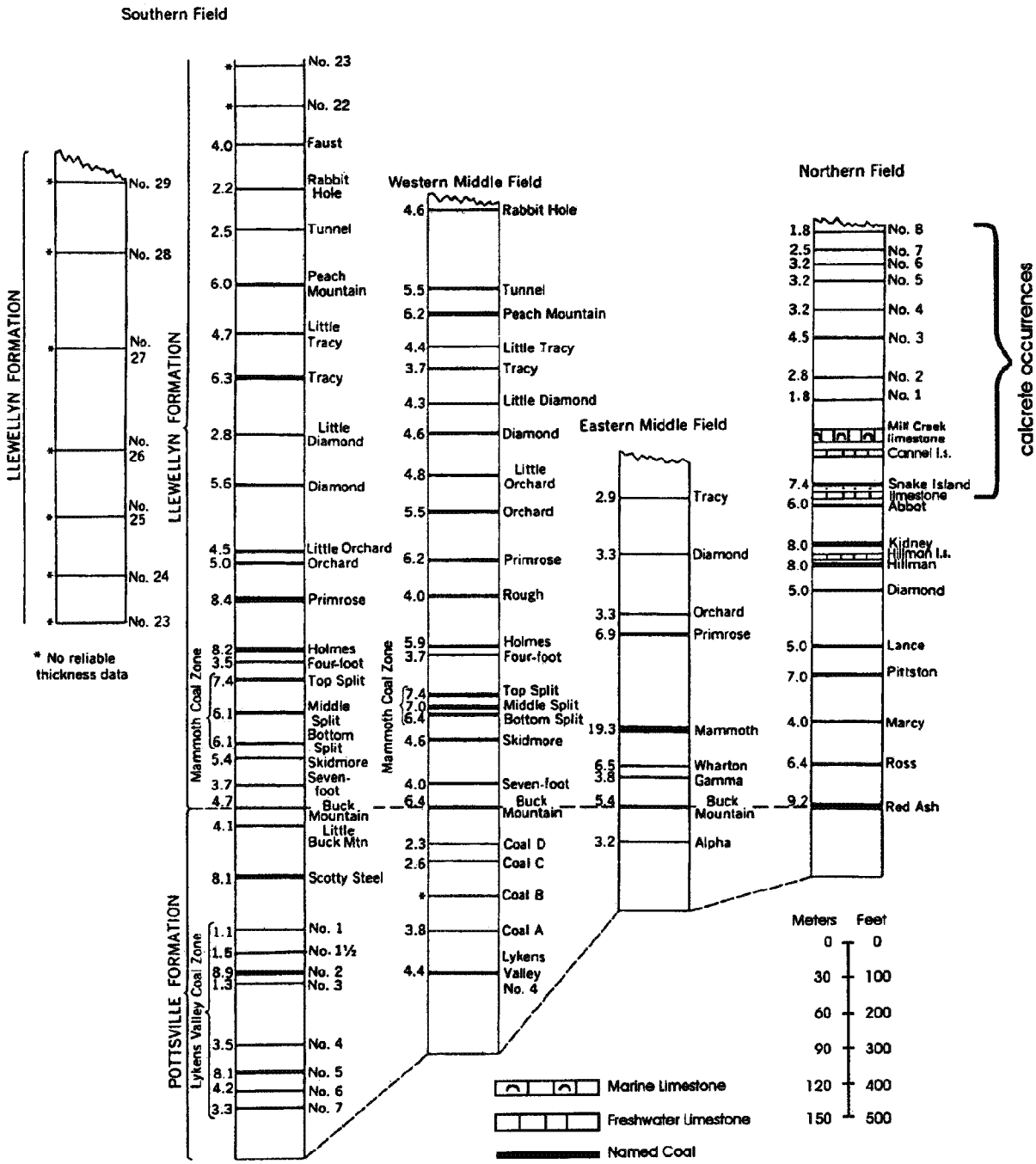


Figure 8.35 Generalized columnar sections showing names, average thickness of coals (in ft), and intervals between coal beds in the Pennsylvania Anthracite fields. Figure is primarily from Wood et al. (1986). Information on calcareous zones in the Northern Field has been supplemented by data from Edmunds et al. (1998) and Inners and Fabiny (1997).

Mill Creek Limestone is a one- to three-ft (0.3 m to 1 m), richly fossiliferous marine limestone (Chow, 1951). The Llewellyn Formation contains several other nonmarine limestones in the Northern Field including the Cannal and Hillman limestones (Chow, 1951, and Edmunds et al., 1998). Additionally, Inners and Fabiny (1997) have identified calcareous paleosols ("calcrete") in the uppermost Llewellyn Formation in the Northern Field. They have tentatively correlated this portion of the stratigraphy with the Conemaugh of western Pennsylvania. The calcretes are indicative of "seasonally semi-arid conditions" (Inners and Fabiny, 1997, p. 85). The calcretes are often associated with siderite. Kochanov (1997) has found calcareous sandstones in the lower part of the Llewellyn in the Northern Field. Siderite nodules are also common in the lower Llewellyn (Kochanov, 1997, personal communication).

The identification and mapping of limestone and other calcareous rocks in the Southern and Middle Fields have not been reported in the literature; however, some large mine pool discharges such as the Wadesville Colliery (see Table 8.14), have alkalinity of several hundred milligrams per liter, which must be attributed to some carbonate minerals in the overburden. Discharges in the Eastern Middle Field have little if any alkalinity (see Table 8.14). This strongly suggests a lack of calcareous rock in this coal field. Study of carbonate minerals and identification of calcareous lithologic units in the Southern and Middle Fields is needed.

Pleistocene Sediments

Based on permits issued by the Department of Environmental Protection in glaciated regions in northwestern Pennsylvania, glacial sediments are most likely to be encountered where mining of the Brookville/Clarion, lower Kittanning and middle Kittanning coals takes place. These sediments affect mine water quality because they contain calcareous clasts. Lower Freeport permits have also been issued in glaciated regions. For Clarion/Brookville coal mines, it can be difficult to assess the impact of glacial sediments on postmining water quality because the Vanport limestone is often part of the overburden. Figure 8.36 shows the area of overlap of glacial sediments, Vanport limestone, and coal areas. The Vanport limestone becomes thinner and more discontinuous near its northern limit.

Glacial overburden in surface coal mines can exert a different influence on mine drainage quality than does bedrock. The texture, composition (mineralogy), and structure of glacial overburden differs from that of bedrock. Much information on the glacial geology and sediment composition exists for northwestern Pennsylvania.

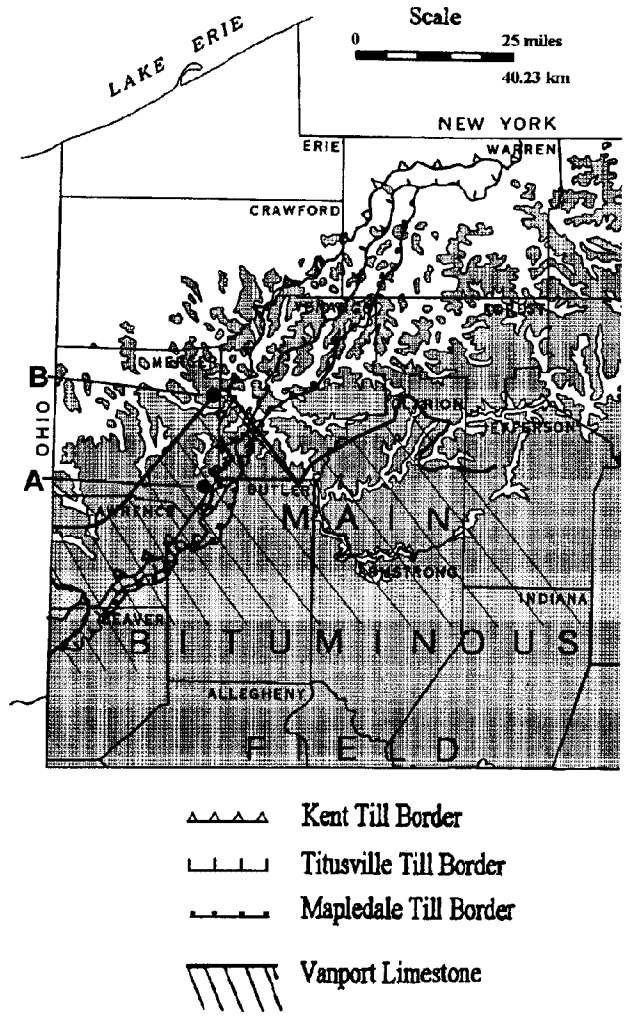


Figure 8.36 Map showing the locations of glacial borders, Vanport limestone, and Pennsylvanian Period rocks and location of sites with glacial overburden that are discussed in the text.

Because of a lack of carbonate source rock, glacial sediments in northeastern Pennsylvania are typically low in carbonate. The only exception is in an area near the Delaware River, east of the anthracite fields (William D. Sevon, personal communication, 1994; Epstein, 1969). Several overburden holes have encountered till in the semi-anthracite Bernice Basin,

Sullivan County. The till ranges in thickness from 0 ft (m) to 32 ft (9.8 m). The highest NP and sulfur (out of 32 samples) was 3 ppt $CaCO_3$ and 0.04 percent respectively, i.e., negligible. There are no overburden analyses of glacial sediments in the anthracite coal fields. Duane Braun (Bloomsburg University, personal communication, November 18, 1997) has done field work in the northern Field and has not observed any till reacting visibly to HCl. Available data suggests that glacial sediments are generally not a source of NP in northeastern Pennsylvania. Therefore, glacial sediments in northeastern Pennsylvania will not be discussed further.

Northwestern Pennsylvania has been glaciated a number of times during the Pleistocene. At least 8 tills have been identified on the Appalachian Plateau of northwestern Pennsylvania (White and others, 1969) and northeastern Ohio (White, 1982) (Table 8.3). The glaciations range in age from pre-Illinoian (> 500,000 ya) to late Wisconsinan (about 15,000 ya). Generally, each advance was less extensive than the previous. The last glacier to advance into Pennsylvania, the Ashtabula advance, stopped at the northwestern edge of the Appalachian Plateau, just south of Lake Erie. The Titusville glaciation deposited the bulk of the glacial sediment in northwestern Pennsylvania. Stacking of multiple Titusville sheets makes up the bulk of the main end moraine, the Kent Moraine (White and others, 1969; White, 1982).

Table 8.3 Pleistocene tills, from youngest to oldest and carbonate content in the clay fraction of those tills in northwestern Pennsylvania. Data from White and others (1969) and White (1982).

Till	Carbonate Content
Ashtabula	Calcareous. Oxidizes dark brown
Hiram	Total carbonate up to 17%
Lavery	Total carbonate > 10%
Kent	Calcite = 1.4% Dolomite = 1.8%
Titusville	Calcite = 1.1% Dolomite = 1.3%
Keefus (NE Ohio)	Not quantified, but highly calcareous
Mapledale	Calcite = 0.7% Dolomite = 0.6%
Slippery Rock	Unknown - all samples weathered and leached

Individual tills in northwestern Pennsylvania are generally only a few feet (~1 m) to a few tens of feet (10s of m) thick, but can be over 100 feet (30 m) thick (White, 1982). Multiple tills of different composition may be encountered in the overburden during mining. White et al. (1969) show this for the Ambrosia mine near Grove City, PA (Figure 8.37). The Mapledale, Titusville, Keefer and Kent tills are present. The upper portion of the Mapledale and Titusville tills are leached of carbonates, where the unweathered portions contain

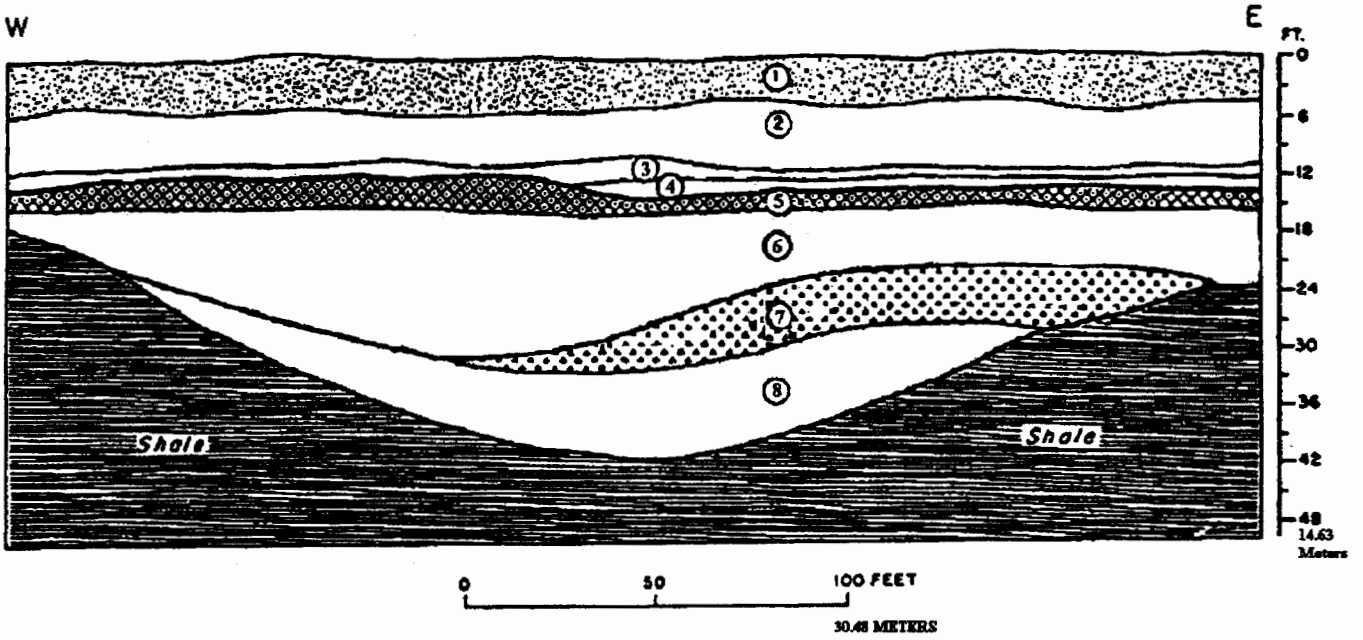


Figure 8.37 Sketch of overburden in Ambrosia strip mine near Grove City. 1. Soil in till and colluvium, noncalcareous. 2. Kent Till, calcareous. 3. Kent Till, calcareous. 4. Sand, calcareous. 5. Keefus Till, calcareous. 6. Titusville Till, noncalcareous. 7. Titusville Till, calcareous. 8. Titusville Till, calcareous. 10. Mapledale Till, noncalcareous. 11. Mapledale Till, noncalcareous. 12. Mapledale Till, slightly calcareous. Site is located at "A" on Figure 8.36.

calcareous minerals. Figure 8.38 shows the variable carbonate contents of tills in mines near the Ambrosia site.

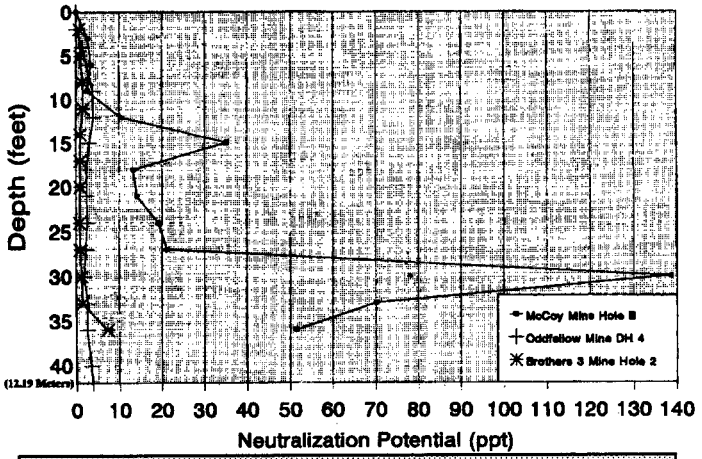


Figure 8.38 Distribution of neutralization potential for glacial overburden from mine sites southeast of Grove City. Sites are located at "A" on Figure 8.36.

Geochemistry of Glacial Sediments

The compositions of sediments from different glaciations are determined by the source materials eroded by the glacier and incorporated into the sediments. Glaciers advancing into northwestern Pennsylvania advanced from the Lake Erie basin. The bedrock in the basin, which was the source for the glacial sediments, consists of a large amount of limestone and dolomite. Therefore, the sediment contained in the glaciers was high in carbonate minerals (calcite and dolomite) when it entered Pennsylvania. Early glaciers advanced far to the south of the Lake Erie basin over a surface of weathered siliceous bedrock and soil, resulting in dilution of the carbonate rich sediment by carbonate poor sediment. The resulting glacial deposits are relatively low in carbonate. Later glaciers advanced less far out of the Lake Erie basin over unweathered bedrock (the weathered horizons having been removed by previous glaciations), and over previously deposited glacial sediments. These glacial sediments were diluted less by the siliceous bedrock south of the Erie basin and are relatively high in carbonate, more characteristic of the source limestone and dolomite rocks in the Lake Erie basin (White, 1982).

Till in the coal fields, near the glacial margins, is probably lower in carbonate content than the average for that till. Because of the difference in source materials for succeeding glaciations, carbonate content generally increases from older tills to younger tills (White et al., 1969) (Table 8.3).

The Mapledale Till is the only till that has such a low carbonate content that unweathered till will not act visibly with dilute hydrochloric acid. It is completely leached of carbonates in the clay fraction in : outcrop area (Gross, 1967). Unfortunately, from a surface mining standpoint, only the older glaciations mainly the Mapledale, Titusville, and Kent, advanc far enough to reach the coal fields of Pennsylvania. The higher carbonate tills (Ashtabula, Hiram) occu mainly in Crawford and Erie Counties (Figure 8.36) Although the Kent and Titusville Tills, in addition t the Mapledale Till, occur beyond the Kent Moraine, little neutralization benefit will be realized from gla sediments beyond the Kent Moraine because they a all thin, discontinuous, and weathered. Fortunately, overburden data suggests that the amount of iron su fide in glacial sediments is negligible (Figure 8.39), thus enabling the till to contribute a generally net pc tive influence on mine water quality. The highest su fur in any of the tills is 0.38% in OB 3-Spag. All o till samples had less than 0.25% sulfur.

By comparison, in the Illinois Basin, most of the coal field is within the glaciated region and the bulk of the tills have carbonate contents greater than 10% in the clay fraction, and up to 64% in the coarse sand fraction (Fleeger, 1980), similar to the Pennsylvania tills near Lake Erie. The presence of glacial deposits is much more significant to the coal mining industry for the prevention of AMD in Illinois than in Pennsylvania. Although coal and associated strata in the Illinois Basin are high sulfur (Maksimovic and Mowrey, 1993), acid streams (pH < 6) were only identified south of the glacial border (Hoffman and Wetzel, 1993, 1995).

Tills have characteristic grain size distributions (Shepps and others, 1959). All have a significant amount of fine-grained material, that is, sand size and smaller. Groundwater movement through glacial sediments differs from that through consolidated bedrock in the Appalachian Plateau. The majority of groundwater movement through bedrock is along fractures and bedding planes. In glacial sediments, much more of the groundwater movement is intergranular, although some movement does occur through fractures in dense tills. The small grain size, poor sorting, and lack of fractures and bedding planes in tills results in low permeability. Water moves through tills very slowly, increasing the amount of time that the groundwater remains in contact with the mineral grains. Like the increased surface area, the increased residence time

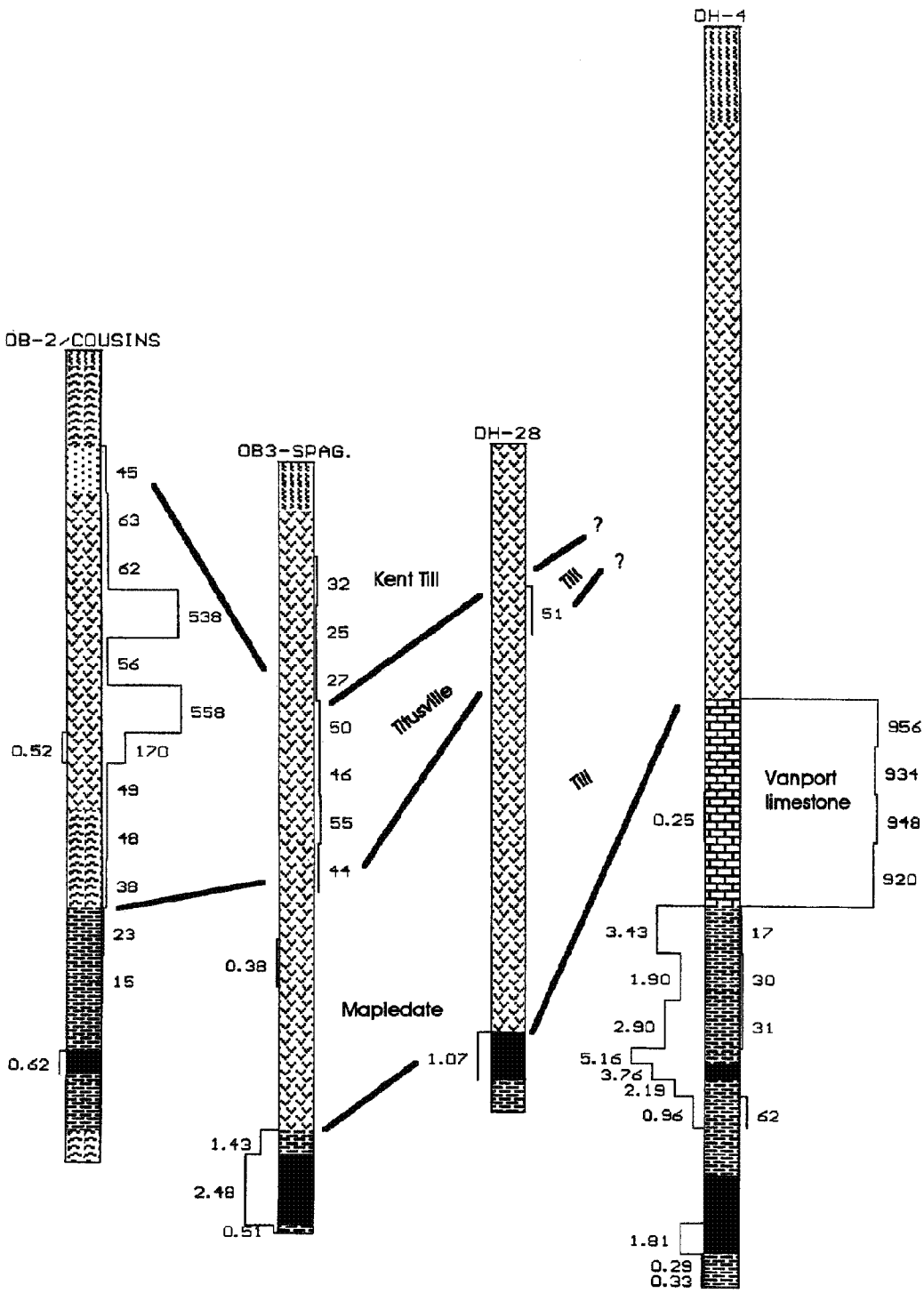


Figure 8.39 Till overburden above the Brookville/Clarion coal at Sites 21 in Millcreek Township (OB1-SPAG and OB3-SPAG) (site B on Figure 8.36) and Site 22 in Pine Township (DH-28 and DH-4) (site A on Figure 8.36), Mercer County. Probable till correlations are shown. This figure shows the variable thickness of tills that can occur within the same mine, wide variation in neutralization potential of tills and differences in the amount of erosion of underlying bedrock.

Table 8.4 Water quality parameters at the Spagnolo and Owens Mines. The unit for specific conductance is µS/cm, and units for other parameters, with the exception of pH, are in mg/L.

	N	Lab pH	Specific Conductance	Alkalinity	Acidity	Fe	Mn	Al	SO_4
Spagnolo Pre-mining	9	6.5	94	29	2	0.98	0.09	0.34	17
Spagnolo During-Mining	9	6.78	100	34	3	0.33	0.09	0.15	20
Owens Postmining	10	7.13	391	110	0	0.19	0.04	0.39	122

allows for greater reactivity in tills than in shallow, fractured bedrock.

The neutralizing capability of a till varies considerably and is reported in the literature in various ways. Published carbonate values for tills of northwestern Pennsylvania are for the clay fraction only, and not representative of the till as a whole. In addition, the carbonate content of any size fraction varies areally due to dilution by local bedrock, and vertically due to dilution and weathering (White, 1969). The published mean carbonate contents for the clay fraction of tills likely to be encountered in mines in northwestern Pennsylvania are based on limited numbers of sample analyses (3 Kent, 9 Titusville, and 9 Mapledale) (Gross, 1967). For these reasons, converting published carbonate values for tills in northwestern Pennsylvania into NP values is not valid, and site-specific testing and analyses are required.

Four mines near Grove City in Mercer County (Location A on Figure 8.36), including the Ambrosia mine, demonstrate the variability that till can have. All are within the Kent Moraine. All mined the Brookville/Clarion coals. About 50% of the glacial overburden in the Ambrosia Mine (Figure 8.37) is calcareous. Two nearby sites, Oddfellow Mine (Figure 8.36 and Figure 8.38) and Brothers 3 Mine (Figure 8.37), have very little NP > 30, even though the depth of the glacial overburden is up to 60 feet (18 m). The fourth site, McCoy Mine (Figure 8.38), did have significant NP in the glacial overburden.

Carbonate minerals in tills with NP less than 30 ppt CaCO3 can probably dissolve to produce alkalinity. Calcareous minerals in till probably react more completely than those in bedrock because of the greater surface area of particles in till. Because of the source area (Erie Basin) the NP of glacial sediments is less likely to be complicated by siderite, and reflects actual neutralizing potential.

Importance of Glacial Sediments in Mine Drainage Water Quality

The overlap of the main bituminous coal field and glaciated region is mainly in Beaver, Lawrence, Butler, Mercer, and Venango Counties (Figure 8.36). The Slippery Rock, Mapledale, Titusville, and Kent Tills are present in these areas. Rare thin patches of Lavery Till may also be encountered in northwestern Lawrence County.

In glaciated areas of Pennsylvania, postmining water quality is frequently good, presumably due to the carbonate content of glacial sediments. Overburden for the Spagnolo mine is shown in Figure 8.39, and the location of this and the Owens mine are shown in Figure 8.36. Water quality at the Spagnolo Mine, at the time of this writing, has not changed significantly from the premining background quality Table 8.4. However, the Spagnolo Mine reclamation was completed about the time this was written. Thus, there has not been sufficient time to collect and evaluate the postmining water quality.

The Owens Mine, about 6,000 feet (1,830 m) from the Spagnolo Mine (Location B on Figure 8.36) was mined in the late 1960's and early 1970's, and left partially unreclaimed. No acid-base accounting data are available for this site. Its geology, however, is likely similar to the Spagnolo Mine, although, as has been previously shown at Grove City, there can be rapid lateral variability in the mineralogy of glacial sediment. Both are located within the Kent Moraine, have similar drift thickness (Schiner and Kimmel, 1976), and mine the same coal. Postmining water from the Owens mine in 1990 was higher in specific conductance, alkalinity, and sulfates than the pre- or during-mining water from the Spagnolo site Table 8.4. The Owens water is characteristic of neutralized mine drainage. Other parameters are largely the same as the Spagnolo site water quality. Not all mines in glacial overburden will have alkaline drainage. Older tills, especially in their outcrop area, are low in carbonate and may not exert much neutralization effect.

In summary, glacial overburden can be beneficial in preventing acid mine drainage if it is calcareous. Because of the small grain size, unlithified nature, and the source of carbonates in glacial sediments, the NP determinations of glacial overburden probably more accurately reflect the ability of the glacial sediments to prevent and neutralize acid mine drainage than is sometimes the case with bedrock overburden. Site specific data are required to determine the NP of glacial sediments because of their variability in the texture and composition due to dilution and weathering.

Discussion on Stratigraphy

Several lithologic and mineralogic trends for the coal-bearing rocks of western Pennsylvania are evident from examination of Figure 8.2. The clay/shale content increases upward from a low of about 25% in the Pottsville Group to highs of 70 to 80% in the Dunkard Group. In general, there is a reverse relationship with sandstone, with sandstone increasing from ~20% or less in the higher Groups (with the exception of the lower Waynesburg Formation) to a high of 50% in the Pottsville. The percent calcareous rocks increases upward. The Pottsville Group has less than 1% calcareous rock. The lower Allegheny is less calcareous (6%) than the upper Allegheny Group (14%). Rocks of the Casselman Formation and higher are greater than 50% calcareous. The percentage of sandstone that is calcareous is generally similar to the percentage of overall rock that is calcareous. The uppermost Dunkard Group rocks contain the least amount of siderite, whereas over 20% of the rocks in the Allegheny Group and Glenshaw Formation are sideritic. Within the Allegheny and Pottsville Groups sideritic rocks are more abundant than calcareous rocks (Figure 8.2).

Some stratigraphic trends are also worth discussing. The Allegheny Group was divided into upper and lower Allegheny based on the presence of marine and brackish zones below the Johnstown limestone and the occurrence of freshwater limestones in the upper Allegheny, which are rare or absent in the lower Allegheny. The Conemaugh Group, like the Allegheny is divided such that the Glenshaw Formation contains most of the marine rocks, whereas the Casselman is primarily of freshwater origin. Mineable coals are generally restricted to the Allegheny and Monongahela Groups, although coals in the other groups are occasionally mineable.

The important geologic relationships, from a mine drainage standpoint, are the location of marine zones and distribution of calcareous rocks. The marine rocks are frequently associated with high sulfur strata, but can also have calcareous zones. Brackish rocks tend to have high sulfur and a lack of calcareous minerals. The conchostracan-bearing rocks frequently have less sulfur than their marine and brackish counterparts. Truly freshwater sediments tend to have calcareous minerals and limestone. These topics are discussed below in detail.

Little is known about the overburden mineralogy of the anthracite region. The Llewellyn Formation of the Northern Field is known to contain calcareous rocks. Some of the water quality reflects this source of alkalinity. Although stratigraphic studies have not yet identified calcareous rocks in the Southern and Western Middle Fields, highly alkaline mine waters imply that calcareous rocks exist. The lack of alkaline drainage in the Eastern Middle Field suggests a dearth of calcareous strata in this anthracite field.

Pleistocene glaciation in the bituminous coal field only came as far south as the northwestern corner of the field. Tills, where calcareous, can contribute significantly to the alkalinity of postmining water quality. Tills in the Northern Anthracite Field are not calcareous and would not contribute alkalinity to water.

The only places where the stratigraphy is important from a mining standpoint is where these strata will be disturbed by surface mining. Ultimately, postmining water quality is related to the mineralogy of these rocks.

Mineralogy of Mine Site Overburden

Coal overburden is composed of many different minerals in varying abundance. As mentioned previously, mining accelerates the weathering of these minerals by exposing fresh rock surfaces, and from a mine drainage or soil reclamation standpoint, two groups of minerals are overwhelmingly important. These are the acid-forming iron sulfides and the acid- neutralizing carbonates. The weathering of these two groups of minerals dictate whether the mine spoil will produce alkaline or acidic water. These minerals need only be present in an abundance of a few percent or less to be significant. By comparison the other 95% or so of overburden minerals play only a minor role.

Iron sulfide (pyrite) oxidizes and dissolves to create acidic water. Calcareous minerals (Ca-rich carbonates, such as calcite) can dissolve to neutralize and inhibit acid production (Chapter 1). The inhibitory effect is probably due to neutral pH conditions reducing the

catalytic effects of pyrite oxidizing bacteria, and the virtual elimination of pyrite oxidation by Fe^{+3} because of low solubility at near neutral pH. An example of the interaction between pyrite and a calcareous mineral (calcite) can be represented by:

$$FeS_2 + 2\ CaCO_3 + 3.75\ O_2 + 1.5\ H_2O \Rightarrow Fe(OH)_3 + 2\ SO_4^{2-} + 2\ Ca^{2+} + 2\ CO_{2(g)} \quad (8.1)$$

In the above equation the acid generated by the pyrite is neutralized by the calcite. The ultimate products of this reaction are iron hydroxide, sulfate, calcium and carbon dioxide gas. Other equations can be written and other products produced, and these are discussed in Chapter 1. For the present chapter it is simply necessary to recognize that weathering of pyrite makes acid, and dissolution of calcareous minerals will neutralize acid and possibly inhibit pyrite oxidation.

Pyrite, Other Forms of Sulfur, and Acid Production

In this section we will discuss the influence of forms of sulfur, pyrite morphology, and pyrite genesis as they relate to the production of acid-sulfate weathering products. Forms of sulfur that occur in coal overburden are sulfide, sulfate and organic. As discussed above, iron sulfide minerals (principally pyrite) are the culprit in the formation of acid mine drainage. Pyrite occurs in several crystal morphologies, ranging from micron-size framboids to millimeter (or larger) size euhedral crystals and coatings. Pyrite genesis has been suggested as a factor influencing pyrite reactivity, for example sedimentary pyrite is more reactive than hydrothermal pyrite (Hammack et al., 1988). Pyrite associated with Pennsylvania's bituminous coal seams and overburden is sedimentary in origin.

Chemical Forms of Sulfur (Sulfur Mineralogy) in Overburden Rock - When overburden is analyzed, weight percent total sulfur is generally determined as a means of estimating pyritic sulfur and thus the acid-producing potential of the rock. Forms of sulfur can be determined as described in Noll et al. (1988), however because of difficulties with analytical methods, added cost of analysis, and the fact that most sulfur in overburden rock is pyritic, typically only total sulfur is determined.

Although pyrite may comprise only a few percent, or even a fraction of a percent, of the overburden rock, its importance to postmining water quality far outweighs its seemingly minor presence. An overburden that averages just a fraction of a percent sulfur, in the absence of neutralizing rocks, can create significant postmining water quality or revegetation problems if not dealt with properly.

Sulfide Sulfur - Two iron-sulfide minerals occur in bituminous coal and overburden. They are pyrite and marcasite. Both have the chemical formula FeS_2 and are 53.4 percent sulfur with the remainder being iron, but the two minerals have different crystallinity. For simplicity we will refer to iron sulfide minerals as pyrite.

The oxidation of pyrite results in the production of sulfuric acid and iron. This acid can dissolve other minerals and thus release undesirable ions such as aluminum and manganese. The oxidation and acid-weathering processes are discussed in Chapter 1. A summary equation for the process can be described as follows:

$$FeS_2 + 3.75\ O_2 + 3.5\ H_2O \Rightarrow Fe(OH)_3 + 2\ SO_4^{-2} + 4\ H^+ \quad (8.2)$$

As seen above, one of the products of pyrite oxidation is aqueous sulfate. Under evaporative conditions sulfate minerals can form.

Sulfate Sulfur - Sulfate minerals are generally secondary weathering products of pyrite oxidation. Nordstrom (1982) shows the sequence by which these minerals can form from pyrite (Figure 8.40). Many sulfate minerals have been identified in Pennsylvania overburden (Table 8.5). They are divided into acid-producing and non-acid-producing. These minerals (with the exception of barite) are typically very soluble and transient in the humid east. They form during dry periods and then are flushed into the groundwater system during precipitation events. The phases that contain aluminum or iron are essentially stored acidity and will produce acid when dissolved in water. Gypsum, which is not acid forming, is relatively uncommon in Pennsylvania, whereas other sulfate minerals such as pickeringite and halotrichite occur more commonly.

The dissolution of coquimbite will be given as an example of how dissolution of sulfate minerals can create acid:

$$Fe_2^{3+}(SO_4)_3 \cdot 9H_2O \Rightarrow 2Fe(OH)_3 + 3\ SO_4^{2-} + 3\ H_2O + 6\ H^+ \quad (8.3)$$

Furthermore, Cravotta (1991, 1994) showed how the dissolution of roemerite could oxidize pyrite in the absence of oxygen, and thus create acid.

$$FeS_2 + 7\ Fe^{2+}Fe_2^{3+}(SO_4)_4 \cdot 14H_2O \Rightarrow 22\ Fe^{2+} + 30\ SO_4^{2-} + 16\ H^+ + 9\ H_2O \quad (8.4)$$

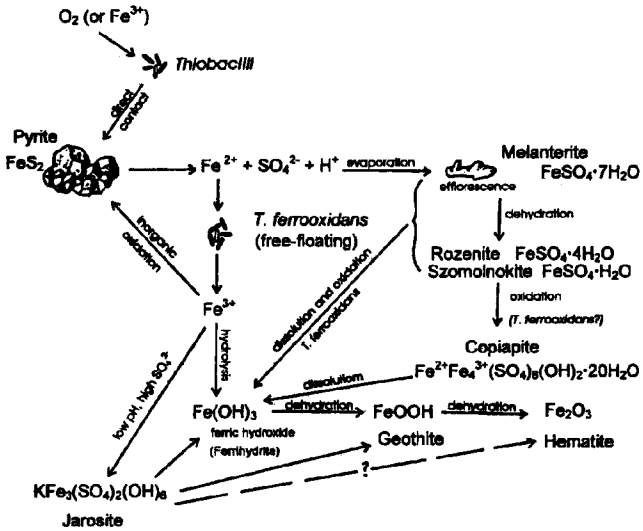


Figure 8.40 The overall sequence of mineral reactions for pyrite oxidation showing the relationships between oxidizing agents, catalysts and mineral products. From Nordstrom (1982).

The bottom line is that in Pennsylvania sulfate sulfur should be assumed to be acid producing unless the mineral can be verified as a non-acid producing one.

No systematic work has been done in Pennsylvania on pyrite weathering products, so the list in Table 8.5 is by no means exhaustive. Sulfate minerals are common to coal mine environments and have been reported from (among other places) Texas (Dixon et al., 1982) and Indiana (Bayless and Olyphant, 1982). Dixon et al. (1982) provide a list of 26 sulfate minerals "related or potentially related to lignite mine spoil..." A more complete list for Pennsylvania coal overburden would likely include most of the same minerals.

Organic Sulfur - Organic sulfur is sulfur that is tied up in organic molecules. This sulfur can originate by two processes. It can be associated with the original plant material, and it can be complexed with organic molecules during diagenesis. Casagrande et al. (1989) concluded that organic sulfur is not acid forming. Harvey and Dollhopf (1986) concluded that some forms of organic sulfur are acid producing, although the amount of acid produced in two leaching tests showed that organic sulfur contributed only 6 and 19 percent of total acidity. They showed, however, that theoretically some forms of organic sulfur should be capable of creating more acid than pyrite, whereas other forms are comparatively inert. Few, if any, other studies have been conducted on acid potential of organic sulfur.

Table 8.5 Secondary sulfate minerals identified in western Pennsylvania mine spoil and overburden. (Minerals from L. Chubb and R. Smith (PA Geologic Survey, personal communications, various years), Cravotta (1991, 1994), and observations by the authors. Mineral chemistries are from Roberts et al. (1990).

Acid-Producing

Pickeringite:	$MgAl_2(SO_4)_4 \cdot 22\ H_2O$
Halotrichite:	$Fe^{+2}Al_2(SO_4)_4 \cdot 22\ H_2O$
Alunogen:	$Al_2(SO_4)_3 \cdot 17\ H_2O$
Copiapite:	$Fe^{2+}Fe^{3+}(SO_4)_6(OH)_2 \cdot 20\ H_2O$
Copiapite Group:	aluminocopiapite with magnesium?
Coquimbite:	$Fe_2(SO_4)_3 \cdot 9\ H_2O$
Roemerite:	Fe2+Fe23+$(SO_4)_4 \cdot 14$ H2O
*Jarosite:	$KFe_3^{+3}(SO_4)_2(OH)_6$

Non-Acid-Producing

Gypsum:	$Ca(SO_4) \cdot 2\ H_2O$
Epsomite:	$MgSO_4 \cdot 7\ H_2O$
Barite:	$BaSO_4$

*Jarosite is less soluble than the other acid-producing sulfate minerals.

One factor complicating organic sulfur estimates is that organic sulfur is usually determined by "difference" (Noll et al., 1988). That is, total weight percent sulfur minus pyritic sulfur and sulfate sulfur. If pyritic sulfur or sulfate sulfur are incorrectly determined during analysis, organic sulfur will also be incorrect. In any event, acid production from organic sulfur is probably much smaller than from sulfide or sulfate sulfur.

It might be expected that rocks with high organic content would have greater amounts of organic sulfur compared with rocks with lesser amounts of organic matter. This appears to be true for coals, but not so for other rock types. A study by Brady and Smith (1990) examined the percentage of pyritic sulfur in relation to total sulfur for various rocks. Carbonalith (i.e., an organic-rich rock) did not have significantly different pyritic sulfur in relation to total sulfur than other rock types such as shale, sandstone and clay. The lack of higher amounts of organic sulfur in organic-rich rocks may be allied to the relationship between organic matter and pyrite formation, which is discussed below.

Pyrite Morphology - A considerable effort has been expended over the years looking at pyrite morphology and attempting to relate this to acid mine drainage generation. Some of the earliest work is by Caruccio (e.g. 1970), however numerous other individuals have also examined this issue. This seems like a logical thing to

look at because pyrite is what causes acid mine drainage.

Morrison (1988) defined nine "classes" of pyrite morphology, end members being framboids and euhedral crystal structures. Framboids tend to be small (< 1 micron size), and euhedral are generally larger (tens to thousands of microns). For any given percentage of sulfur, framboids would have a proportionally larger surface area than euhedral crystals. Other classification systems have also been discussed (e.g., Arora et al., 1978; Hawkins, 1984). Caruccio (1970) and Morrison (1988) found a relationship between relative surface area and acid production, with the small particles more reactive than large particles. Hornberger and associates (1981,1985) found a statistically significant difference in the abundance of framboidal pyrite (i.e. framboids and framboidal clusters <10 microns) in lower Kittanning coal samples from marine and freshwater paleoenvironments. There were almost no discrete framboids in point counts of the freshwater samples, but the marine samples had many. However, some of the freshwater samples produced as much acidity and sulfate in leaching tests as the marine samples. One LK sample from a brackish paleoenvironment produced by far the highest acidity and sulfate of all of the LK coal samples tested, despite having a dearth of framboids (and total and pyritic sulfur contents similar to the marine samples). It seems reasonable that surface area would have an effect on reactivity, but it is not by any means the only factor controlling reactivity.

Discussion on Sulfur Minerals and their Relation to Acidic Water - Typically in Pennsylvania determination of total sulfur will adequately serve as a proxy for acid potential. This is because it includes the sulfur from acid-generating sulfide and sulfate minerals and typically the amount of organic sulfur in overburden rock is insignificant. In locations where gypsum, and other sulfur-bearing non-acid-forming materials are abundant, accurate determination of sulfide sulfur should provide a better prediction of acid potential.

Formation of Pyrite

This section will discuss the factors involved in the formation of pyrite. These factors are responsible for the amount of pyrite present in a stratigraphic interval, and thus that rock's acid-producing potential. Pyrite consists of iron and sulfur, so clearly these ingredients are required. Other factors that influence the creation of pyrite are the presence of organic matter decomposable by sulfate-reducing bacteria (essential for creating reducing conditions), sedimentation rate and bioturbation.

Sulfur and Iron - Sulfate, the typical aqueous form of sulfur, is the source of sulfur in most sediments. The sulfur in sulfate is oxidized and must be reduced to sulfide to become part of pyrite. Ocean water contains about 2700 mg/L SO_4. Freshwater, on the other hand, is typically low in sulfate. An average river transports about 8 mg/L sulfate (Hem, 1985), although rivers draining arid and semi-arid regions can have much higher sulfate (hundreds of mg/L). Another source of sulfate that has been suggested as a source of sulfur for pyrite is sulfate from eroded evaporites. Erosion of upstream evaporites containing gypsum has been espoused by Querol et al. (1991) as the source of sulfur for some high sulfur coals in Spain and by Gibling et al. (1989) for high sulfur coals in the Maritime basin of Canada. Most studies of sulfur in rocks have dealt with marine sediments, where the water column provides a nearly unlimited supply of sulfate sulfur. Few studies are available for freshwater rocks and the formation of pyrite. The few that do exist seem to indicate that sulfur is low in freshwater sediments.

The concentration of iron in ocean water is very low (<.01 mg/L), whereas iron associated with fresh water is comparatively high (~0.7 mg/L average) (Hem, 1985). Iron can also be transported as detridal iron-bearing minerals (e.g., iron oxides) and bound to clay minerals. Thus iron can be transported into a marine or marginal marine environment by iron-bearing water and sediments.

It has been suggested that the most optimum environment for pyrite formation would be a brackish environment, where freshwater high in iron mixes with marine water high in sulfate (Guber, 1972). The subject of paleoenvironmental controls on pyrite formation are discussed later in this chapter.

Organic Carbon and its Relationship to Sulfur - Sulfate can only be reduced to sulfide in sediments by bacterial activity in the absence of oxygen. The bacteria oxidize organic carbon to provide energy for their metabolic processes and sulfate is the terminal electron accepting reactant. The sulfate is reduced to sulfide. Suitable reducing environments are typically found below the sediment-water interface. Although pyrite is the end product, intermediate iron sulfide minerals are created first (e.g., mackinawite (FeS); greigite (Fe_3S_4)). A schematic of this process is shown in Figure 8.41 (Goldhaber and Kaplan, 1982). Pons et al. (1982)

have described this process with the following overall equation (CH_2O represents organic matter):

$$Fe_2O_3 + 4\ SO_4^{2-} + 8\ CH_2O + \tfrac{1}{2}\ O_2 \Rightarrow 2\ FeS_2 + 8\ HCO_3^- + 4\ H_2O \qquad (8.5)$$

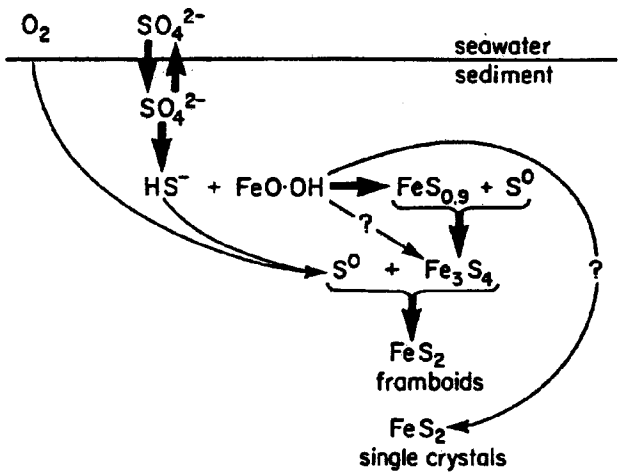


Figure 8.41 Pathway of sedimentary pyrite formation. From Goldhaber and Kaplan (1982).

A positive linear relationship has been shown between percent organic carbon and percent sulfur for Recent and Pleistocene marine sediments (Goldhaber and Kaplan, 1982; Raiswell and Berner, 1986). Fairly strong positive linear relationships exist for marine sediments back in time to at least the Jurassic (Holocene and Pleistocene, correlation coefficient (r) = 0.95; Upper Cretaceous, r = 0.73; Jurassic, r = 0.91), but more random scatter seems to be the case during the lower Carboniferous of Europe (Mississippian Period in the US) with r = 0.39 (Raiswell and Berner, 1986). The reason for the poor correlation between carbon and sulfur during the Carboniferous is not discussed. But the correlation coefficient of 0.39 indicates that carbon abundance explains only 15% of the variation in sulfur, while carbon explains 90% of the variation of sulfur in the Holocene and Pleistocene samples.

Despite the importance of pyrite and the abundance of organic matter in coal-bearing rocks of Pennsylvanian age, studies of the relationship between organic carbon and sulfur in these rocks are rare. No studies are known from Pennsylvania. Gilb (1987) looked at the relationship between organic carbon and sulfur in the Pennsylvanian Breathitt Formation of eastern Kentucky. Gilb separated the lithologies into carbonaceous shale (organic carbon between 5 and 30%), mudrock with calcareous concretions, and mudrock without calcareous concretions. Chesnut (1981) concluded that mudrocks with calcareous concretions were of marine origin. Gilb proceeded on this assumption, plus the assumption that the mudrocks lacking concretions are freshwater. The carbonaceous shale shows a positive relationship (slope = 0.13) between percent sulfur and percent organic carbon (% Org. C), with a correlation coefficient (r) of 0.60. The mudrocks with calcareous concretions also have a positive slope (0.6) and r = 0.72. The relationship between sulfur and organic carbon in mudrocks not having calcareous concretions is essentially random. Of 38 samples, all but four are less than 0.4% sulfur and most are less than 0.1% sulfur. It must also be remembered that these rocks were defined as "freshwater" based on negative evidence (lack of calcareous concretions), so the few high sulfur rocks (and perhaps some of the low sulfur rocks) may have a marine origin. Some of the samples Gilb included in his study had carbon less than 1%. Berner (1984) cautions that the use of sulfur to carbon ratios as a paleoenvironmental indicator should only be used for sediments with organic carbon greater than 1%.

Studies of pyrite formation in freshwater sediments are few in number. Most suggest that sulfur values will be low because sulfate availability is limited to only a small percentage of that present in marine waters (e.g., Berner and Raiswell, 1984; Davison, 1988). Berner and Raiswell (1984) have suggested that the carbon to sulfur ratio (C/S) can be used as a means of distinguishing freshwater from marine sediments. They found that marine rocks are characterized by C/S values of 0.5 to 5 and that freshwater rocks had C/S values >10 (Figure 8.42). This difference is attributed to the low sulfate levels of freshwater being limiting on pyrite production. They cautioned that this method should (1) only be applied to rocks with greater than 1% organic carbon, (2) not be applied to nearly pure limestones because low amounts of iron probably limited pyrite formation and (3) not be applied to coal because organic sulfur could be mistaken for pyritic sulfur in total sulfur analyses and the "superabundance of organic matter" would create a situation where pyrite formation becomes limited by iron availability. Also "...at such high organic-carbon concentrations, high C/S ratios can result even at high salinities." Gilb (1987) adds a further caution regarding the use of C/S ratios for coal. He points out that many swamp environments have low pH. This is not conducive to sulfate-reducing bacteria, which prefer neutral water conditions. "Therefore peat deposited in swamps hav-

ing low pH may form low sulfur coal regardless of sulfate and iron availability" (p. 13). It would be interesting to see the results of a study of C/S for Pennsylvania's Pennsylvanian rocks and compare these results with the other studies.

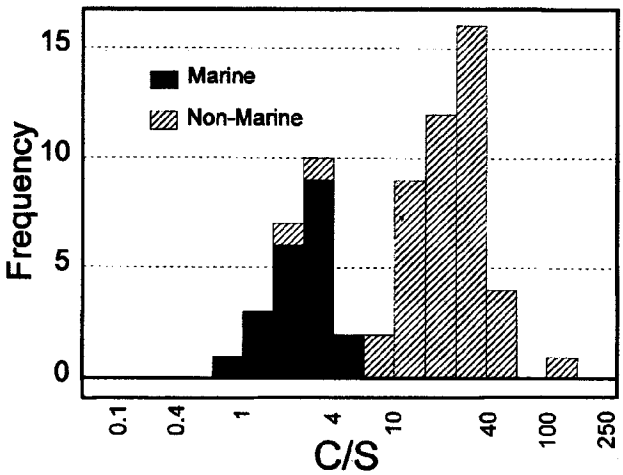


Figure 8.42 Frequency distribution of C/S weight ratios (plotted on a logarithmic X-axis) for British Carboniferous siltstones, mudstones and shales that were determined to be marine or non-marine by independent means. From Berner and Raiswell (1984).

The Berner and Raiswell (1984) study included modern freshwater lake sediments and British Carboniferous freshwater sediments. The freshwater sediments (modern and ancient) were, with few exceptions, low in sulfur (<0.5%). This fact differs from what we see in Pennsylvania, where presumed "freshwater rocks," especially organic-rich rocks, frequently exceed 0.5 % sulfur (for example see Figures 8.15, 8.17, 8.18, 8.19, 8.20, 8.21, 8.26, and 8.31). As discussed earlier, the upper Allegheny "freshwater rocks" are believed to have been deposited in a slightly-saline, marginally-brackish environment. For a comparison with marine and brackish rocks from the Allegheny and Conemaugh Groups, see Figures 8.7, 8.12, 8.13, 8.14, 8.23, and 8.24. It does appear, however, within the Allegheny Group and Conemaugh Group that high-sulfur, marginally-brackish strata overlying coals are typically not as thick as the high-sulfur strata associated with brackish and marine environments. For example the high sulfur (>0.5% S) associated with the UK, LF and UF in Figures 8.15, 8.17, 8.18, 8.19, 8.20, 8.21, and 8.26 is one to 5 ft (0.30 to 1.5 m) thick, whereas the thickness of the high-sulfur strata in marine and brackish environments (Figures 8.7, 8.12, 8.13, 8.14, 8.23, and 8.24) can be up to 30 ft (10 m). Freshwater rocks associated with coals of the Monongahela and Dunkard Groups (Figures 8.31, 8.32, and 8.34) seem to have thicker sequences of high-sulfur strata than the Allegheny overburden. Since there seems to be no evidence of marine influence within this section, this may be due to more arid conditions resulting in higher sulfate levels in surface water and groundwater. A modern relationship between aridity and high dissolved solids, including sulfate, has been noted in the arid and semi-arid western United States. Hem (1985) notes that in semi-arid regions, the amount of sulfate is large in proportion to the water volume in which it is carried away, thus elevated sulfate.

Sedimentation Rate and Bioturbation (Open vs. Closed System) - Sedimentation rate and bioturbation can influence whether the sediment just below the sediment/water interface is an open or a closed system with respect to sulfate in the overlying water column. Bloch and Krouse (1992), studying rocks of the Cretaceous period in western Canada, found the highest sulfur concentrations (>2.75%) associated with bioturbated marine mudstones and siltstones, when compared to mudrocks that were not bioturbated (0.1 to ~2%). Bioturbation irrigated the upper portions of the sediment with sulfate from the overlying water column, thus creating an open-system source of sulfur. They also suggested that some of the low sulfur sediments were due to fast sedimentation rate, resulting in a more closed system where sulfate would be limited to that entrapped within the sediment pore-water. Bloch and Krouse calculated, assuming a porosity of 75% for the original sediment and 100% retention of sulfur (from sulfate) within the sediment, that a closed marine sediment would be limited to 0.1% sulfur. Berner (1970, p. 2) gives a higher figure, saying that "simple burial of sea water and reduction of all included sulfate can provide only about 0.3 percent pyrite sulfur..." For this to be true, the porosity of the sediment would be around 90%. Another important factor is that pyrite sulfur probably only represents a small fraction of the total hydrogen sulfide, H_2S, produced by sulfate reduction (Dean and Arthur, 1989). Jorgensen (1977) in studying a marine sediment in the coastal waters of Denmark found that only 10% of H_2S was fixed as iron sulfide, the remainder was lost by diffusion and reoxidation. The point Berner (1970) and Bloch and Krouse (1992) make is that for sulfur to be higher than a few tenths of a percent, diffusion and/or irrigation by burrowing organisms must occur to permit sufficient sulfate into the sediment to achieve high sulfur values. Movement of H_2S away from sites with high organic matter to other sites with available iron could result in

pyrite formation in the absence of organic matter. This may explain the high sulfur in some sandstones that "cut" down to the coal and overlay the coal. Typically the high sulfur zones occur near the base of the sandstone. Drill Hole A-5 and OB-4 in Figure 8.13 are examples of such a sandstone. The bottom 5 ft (1.5 m) of the sandstone in A-5 has greater than 0.5% S, with the interval from 3 to 5 ft (1 m to 1.5 m) above the coal having greater than 8% S. The base of the sandstone in OB-4 has 6.15% S.

Goldhaber and Kaplan (1982) also recognize the potential importance of bioturbation to increase the amount of sulfate available for reduction. They, however, present an extended argument to show that sulfate reduction rates are greater at higher sedimentation rates. Higher sedimentation rates tend to help preserve organic carbon, a component necessary for bacterial conversion of sulfate to sulfide. Their comparisons of sedimentation rate showing higher sulfide with higher sedimentation rates, are made with H_2S and "acid volatile" sulfides, not pyrite. Goldhaber and Kaplan do not discuss how these rates correspond to final pyrite concentrations. Berner (1984) concluded that "rapid burial enables relatively reactive (organic) compounds and more organic matter in general to become available for bacterial sulfate reduction at depth...These considerations help to explain why there is a crude correlation between sedimentation rate on the one hand, and organic matter and pyrite contents on the other" (p. 607).

Curtis and Spears (1968) looked at iron minerals, principally pyrite and siderite, in sediments of the Carboniferous Period coal measures and of the Jurassic Period in England. Pyrite and siderite both require reducing conditions. In the Carboniferous and Jurassic sediments they observed that pyrite and siderite were not randomly distributed in the sediment, but that siderite-bearing mudstones occurred above shales and mudstones containing pyrite. They concluded that slow sedimentation rates in marine sediments favored pyrite formation (more availability of sulfur) and fast rates favored siderite formation.

It is obvious from the conflicting conclusions that more work on the subject of pyrite formation as a function of sedimentation rates is warranted. High sedimentation rates would tend to create a "closed" system which, in the absence of bioturbation, would result in little input of sulfate from the overlying water column, and limited sulfate available for additional sulfate reduction. High sedimentation rates, however, preserve organic matter that is necessary for bacterial reduction of sulfate. In any event, it appears that bioturbation is important in irrigating the sediment such that additional sulfate is available for reduction.

Discussion on Formation of Pyrite - Although there is a clear positive relationship between percent organic carbon and percent sulfur in Recent and Pleistocene marine sediments, the relationships between these parameters (plus percent iron) in older marine sediments is complex. Raiswell and Berner (1986) examined British Carboniferous marine sediments and found that there was considerable scatter and a low correlation coefficient for C/S ratio. They however suggest that the overall C/S ratio remained relatively constant from the Devonian to Tertiary (~2). It is somewhat higher in more recent sediments (~2.8), and lower (<1.0) in older Paleozoic sediments.

Gild's (1987) findings on the relationships between organic carbon and sulfur are similar to those by Berner and Raiswell (1984). Even though no studies relating sulfur to organic carbon have been performed on Pennsylvanian rocks in Pennsylvania, the general findings of Gilb (1987) and Berner and Raiswell (1984) are probably applicable. Typically there will be a relationship between percent organic carbon and percent sulfur for marine rocks; higher sulfur values will be found in marine mudstones than in freshwater mudstones; and carbonaceous rocks will typically contain more pyrite than noncarbonaceous rocks for any given paleoenvironment. More discussion on paleoenvironmental and rock-type controls on sulfur will be presented later.

The higher the content of organic matter the darker the rock tends to be. If a mudstone is known to be of marine or brackish origin and it is dark in color, there is a good chance that it is also high in sulfur. Carbonaceous rocks (> 5% organic carbon) may be high in sulfur, at least relative to other rocks, regardless of paleoenvironment. This can be useful in helping to identify potentially high sulfur rocks in the field or in drill cuttings/cores.

Alkalinity Producing Minerals: The Carbonates

Carbonate minerals play an extremely important role in determining postmining water chemistry. They not only neutralize acidic water created by pyrite oxidation, but as discussed above, there is evidence that they also inhibit pyrite oxidation (Hornberger et al., 1981; Williams et al., 1982; Perry and Brady, 1995). These processes are discussed more fully in Chapters 1 and 11. Brady, et al. (1994) determined that the pres-

ence of as little as 1% to 3% carbonate (on a mass weighted basis) on a mine site can determine whether that mine produces alkaline or acid water. Although pyrite is clearly necessary to form acid mine drainage, the relationship between the amount of pyrite present and water quality parameters (e.g., acidity) is only evident where carbonates were absent. Neutralization potential, a measure primarily of the carbonate content of the overburden, relates positively to the alkalinity of postmining water.

A knowledge of the distribution, amount, and type of carbonates present on a mine site is extremely important in predicting the potential for postmining problems and in designing prevention plans.

Carbonate Mineralogy - The most common carbonate minerals found in coal mine overburden are listed in Table 8.6. Carbonate minerals are often not "pure" end members, but form solid solution series with cation substitution.

Table 8.6 Common Carbonate Minerals in Mine Overburden, listed in descending order of their capability to neutralize acid.

Mineral	Chemistry
Calcite	$CaCO_3$
Dolomite	$CaMg(CO_3)_2$
Ankerite	$Ca(Fe,Mg)(CO_3)_2$
Mn-Siderite	$(Fe, Mn)CO_3$
Siderite	$FeCO_3$

The above minerals, with the exception of siderite, will neutralize acid generated from pyrite oxidation. An example of this neutralization process is:

$$CaCO_3 + 2H^+ \Rightarrow Ca^{2+} + CO_2 + H_2O \qquad (8.6)$$

Not all carbonates are created equal when it comes to neutralization of acid. Calcite is more soluble than dolomite although the overall dissolution is similar to that shown for calcite (Geidel, 1982). Both calcite and dolomite will neutralize acid, and potentially inhibit pyrite oxidation. Siderite is less soluble than calcite and dolomite, and its role as an acid-neutralizer is either limited or non-existent as discussed below.

Siderite is a very common mineral in coal measures (e.g., Texas - Senkayi et al. 1986; and Japan - Matsumoto, 1978), including those in Pennsylvania (Morrison et al, 1990a, 1990c; and Figure 8.2). Siderite will form preferentially to calcite where iron is abundant (Blatt et al., 1972). It forms under reducing conditions where sulfur availability (as sulfate) is limited (e.g., Curtis and Spears, 1968; Postma, 1982). Where reduced sulfur is abundant, pyrite will form in preference to siderite. Dissolution of siderite can create weakly acid conditions in a closed system (Barnes and Romberger, 1968; Cravotta et al., 1990):

$$FeCO_3 + 0.25\ O_2 + 2.5\ H_2O \Rightarrow Fe(OH)_3 + H_2CO_3 \qquad (8.7)$$

Even in an open system, the weathering of siderite, because of the hydrolysis of iron, has no net neutralizing effect. As discussed in Chapter 6 (see also Skousen et al., 1997), tests for neutralizing potential can give misleading results if siderite is present. Siderite may cause the test to appear positive for neutralizers. Additionally, siderite can contribute iron to water, and is probably responsible for at least some, and possibly much of the Mn observed in some mine waters. Mn is a common substitute for iron in siderite (Morrison, et al., 1990c).

Curtis and Spears (1968) attributed whether pyrite or siderite formed to the relative anion concentrations. A factor that may contribute to the bicarbonate ion concentration is that bicarbonate is produced during sulfate reduction (equation 8.5). Presley and Kaplan, (1968) observed an increase in bicarbonate with a corresponding decrease in sulfate in some modern nearshore marine sediments. Under reducing conditions and a more or less closed system, sulfate reduction would occur first with iron fixed as pyrite; once the sulfate was consumed, and assuming iron is available, siderite could form. A variety of factors may result in no clear relationships between the relative amounts of pyrite and siderite. For example, pyrite forms under slightly acidic to alkaline conditions, thus bicarbonate may have been present in the pore waters even before sulfate reduction. Also, Presley and Kaplan (1968) found more biogenically produced bicarbonate than could be explained solely by sulfate reduction. They attributed this to other biologic processes such as fermentation. The potential loss of sulfide due to oxidation or diffusion and the presence of preexisting bicarbonate may also result in a lack of relationships. No work similar to that by Curtis and Spears (1968) has been done in the Pennsylvanian of Pennsylvania.

The presence of siderite does not by itself reflect a particular depositional environment. Siderite occurs in sediments of freshwater, brackish, and marine origin (Matsumoto, 1978; Mozley, 1989; Morrison, 1988). Siderite is normally an early diagenetic mineral, formed below the sediment-water interface. Siderite can also

form in terrestrial soil forming processes and is associated with some underclays (Gardner et al., 1988).

Mozley (1989) looked at compositional variabilities of siderite from marine and freshwater sediments. He found that marine siderite is impure with no more than 90 mole percent (mol %) $FeCO_3$. It can have Mg substituting up to 41 mol %, and Ca up to 15 mol % in the siderite crystal lattice. Freshwater siderite is commonly very pure (> 90 mol % $FeCO_3$), and can have higher Mn concentrations compared to marine siderite. Unfortunately Mozeley did not discuss siderite from brackish environments, and did not study "(s)iderite from complex depositional sequences with intercalated marine and nonmarine strata (e.g., coal-measure siderite)...", because of the possible early mixing of pore waters from different paleoenvironments. No efforts similar to Mozley's have been conducted in the Pennsylvanian of Pennsylvania. It would be interesting to see if siderite composition varied by paleoenvironment. A better understanding of siderite composition would be useful for a variety of purposes. First, impure siderite may offer some neutralizing capacity; second, it would be a step in determining to what extent siderite contributes to Mn in mine waters; and third it may offer insight into paleodepositional environments.

Distribution of Carbonates in the Pennsylvanian of Western Pennsylvania - Within the Allegheny Group in Pennsylvania, siderite is the most common carbonate mineral (Morrison, 1988; and Figure 8.2). It occurs throughout the Pennsylvanian of Pennsylvania, regardless of paleoenvironment (Figure 8.2). An important aspect of siderite, in terms of mine drainage, is that it is the only carbonate that normally occurs in brackish sediments (see Table 8.15 in Appendix). This, coupled with the high sulfur content of brackish rocks, often leads to poor quality water from mines developed in brackish sediments.

Calcite and dolomite occur in the freshwater limestones of the Allegheny, Conemaugh, Monongahela, and Dunkard Groups. Additionally, in the Monongahela and Dunkard Groups, calcite and dolomite are the most common carbonate minerals present in other rock types (Figure 8.2). Marine limestones and associated rocks (Allegheny and Conemaugh Groups) can have a high carbonate content. As shown previously the Vanport limestone can be over 90% $CaCO_3$.

Chemical composition data for the Vanport limestone and other Pennsylvanian limestones and dolomites are shown in Table 8.7. Data from a few Cambrian and Ordovician limestones and dolomites, including the Valentine limestone from Centre County are included for comparison, as these high-calcium limestones are well known for their purity and industrial significance (see chemical composition data and additional discussion in O'Neill, 1964, 1976; Rones, 1969; and Chapter 7 in this volume). Table 8.7 shows that some marine and freshwater limestones of the Pennsylvanian Period exceed 90% calcium carbonate, which is also evident from NPs exceeding 900 ppt on Figures 8.7, 8.18, 8.20, and 8.39. Chemical composition data for the freshwater Fishpot, Redstone and upper Freeport limestones are shown in Table 8.7. These freshwater limestone samples typically have lower calcium carbonate contents than the Vanport limestone samples included in Table 8.7. NPs in the range of 500 to 875 ppt $CaCO_3$ for some of these stratigraphic intervals are also shown in Figures 8.17, 8.18, 8.19, 8.20, 8.25, 8.26, and 8.32. The origins of limestones and other calcareous rocks will be discussed in more detail in a following section of this chapter.

Not much is known about limestones and other calcareous rocks of the Anthracite Region. As mentioned earlier and shown on Figure 8.35 one marine limestone and several freshwater limestones occur in the northern field. No analyses of these limestones are known. Siderite, at least in the form of nodules, is fairly common in the Anthracite Region. Another possible source of calcite is secondary mineralization along fractures.

Other Neutralizing Minerals and Processes

The most effective minerals, in terms of acid neutralization, are the carbonates. Some other minerals, however, can also neutralize acid. For example silicate minerals can neutralize acid, but the reaction rates at near neutral pH tend to be slow. Quartz, the most common silicate, is for all practical purposes inert. Many of the other silicate minerals, however, can provide buffering at low pH's (Stumm and Morgan, 1981; Lapakko, 1992). The following example shows how anorthite can neutralize acid.

$$CaAl_2Si_2O_{8\,(s)} + 2\,H^+ + H_2O \Rightarrow$$
(anorthite)
$$Ca^{2+} + Al_2Si_2O_5(OH)_{4\,(s)}$$
(kaolinite) (8.8)

Another source of neutralization is cation exchange on clay particles. Clay particles tend to have negative charges at their surfaces. These attract positively charged ions. Thus, H^+ can adhere to the clay surfaces and raise the pH of the solution.

Table 8.7 Chemical composition of limestones and dolomites from Pennsylvania.

Limestone/Dolomite Name	Geologic Period	Formation	County	$CaCO_3$	$MgCO_3$	SiO_2	Al_2O_3	Fe_2O_3	R_2O_3	Insol.	S	Year of analysis	Source
Upper Washington	Permian	Washington	Washington	72.9	3.8				2.9	17.4	0.16	1876	1
Benwood	Upper Penn	Monongahela	Westmoreland	85.8	2.3	6.4	1.0	1.4				1925	1
Fishpot	Upper Penn	Monongahela	Somerset	67.7	12.3					15.6		1997	2
Redstone	Upper Penn	Monongahela	Somerset	69.4	11.5					13.4		1997	2
Redstone	Upper Penn	Monongahela	Somerset	86.6	6.2					4.0	0.09	1879	1
Upper Freeport	Middle Penn	Allegheny	Westmoreland	71.6	1.7					24.8		1997	2
Upper Freeport	Middle Penn	Allegheny	Westmoreland	68.5	1.7					27.2		1997	2
Upper Freeport	Middle Penn	Allegheny	Indiana	84.4	2.8				2.1	9.2	0.20	1878	1
Upper Freeport	Middle Penn	Allegheny	Jefferson	90.0	2.9				1.3	3.5		1946	1
Upper Freeport	Middle Penn	Allegheny	Jefferson	66.5	12.4	12.7						1946	1
Vanport	Middle Penn	Allegheny	Armstrong	94.2	1.4	1.4	0.4	1.4				1934	1
Vanport	Middle Penn	Allegheny	Armstrong	93.4	2.0	1.2	0.4	1.1			0.05	1927	1
Vanport	Middle Penn	Allegheny	Butler	94.9	1.5	1.5	1.0	0.7				1934	1
Vanport	Middle Penn	Allegheny	Butler	95.8	1.8	1.6			2.2			1934	1
Vanport	Middle Penn	Allegheny	Clarion	91.7	1.6	3.9	2.7					1963	1
Vanport	Middle Penn	Allegheny	Lawrence	95.0	0.9	2.2	1.5	0.6			0.05	1929	1
Vanport	Middle Penn	Allegheny	Lawrence	94.6	1.4	2.1	0.6	0.7			0.03	1963	1
Valentine	Ordovician	Benner	Centre	98.5	1.1	0.6	0.3	0.1			0.04	1955	1
Valentine	Ordovician	Benner	Centre	97.2	1.1	0.8	0.3	0.1		0.6	0.00	1963	1
Valentine	Ordovician	Benner	Centre	98.6	0.3	0.6			0.5			1955	1
Valentine	Ordovician	Benner	Centre	96.9	1.8	0.9			0.4	0.6		1963	1
Ledger	Cambrian	Ledger	Chester	52.9	43.7	1.4	0.5	0.3		0.6	0.00	1963	1
Ledger	Cambrian	Ledger	Chester	51.4	42.9	3.7			2.0			1959-60	1
Ledger	Cambrian	Ledger	Montgomery	53.8	44.5	1.1	0.2	0.5				1963	1
Kinzers	Cambrian	Kinzers	York	93.0	6.5	0.5			0.4	0.6	0.00	1963	1
Kinzers	Cambrian	Kinzers	York	99.2	0.4	0.2			0.2			1934	1

* 1=O'Neill, 1964, PA Geological Survey Report M 50

2=R.C. Smith II, PA Geological Survey, unpublished data

Silicates neutralize acid by dissolving (often incongruently, as in the above example). This dissolution releases elements such as aluminum and magnesium, to name two of the more common elements seen in mine drainage. Thus, although their role may not be significant at near neutral pH, at low pH they can also contribute to the dissolved solids content of the mine water and provide some buffering. The role of silicate neutralization may explain why overburden that is low in percent sandstone and therefore high in finer-grained sediment (and feldspar and clay minerals) frequently produce alkaline drainage. This subject will be discussed more fully in the section relating lithology to water quality.

Geologic Controls on Overburden Mineralogy in the Appalachian Basin

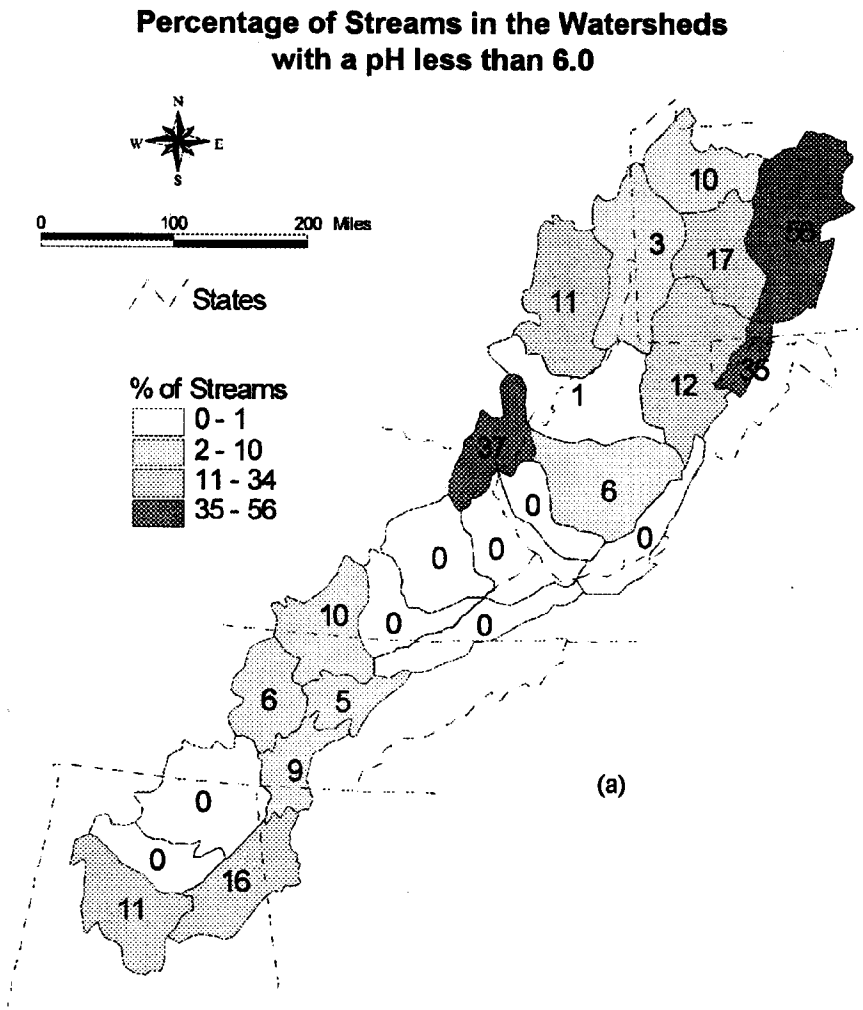
The Appalachian Regional Commission (1969) and Wetzel and Hoffman (1983, 1989) observed that acid mine drainage was a regional problem, and upon closer inspection they determined that it is most prevalent within the Allegheny Group. Figure 8.43 illustrates the distribution of pH and sulfate problems for surface waters in the Appalachian basin. Although these maps show in a general way the distribution of water quality problems, some caution must be used in their interpretation. For instance, it must be kept in mind that some watersheds are much more intensely mined than other watersheds, and some watersheds on the periphery of the basin may have little or no coal. Some general statements can be made. The West Branch Susquehanna River has the highest percentage of streams with pH less than 6.0 (56 %). This watershed has a correspondingly high percentage of streams with sulfate above 75 mg/L, thus indicating that the proportionally low pH is mining influenced. The other two watersheds with greater than 35% of the streams having a pH less than 6.0 occur where mining would have encountered the Allegheny Group. The watersheds with greater than 35% of streams with sulfate greater than 75 mg/L in southern West Virginia and Kentucky illustrate that high sulfate does not necessarily correspond with low pH. None of the sampled streams have a pH less than 6.0. Figure 8.43 would be made more useful if bedrock geology and the percentage of each watershed that has been disturbed by mining could be plotted. Because of the limitations, Figure 8.43 should only be used to discern broad trends.

Although there is a general relationship between geology and mine drainage quality, no comprehensive study relating geology and coal mine drainage quality has been attempted for the entire Appalachian basin. An examination of geologic studies suggests some significant differences in mineralogy for the southern Appalachian (Pottsville) strata and the northern Appalachian (Allegheny through Dunkard) strata (e.g., Cecil et al., 1985; Donaldson et al., 1985a). Several geologic processes have contributed to the variability of coal properties and the chemistry/mineralogy of intervening strata. These processes are paleoclimate, paleodepositional environment, and recent surface weathering. The discussions below will attempt to address the geologic factors that contribute to water quality differences.

The paleoclimatic and paleodepositional environmental influences on rock chemistry in the northern Appalachians resulted in the formation of coal overburden with greatly variable sulfur content (0% to >10% S) and calcareous mineral content (0% to >90% $CaCO_3$). The wide variations in rock chemistry contribute to the wide variations in water quality associated with Pennsylvania's surface coal mines. Figure 1.2 in Chapter 1 shows the frequency distribution (i.e., range) of pH and net alkalinity of mine discharges in western Pennsylvania.

Conventional wisdom, and early research in the northern Appalachians, has suggested that high sulfur coal and rocks are associated with marine environments (Williams, 1960; Guber, 1972). Coals in the northern Appalachians are higher in sulfur than those in the central Appalachians (Cecil, et al., 1985). This difference in coal composition can not be due simply to paleodepositional environment. Marine sediments in the southern Appalachian (Pottsville) rocks are very common. Chestnut (1981), for example, identifies 49 marine zones in the Lee and Breathitt Formations of Kentucky. As a comparison, the number of recognized marine and brackish zones in the Pennsylvanian of Pennsylvania is ~13 (Skema, personal communication, October 13, 1995). If depositional environment was controlling sulfur content in the southern Appalachian coals and rocks, the sulfur should be high, but it is not. Also, acid mine drainage typically is less of a problem in the southern Appalachians than in the northern Appalachians (Figure 8.43) (Wetzel and Hoffman, 1983; Appalachian Regional Commission, 1969).

One aspect of southern Appalachian geology that seems to have received little attention is that calcareous marine zones occur within the Pennsylvanian in Kentucky and southern West Virginia. Chestnut (1981) in discussing marine units in Kentucky with calcareous



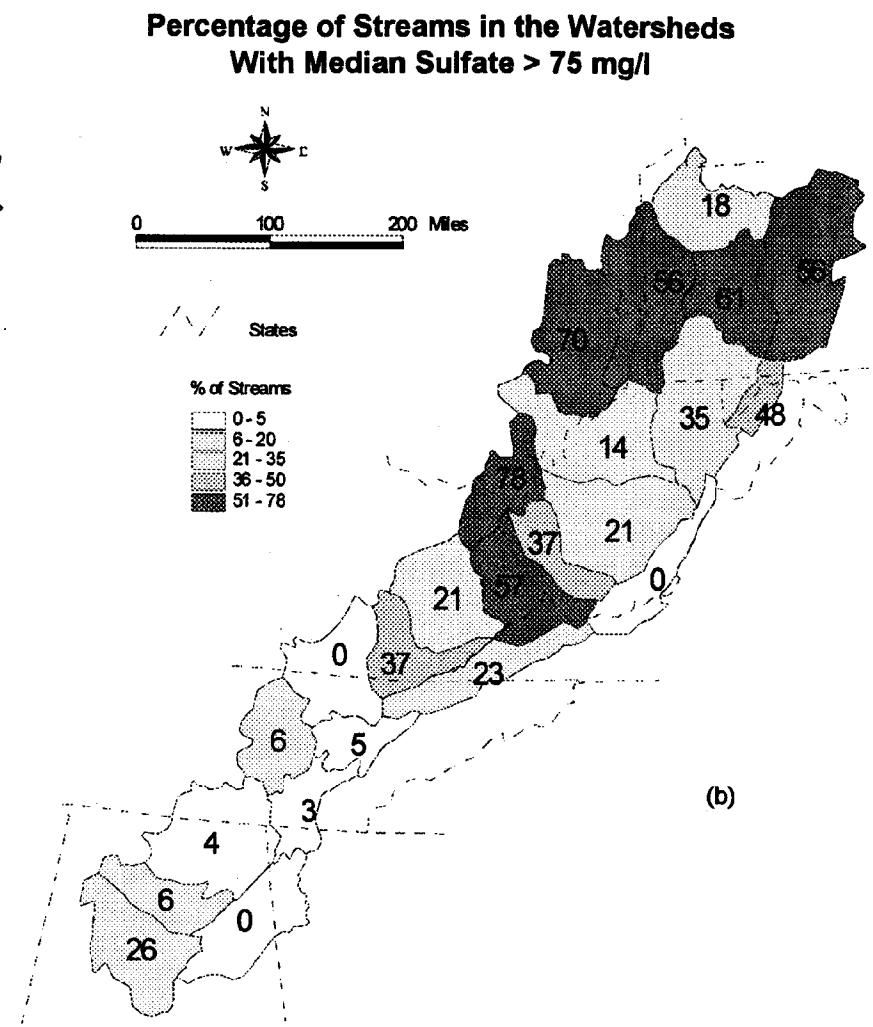


Figure 8.43a and b Percentage of surface water sample stations that had pH < 6.0 (figure a) and sulfate greater than 75 mg/L (figure b) for 24 watersheds in the Appalachian Basin. Data are from Wetzel and Hoffman (1983).

calcareous concretions says "(c)alcite is often in great enough proportion to classify the rock a limestone..." Martino (1994) refers to several calcareous marine zones in southern West Virginia.

Cecil et al. (1985) indicate that sandstones with calcareous cement are absent in the central Appalachians. More recent studies of central Appalachian sandstones indicate otherwise. Englund et al. (1986) describe the sedimentology of the lower Pennsylvanian Pocahontas Formation in southwestern Virginia and southern West Virginia. They indicate that 70 percent of the formation is sandstone which is "in part, calcareous." Chesnut (1992) also identifies calcareous sandstones and siltstones in the Breathitt Group of Kentucky. Powell and Larson (1985) likewise indicate that "calcite is present as a cement and as clasts in some of the sandstone" in the Norton Formation of Virginia. The literature does show that calcareous rocks are present in the southern and central Appalachian Pottsville Group. These calcareous strata along with the low concentrations of sulfur probably explain the lower abundance of acid mine drainage problems in the southern Appalachians.

Paleoclimatic Influences on Terrigenous Rock Mineralogy

Various attempts have been made to reconstruct the paleoclimate of the northern and central Appalachian Basin during the Pennsylvanian. Donaldson et al. (1985a) and Cecil et al. (1985) interpreted paleoclimate from the depositional characteristics and the chemistry of terrigenous sediments within the coal-bearing stratigraphic sequence of the central and northern Appalachians. Phillips et al. (1985) and Winston and Stanton (1989) derived their interpretations of climate from vegetational changes. Figure 8.44 shows a side by side comparison of these various climatic interpretations. As can be seen, there is less than a consensus, especially within the Pottsville Group. We will, however, only concern ourselves with the uppermost Pottsville and higher strata; that is, the strata that occurs in Pennsylvania. The four models differ as to how wet or dry the upper Pottsville was, but they agree that at the time of deposition of the Allegheny Group, the climate was moderately wet, although drying upward. All models agree that during deposition of the Conemaugh Group, it was dry. The base of the Monongahela was wet, and probably became drier higher up in the section. Cecil et al. (1985) and Donaldson et al. (1985a) concluded that the period during which the Dunkard was deposited was comparatively dry.

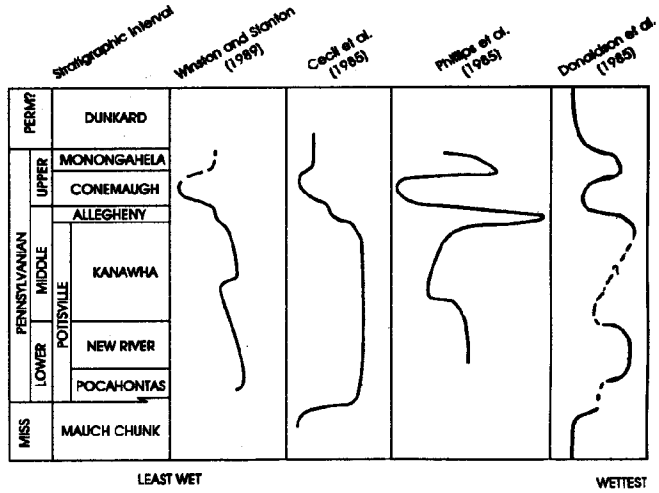


Figure 8.44 Comparison of paleoclimatic interpretations during the late Mississippian through Permian? from four studies. Curves show relative wetness. Wetter periods were probably "ever-wet", i.e., wet year-round (Pottsville time in southern Appalachians), the driest period (Conemaugh time) was probably semi-arid, and in-between curves represent yearly climate that was seasonally wet and dry. Sedimentological features in the Monongahela and Dunkard Groups also indicate periods that were semi-arid. Each curve is relative only to itself. The Cecil et al. and Donaldson et al. curves are based on sedimentological characteristics, and the Phillips et al. and Winston and Stanton curves are based on paleobotanical interpretations.

Cecil et al.'s (1985) interpretation was that the climate was an "ever-wet" tropical one during deposition of the early Pennsylvanian Pottsville Group (the Kanawha, New River, and Pocahontas Groups of southern West Virginia), but was more seasonally "wet-dry" in the stratigraphically higher sections. Cecil et al. (1985) suggest that climate affected the shape of the peat deposit, which in turn affected the chemistry of the swamp (and ultimately the chemistry of the coals). During the early Pennsylvanian (Pottsville Group coals), the ever-wet conditions resulted in domed peat swamps which had rainfall as their source of water. The swamp water would be low in dissolved solids, and nutrients and the low pH (<4) conditions would not be conducive to pyrite formation or accumulation of solids (ash). During the middle and later Pennsylvanian (Allegheny, Conemaugh, and Monongahela coals) the swamps were planar and water entered the swamp from ground and surface sources. This resulted in a swamp with higher pH (4 to ~7), more dissolved solids, and greater availability of nutrients (Cecil et al., 1985). Additionally, periodic dry conditions would allow the surface of the peat to dry, oxidize and de-

grade, thus increasing ash content. These conditions, taken together would result in higher sulfur and ash in the northern Appalachian coals. Cecil et al. use this theory to explain why the coals of the southern Appalachian Pottsville Group are lower in sulfur (typically <1% sulfur) and ash (typically lower than 10% ash) than the younger coals of the northern Appalachians (typically >1% sulfur and >10% ash) (Figures 8.45 and 8.46, and Table 8.8).

Sulfur in Pennsylvania's anthracite is much lower than in coals of the bituminous region. On average the sulfur is about 0.8% (Wood et al., 1986).

As with coal quality, Cecil et al. (1985) and Donaldson et al. (1985) conclude the associated terrigenous rocks are also influenced by paleoclimate. Figure 8.47 (Cecil et al., 1985) and Figure 8.48 (Donaldson et al., 1985a) show the distribution of important rock types and minerals throughout the Pennsylvanian and lower Permian. The drier conditions during the Upper Pennsylvanian (upper Allegheny and younger strata) resulted in the common occurrence of freshwater limestones, calcareous cements, and calcareous concretions in nonmarine sandstones and shales.

Figure 8.49 presents plots of percent sulfur in roof rock and floor rock as functions of percent sulfur in coal for 12 coal seams from four different coal fields.

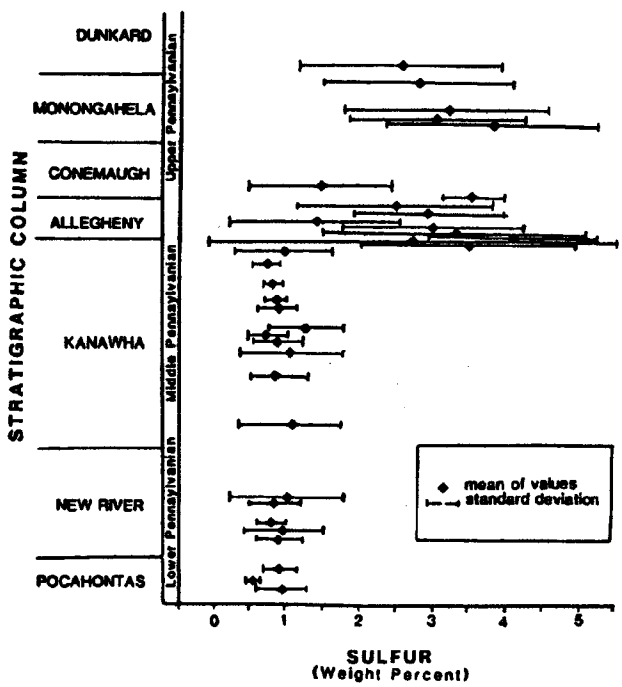


Figure 8.45 Stratigraphic variation of sulfur content of 34 coal beds of the central Appalachians, including Pennsylvania. Figure from Cecil et al. (1985).

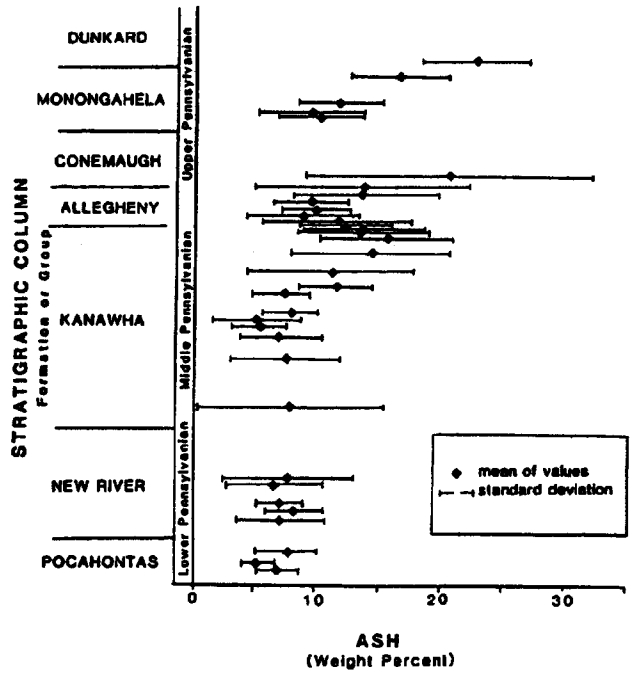


Figure 8.46 Stratigraphic variation of ash content of 34 coal beds of the central Appalachians, including Pennsylvania. Figure from Cecil et al. (1985).

Table 8.8 Means (x) and standard deviations (sd) for coals by formation/group in the Pennsylvanian of the northern Appalachian Basin. (Adapted from Cecil et al., 1985).

		Total Sulfur		Ash	
Formation	**Number of Samples**	**x**	**sd**	**x**	**sd**
Monongahela	159	3.4	1.4	10.8	4.2
Conemaugh	8	2.2	1.3	18.1	10.6
Allegheny	296	2.9	1.5	11.2	5.5
Kanawha	73	0.9	0.5	9.2	5.3
New River	74	0.9	0.4	7.1	3.5
Pocahontas	21	0.8	0.3	6.8	2.1

Although the sample is small, the data from the Appalachian Basin is consistent with the findings of Cecil et al. (1985) in that pyrite is rare in the older sediments of the southern Appalachians, but common in the younger sediments of the northern Appalachians (Figure 8.47). For comparative purposes, data from the Powder River Basin and the Illinois Basin are also shown in Figure 8.49. The low sulfur of the freshwater-deposited Powder River Basin sediments and the high sulfur of the mostly marine-deposited Illinois Basin sediments are consistent with paleodepositional models, which will be discussed in the next section. Assuming the data in Figure 8.49 is representative, it appears that low-sulfur coals, such as in the southern Appalachian and Powder

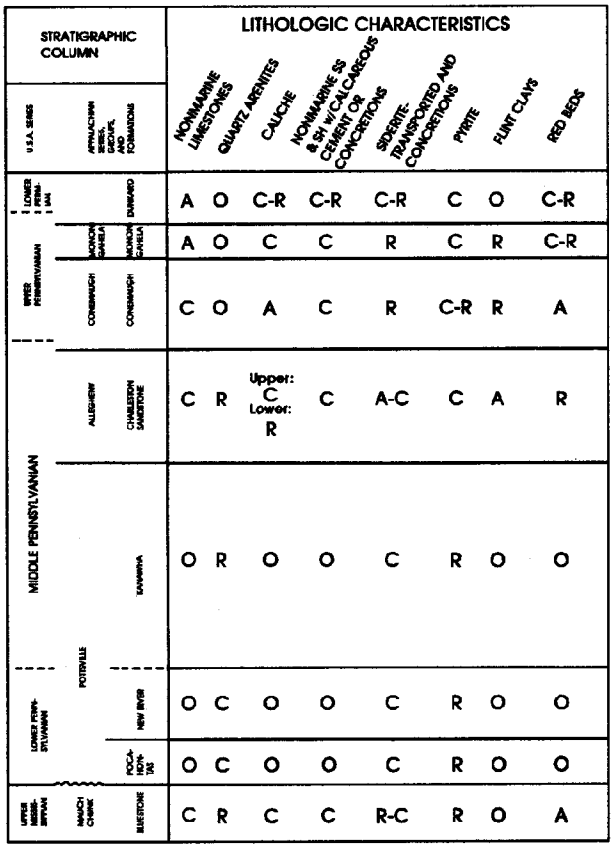


Figure 8.47 Characteristics of lithologies from strata in the central Appalachian Basin, including Pennsylvania (A = abundant; C = common; R = rare; O = absent). Figure from Cecil et al. (1985).

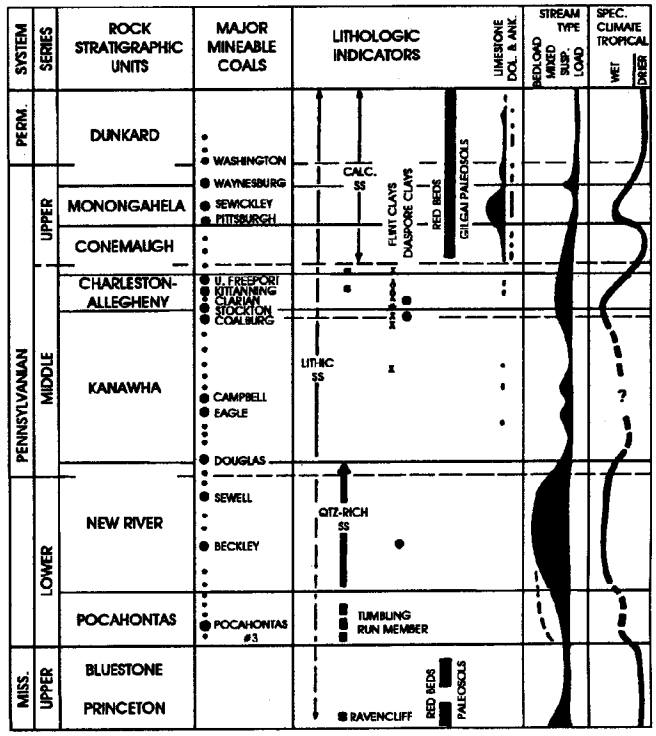


Figure 8.48 Lithologic indicators of paleoclimate in the Appalachian basin, including Pennsylvania. Modified from Donaldson et al. (1985).

River Basins, are associated with low-sulfur roof and floor rock. High-sulfur coals, such as those in the northern Appalachian and Illinois Basins, may or may not have high sulfur roof and floor rocks.

Paleodepositional Environmental Influences on Rock Mineralogy

A second category of geologic processes that influenced the chemistry and mineralogy of Pennsylvanian Period coal-bearing sediments, including the distribution of calcareous and pyritiferous rocks, was paleodepositional environment. Typically, within the Pennsylvanian of Pennsylvania, paleoenvironment is classified into three categories (Williams, 1960): freshwater, brackish, and marine. These three categories are not evenly distributed geographically or stratigraphically. Figure 8.2 shows that marine and brackish units are restricted to the upper Pottsville/ lower Allegheny and lower Conemaugh Groups. Freshwater limestones are principally found above the middle of the Allegheny Group. As discussed in the section on the Allegheny Group, conchostracans probably represent marginal brackish, rather than continental (fresh-water) conditions. These paleoenvironmental influences are only important, from a mine drainage standpoint, where there are economic coals; i.e., the Allegheny and Monongahela Groups (Figure 8.2). Figure 8.50 is a schematic showing "rule-of-thumb" trends in stratigraphy, and acid-potential, of the lower Allegheny and upper Allegheny strata. In general, the lower Allegheny becomes more marine influenced to the west.

Many researchers (Hornberger et al., 1981; Williams et al., 1982; diPretoro, 1986; Brady et al., 1994; and Perry and Brady, 1995) have concluded that the key factor regarding the prediction of mining-associated water quality is the amount of calcareous material encountered. The amount of sulfur (pyrite) present is of secondary importance. Paleoenvironment is an important control on the distribution of carbonates and pyrite. Marine limestones, such as the Vanport and Brush Creek can have significant alkalinity generating capability, and mines that encounter these limestones generally produce alkaline drainage. Freshwater limestones are common in the upper Alle-

gheny and Monongahela Groups. Mines that encounter these limestones, likewise, routinely produce alkaline drainage. Brackish environments typically lack calcareous minerals, with siderite being the only carbonate present. Coal overburden of marine and brackish origin often have much greater thicknesses of high sulfur strata than overburden of "freshwater" origin. Brackish environments therefore frequently have the unfortunate attributes of high sulfur rock with a lack of calcareous minerals, which often results in acid mine drainage. These paleoenvironmental influences on the distribution of carbonates and sulfur (pyrite) will be examined in detail below.

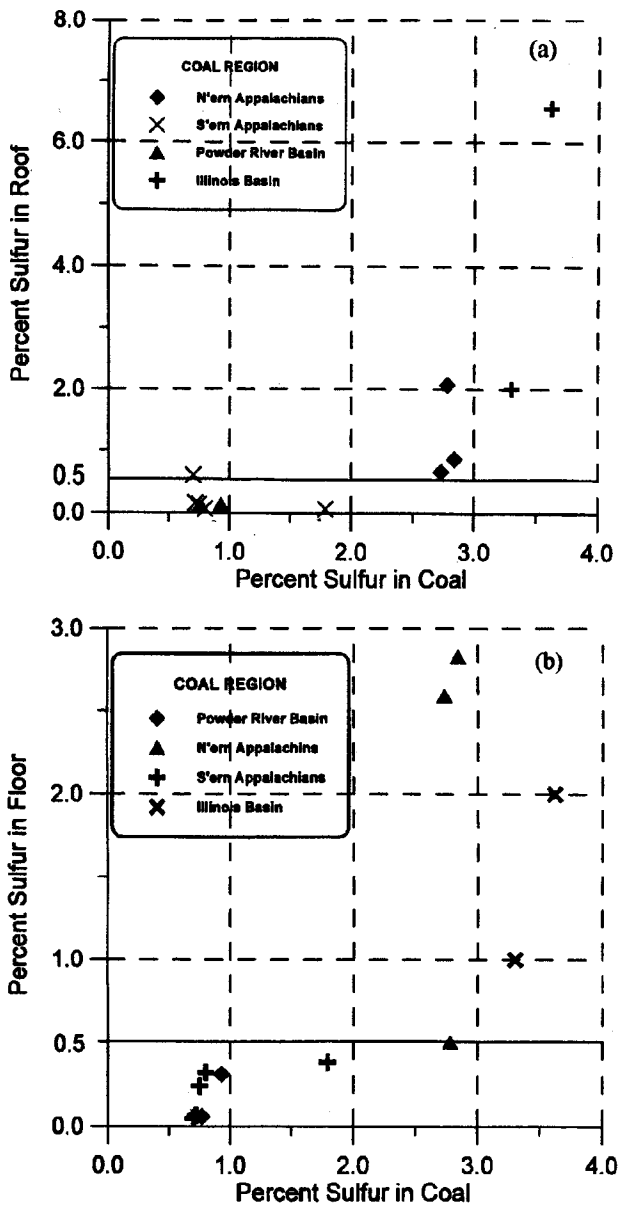


Figure 8.49 Plots of sulfur in coal and sulfur in roof rock (figure a) and floor rock (figure b) for the northern Appalachian, southern Appalachian, Powder River, and Illinois Basin coal fields. The 0.5% sulfur line that intercepts the Y-axis divides "high-sulfur" from "low-sulfur" rock. Data are from Maksimovic and Mowry (1993).

Depositional Environments of Carbonate Minerals - Carbonate minerals form under marine and freshwater environments. Both environments are represented in Pennsylvania's Pennsylvanian stratigraphy.

Marine Carbonates - The climatic models of Cecil et al. (1985) and Donaldson et al. (1985a), discussed above, only consider terrigenous sediments. Marine environments are likewise important in contributing to overburden mineralogy. The formation of limestone, or other calcareous rocks, under marine conditions may have little or nothing to do with climate, but can play a significant role in preventing acid mine drainage in Pennsylvania and elsewhere in the Appalachian Basin. Marine limestones significantly contribute to the alkaline water of the Illinois Basin and the Western Interior Coal Province.

As discussed previously and shown in Figures 8.2, 8.7, and 8.12, marine rocks can be an important component of coal overburden in Pennsylvania. Marine sediments are also very common in the southern Appalachian (Pottsville) rocks [see for example: Alabama - Horsey (1981), Pody (1987), and Demko and Gastaldo (1996); Tennessee - Dorsey and Kopp (1985); Kentucky - Chestnut (1981); and southern West Virginia - Martino (1994, 1996)].

Marine rocks in Pennsylvania occur principally in the lower Allegheny Group and the Glenshaw Formation (Figure 8.2). The rocks represent open marine to marginal marine (brackish) conditions. The open marine facies are frequently limestone or calcareous shales. Brackish facies often lack alkalinity generating calcareous minerals, although siderite ($FeCO_3$) can be abundant. Conchostracans probably represent a marginal brackish environment with some marine influence. If marginal-brackish environments are included, some marine influence is present in Pennsylvanian Period rocks in Pennsylvania from the Pottsville Group through at least the Skelly horizon of the Glenshaw Formation.

The Allegheny Group Vanport member is a good example of the nature of marine limestones. The Vanport horizon, which occurs above the Clarion coal, is often transitional laterally (and vertically) from marine

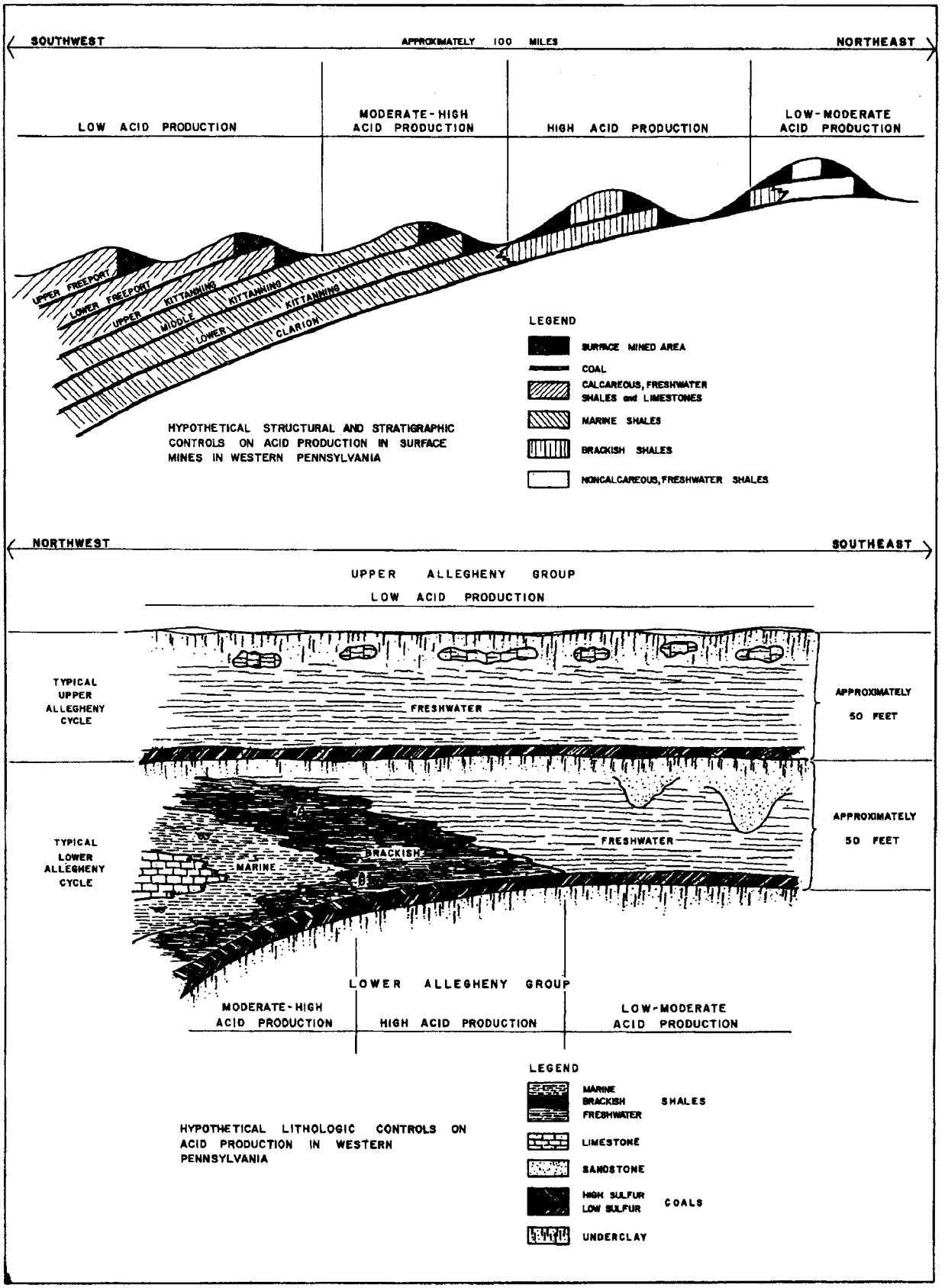


Figure 8.50 Schematic summary of hypothetical lithologic stratigraphic and structural controls on acid mine drainage production for the upper and lower Allegheny Group. From Hornberger (1985).

to brackish conditions. Figure 8.8 shows regional changes in thickness of the Vanport limestone.

Skema et al. (1991, and personal communication, 1997) discussed the facies distribution of the Conemaugh Group Brush Creek marine zone. The Brush Creek Marine zone is present almost everywhere within its outcrop belt. Because the limestone or a calcareous facies is typically present where the Brush Creek coal is of mineable thickness, the drainage is typically alkaline.

In addition to limestones, other marine sediments are often calcareous. This is illustrated by NPs above 30 ppt $CaCO_3$ in Figures 8.7 and 8.12 for marine-deposited lower Allegheny rocks.

Freshwater carbonates - Freshwater calcareous rocks, including lacustrine limestones, occur in the upper portion of the Allegheny Group and throughout the Monongahela and Dunkard Groups (Figure 8.2). The extensive lateral distribution of some of these limestones was discussed in the stratigraphy section of this chapter. These limestones, and other calcareous rocks, are responsible for the alkaline nature of many of the mining associated discharges within these stratigraphic horizons. Freshwater calcareous rocks also occur in the Conemaugh Group, and are important when they occur above the upper Freeport coal. Higher in the section they are typically less important in terms of mine drainage quality because Conemaugh coals are rarely mined. Additionally, they often occur below the coals and can be thin and discontinuous. The discontinuous nature is evident by comparing drill holes DH-12 and DH-3 in Figure 8.25. Both holes were drilled at the same mine site. DH-12 shows the freshwater limestone below the upper Bakerstown coal. The limestone is absent in DH-3. Our experience is that these "limestones" are often "dirty" with a high component of clay and silt. At places this stratigraphic interval is represented by calcareous rocks with less than 50% calcium carbonate, and therefore by definition not a limestone.

In addition to freshwater limestones, the upper Allegheny Group frequently contains an abundance of calcareous claystones, mudstones and siltstones. Figure 8.20 shows a stratigraphic section in Fayette County, between the upper Kittanning and lower Freeport coals. Much of this interval is distinctly calcareous (>10% $CaCO_3$), but only small portions could be classified as limestone (> 50% $CaCO_3$).

As discussed earlier, the Monongahela and Dunkard Groups have numerous thick, laterally persistent, lacustrine limestones. Figure 8.2 shows that >50% of the rocks of the Monongahela and Dunkard Groups are calcareous.

Depositional Environments of Iron Sulfides - Much research on the relationship between sulfur and depositional environment has been done on coal because of its economic importance. Comparatively little research, however, has been done on the paleodepositional relationships to sulfur in the rocks associated with coal, despite its importance in the production of acid mine drainage. The following discussion is based upon work with modern sediments, the few studies that have been done on coal associated rocks, studies of sedimentary rocks that are not coal bearing, and our own observations of coal-bearing rocks. Sulfur in coal will be discussed in most detail because of the plethora of studies on this subject.

Marine, Brackish and Freshwater Environments - Coal swamps and associated sediments form under a variety of depositional environments. These environments include alluvial plain, upper delta plain, lower delta plain, marginally brackish, transitional (brackish), and marine environments.

Guber (1972) found that the highest sulfur in rocks overlying the lower Kittanning coal in north-central Pennsylvania was associated with sediments deposited under brackish conditions (identified using the phosphatic brachiopod *Lingula*). Paleoenvironmental determinations were based on the paleontological work of Williams and Keith (1963) which was supplemented by geochemical studies by Degens et al. (1957). At one location the lower Kittanning coal was directly overlain by shale with conchostracans, and the conchostracan-bearing rock was low sulfur. Guber (1972) also studied a section containing the Brush Creek (Glenshaw Fm.) marine zone. The outcrop had calcareous marine fossil-bearing rocks and brackish *Lingula*-bearing rocks. The brackish rocks were higher in sulfur than the marine rocks. He concluded that a brackish environment provides optimum conditions for pyrite formation, with sulfate derived from the brackish water and iron from the nearby terrestrial sources. These sources, coupled with high organic content, provide optimum conditions for pyrite formation; that is, a reducing environment with an ample supply of sulfur and iron.

A relationship between depositional environment and sulfur in coal has been demonstrated for many ar-

eas. Williams and Keith (1963) in their classic study of sulfur in the lower Kittanning coal of Pennsylvania, demonstrated that the sulfur in the coal was related to the paleodepositional environment of the roof rock. Brackish and marine roof rocks overlay high sulfur coal, whereas non-fossiliferous and conchostracan-bearing rocks [what Williams (1960) referred to as "freshwater"] overlay lower-sulfur coal (Table 8.9). The mean sulfur for coal overlain by marine rocks was 3.15%, for brackish (transitional) rocks 2.45%, and for freshwater (continental) rocks 1.73%. The upper Freeport coal which is overlain entirely by unfossiliferous (no fauna) or conchostracan-bearing rocks was used as a control. It did not show any significant regional differences in percent sulfur. The average percent sulfur for the upper Freeport coal was 2.09%, which is intermediate between the freshwater and brackish values for the lower Kittanning coal. It is interesting to note that at one standard deviation the average sulfur for the upper Freeport shown in Table 8.9 overlaps with the average sulfur for the lower Kittanning. Also the upper Freeport average sulfur is higher than the "freshwater" portion of the lower Kittanning. As stated above, it is not the sulfur content that makes the water associated with the Freeport coals of better quality than lower Allegheny County, but the presence of freshwater calcareous rocks. Our experience has shown that the lower Kittanning overburden even where it is conchostracan-bearing (such as in northeastern Cambria County) lacks calcareous strata and produces moderately acidic drainage.

Table 8.9 Summary statistics of sulfur in the lower Kittanning and upper Freeport coals in the northern bituminous coal field of Pennsylvania. Adapted from Williams and Keith (1963).

SAMPLING UNIT	N	x	s
L. Kittanning coal - total area	255	2.64	1.16
- marine area	71	3.15	1.17
- brackish area	48	2.45	1.03
- freshwater area	125	1.73	0.81
U. Freeport coal - total area	183	2.09	0.85

When Williams and Keith (1960) did their field work, good stratigraphic correlations across the state were lacking. Work by the Pennsylvania Geological Survey from the late 1960's to the present has helped to clarify many correlation problems. Detailed mapping in Clearfield County that post-dated Williams' work was used in the construction of Figure 8.11. Although Figure 8.11 shows somewhat different facies boundaries compared to the map by Williams and Keith (1963), their conclusions are probably still largely correct. Irrespective of correlation mistakes, Williams' conclusions regarding the relationship of roof-rock facies to coal chemistry should be valid, in other words, even if the correlations were incorrect (for example, Clarion or middle Kittanning sampled instead of lower Kittanning), marine-, brackish-, and conchostracan-roofed coals and their respective coal analyses would have been compared and used in the compilation of Table 8.9. Also, it appears from examples in this chapter that shales from the conchostracan-bearing areas have lower sulfur than shales from areas of marine or brackish environments, although a larger sample population is needed to quantify this.

Relationships between sulfur and depositional environment for coal have also been documented in Texas and Australia. The Eocene coals of Texas typically have highest sulfur (1.5 to 2%) associated with coals deposited in marine and brackish lagoonal environments, while alluvial plain coals exhibit the lowest sulfur values (< 1%). Deltaic coals are intermediate in sulfur (1 to 1.5%) (Kaiser 1974, 1978). Permian coals in Australia deposited in lower delta plain facies usually contain > 0.55% sulfur, whereas those associated with braided fluvial facies found further inland, usually on alluvial plains, contain < 0.55% sulfur. Upper delta plain coals, which are located between the lower delta plain and the alluvial plains, are typically of intermediate sulfur (Hunt and Hobday, 1984).

Various studies have looked at the relationship between the distance from the coal to overlying marine rocks. The Pennsylvanian Period Herrin (No. 6) coal in Illinois is high sulfur (>2.5%) where overlain by the marine Brereton Limestone, however where the coal is separated from the limestone by the crevasse-splay deposited Energy Shale the sulfur is lower (<2.5%) (Figure 8.51) (Gluskoter and Hopkins, 1970). Figure 8.52 shows the relationships between the contemporaneous sandstone channel, coal and Energy Shale, and the marine Brereton Limestone. A study of Paleogene coals in Japan similarly shows a relationship between the amount of pyrite present in the coal and the thickness of freshwater sediments separating coal from overlying marine sediments (Figure 8.53) (Shimoyama, 1984). Numerous studies in the Illinois Basin, for various coal seams, relate low sulfur coal to freshwater shale roof-rock (e.g.: Murphysboro coal - Jacobson, 1983; Springfield coal - Eggert, 1984; Herin No.6 coal

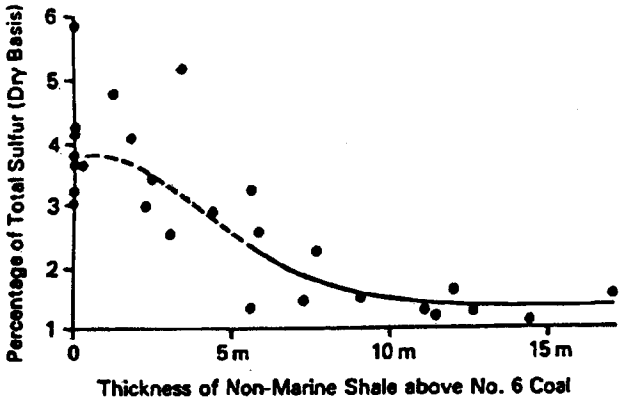


Figure 8.51 Relationship of total sulfur content of the Herrin (No. 6) coal with thickness of non-marine shale which separates the coal from overlying marine sediments. See Figure 8.52 for a cross-section showing relationships between the coal, non-marine Energy shale, and the marine Brereton limestone. After Gluskoter and Hopkins (1970) from McCabe (1984).

- Gluskoter and Hopkins, 1970, Kravits and Crelling, 1981, and Burk, et al., 1987).

The high sulfur (>5%) in Pennsylvanian Period coal in Atlantic Canada (Gibling et al., 1989) and Cretaceous coal in Spain (Querol et al., 1991, 1992) have been attributed to erosion of older upstream evaporite sediments containing gypsum; the sulfate from the gypsum providing the source of the sulfur in the coals. There are Spanish coals with clearly associated marine strata that have lower sulfur than the evaporite influenced coals lacking marine affinities. These studies suggest that dissolved sulfate sulfur eroded from upstream sources can contribute to the sulfur in coal. The high sulfur of the Canadian coals may have another explanation. It was assumed until only recently, after 150 years of research, that because of their association with freshwater biota and alluvial sedimentary

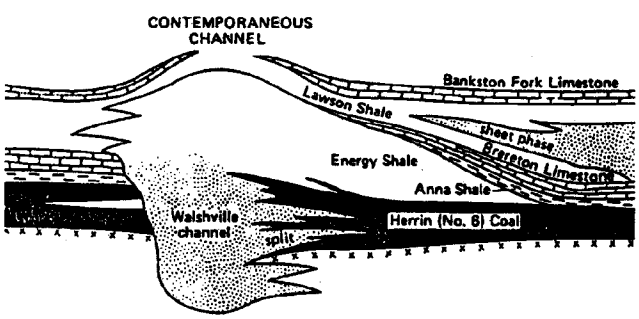


Figure 8.52 Cross-section showing the relationships between the Herrin (No. 6) coal, the contemporaneous Walshville channel, the Energy shale, and Brereton limestone. Modified from Nelson (1983).

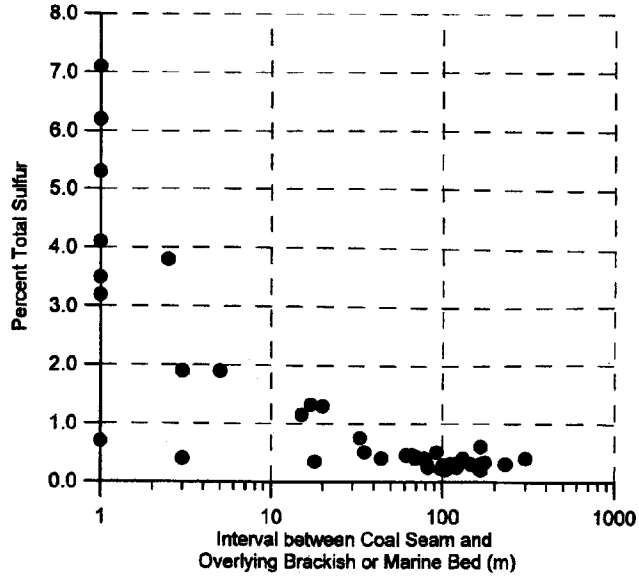


Figure 8.53 Relation of the total sulfur concentration in the main Japanese Paleogene coals to the interval between coal beds and the overlying marine or brackish-water horizons. Modified from Shimoyama (1984).

features that the Atlantic Canada coals were associated with freshwater depositional environments. Wightman, et al. (1993), however, have concluded that deposition took place on a coastal platform, and not the fluvial and lacustrine environments previously proposed. This conclusion was based on the finding of agglutinated foraminifera, which are indicative of marginal marine, tidal-marsh, conditions. These foraminifera are constructed of detrital grains and can remain where calcareous fossils have dissolved. It may be profitable to search for these critters in rocks associated with some of Pennsylvania's high-sulfur "freshwater" coals.

Englund et al. (1986) noted that sulfur in the Pottsville Group Pocahontas No. 3 coal in southern West Virginia and western Virginia was highest at the margins of the deposit (0.9 %) and lowest away from the margins (0.4 %). Two studies of the Allegheny Group upper Freeport coal in southwestern Pennsylvania show similar trends. Skema et al. (1982) found that coal near the margins contained 4 to 5 % sulfur, while coal toward the center of the deposit had 1 to 2 % S. Sholes et al. (1979) found that coal near the margins had 5 to 6 % S, and 3 % or less in the center. In all cases cited above, the coal thins to 0 ft (m) at the margins (i.e., "pinches out"). Thus the thin coal has the highest sulfur. Cheek and Donaldson (1969) also noted an increase in sulfur with decreasing thickness of the upper Freeport coal in northern West Virginia. The upper Freeport coals were deposited in a freshwater (or

more likely a marginal brackish) depositional environment. A couple of factors may contribute to this distribution of sulfur. The margins of the peat swamp would have more access to dissolved solids (e.g., sulfate) carried by streams or estuaries draining the swamps, whereas away from the margins the water would be primarily from precipitation. A second factor is that the margins probably maintained a higher pH due to influence from stream or estuary water compared to the lower pH of the swamp interior. Higher pH is more conducive to pyrite formation (Cecil et al., 1985).

Sulfur in Pennsylvania's anthracite is much lower than in coals from the bituminous region. On average the sulfur is 0.48% organic sulfur, 0.35% pyritic sulfur, and 0.02% sulfate sulfur (Wood et al., 1986). Sulfur generally increases to the west and north, and is highest in the northern field (Figure 8.54). Wood et al. proposed a couple of explanations for the low sulfur. One was that metamorphism may have somehow reduced the sulfur. Another was that the coals, and associated rock, were deposited on an alluvial plain, with virtually no marine influence and therefore away from a source of sulfur. The Mill Creek limestone of the northern field is the only known marine unit. Marine waters may have had more influence in the Northern Field, thus higher sulfur coals.

Some of the examples cited above show well documented relationships between sulfur in coal and paleodepositional environment. However, even where present, the relationships between sulfur and paleodepositional environment are region specific. For example, sulfur in the Eocene Texas coals and Permian Australian coals for a given paleodepositional environment are lower in sulfur than comparable Allegheny Group coals in Pennsylvania. Also, marine rocks commonly overlie coals of the southern Appalachians, but the sulfur is generally lower in these coals than in freshwater coals of the northern Appalachians. The examples from Atlantic Canada and Spain, with a possible upstream source of sulfate, reveal further complexities that may be involved. Therefore, the use of "high" and "low" sulfur as a predictive tool for paleodepositional environment should be used with extreme caution. Only affirmative paleontological and sedimentological evidence should be used to determine paleodepositional environment, and even this can be problematic. It took geologists 150 years to find evidence of marine influence on coals of Maritime Canada (Wightman, et al., 1993) and conchostracans, the "freshwater" indicator in Pennsylvania, are probably marginal-brackish.

Vertical Distribution of Sulfur within a Coal Seam - Changes in percent sulfur have been observed at a more local level than discussed above. Here we will examine vertical variations in sulfur content in coals and the factors which may control this variation.

Shimoyama (1984), in a study of Japanese Paleogene (early Tertiary) coal seams, related depositional environment of roof strata and floor strata with the percent sulfur at the top and bottom of coal seams. Coal seams overlain by marine roof strata had high percentages of sulfur at the top of the seam, and coals underlain by marine sediments had high sulfur at the base of the coal. Coal associated with freshwater deposits had uniform and comparatively low sulfur throughout the coal. Although this may explain the Japanese coals examined, high sulfur at the top and bottom of a coal seam appears to be very common regardless of paleodepositional environment.

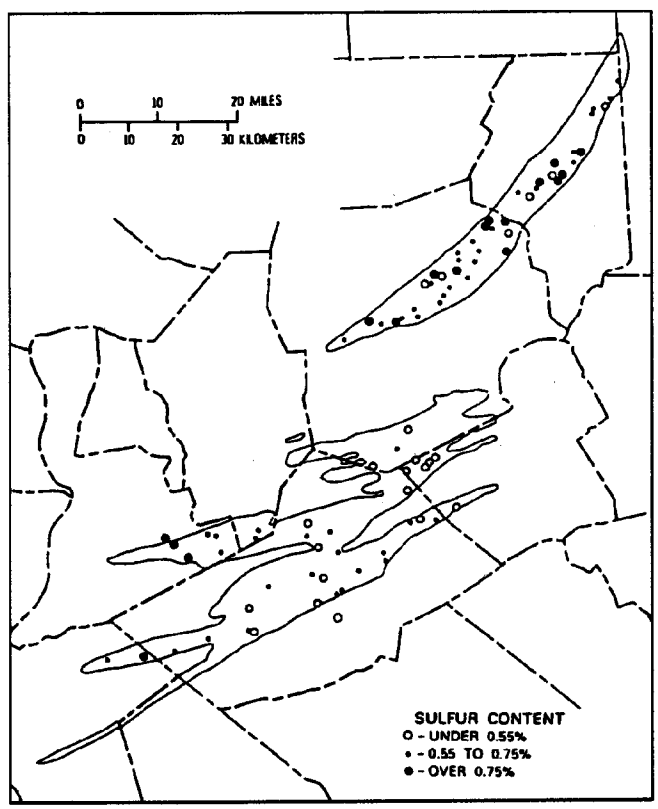


Figure 8.54 Percentage of sulfur in anthracite samples from the Pennsylvania Anthracite region (from Wood et al., 1986).

Numerous studies of the vertical distribution of sulfur in coal have been done for coals around the world, encompassing various geologic periods and coal rank. Increased sulfur at the top and bottom of coal seams appears to be the rule rather than the exception. Suggate (1995) in a study of subbituminous Miocene Epoch coal in New Zealand observed that sulfur content decreased from roof to floor, with a minor increase near the floor. The percent sulfur at the top of coal varied from > 6% to < 2%, however the sulfur in the middle of the coal seam was always 1.5 to 2.0% less. A study of New Zealand Cretaceous coals deposited under marine conditions (Sherwood et al. 1992) also noted higher sulfur at the top of the seam. A bituminous coal of Cretaceous Period from Alberta, Canada averaged only 0.3% sulfur, and the coal was deposited "well removed from marine clastic influences" (Langenberg et al. 1992). This coal showed sulfur elevated at the base and to some extent at the top. The Tertiary "Big George" coal deposit in the Powder River Basin of Wyoming is a 200-ft (60 m) thick subbituminous coal associated with freshwater depositional environments. This coal has total sulfur typically below 0.3%, however the bottom 0.6 ft (0.2 m) has over 1% sulfur (Kent, 1986). The trend of higher sulfur in the upper and lower portions of a coal seam have also been observed in the Eocene lignite coal deposits in Texas (Arora et al. 1980).

Another example in the literature of high sulfur at top and bottom of coal is a coal in the Cherokee Group (Pennsylvanian) in southeastern Iowa (Biggs and Bruns, 1985). The upper 28% of the coal contained 67% of the pyrite, the middle 47% contained 19% of the pyrite and the lower 25% contained 14% of the pyrite. The coal was bounded top and bottom by pyrite-rich shales. The paleoenvironment is not discussed, but most coals in this part of Iowa have associated marine sediments (Howes, 1990).

Similar trends to those described above have been observed in coal seams of the northern Appalachian basin. Reidenour et al. (1967) found higher sulfur at the top and (sometimes) bottom of Clarion and lower Kittanning coals in Clearfield County that have roof rocks that were deposited in a brackish depositional environment. Appalachian coals interpreted to have been deposited in a freshwater depositional environment also show high sulfur at the top and bottom of the seam. This has been observed for the Pittsburgh (Donaldson, et al., 1979) (Figure 8.55), Redstone (Hawkins, 1984), and Waynesburg (Donaldson et al., 1985b) (Figure 8.56) coals of northern West Virginia and southwestern Pennsylvania. High sulfur has also

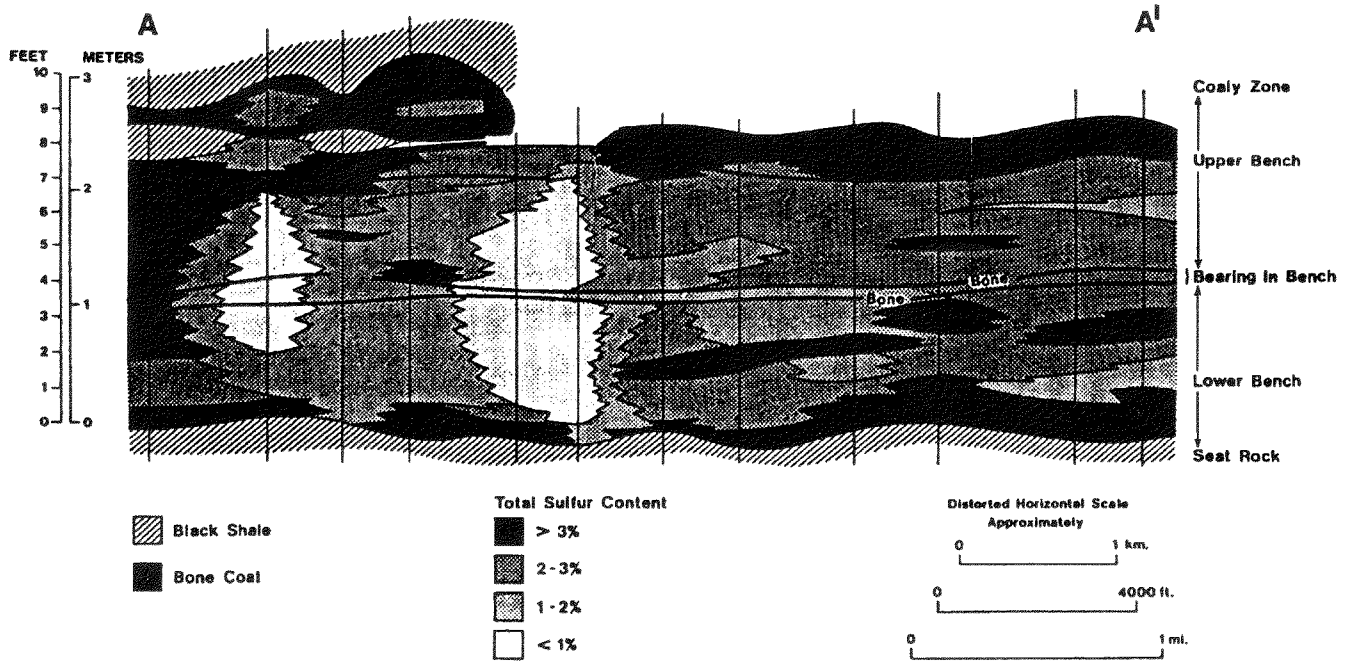


Figure 8.55 Stratigraphic cross-section of total sulfur facies in the Pittsburgh coal. Cross-section is oriented approximately north-south and is located in northern West Virginia and southwestern Pennsylvania. Precise location is not given. Note that the highest sulfur is at the top and bottom of the coal seam. From Donaldson et al. (1979).

been observed at the top and bottom of the upper Freeport coal by Cheek and Donaldson (1969) in northern West Virginia.

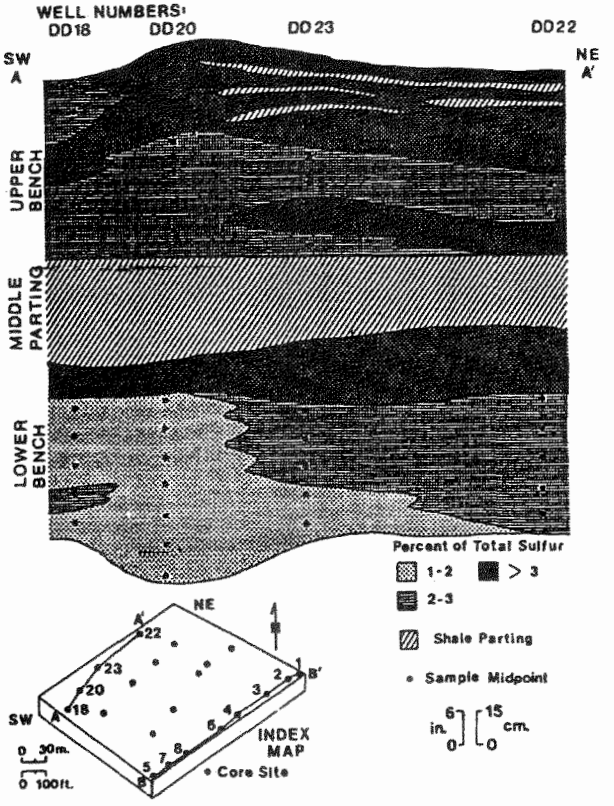


Figure 8.56 Cross-section showing total sulfur content of the Waynesburg coal in a strip mine in northern West Virginia. Note that the highest sulfur is at the top of each of the two benches of coal. From Donaldson et al. (1979).

The findings for vertical variations in sulfur concentration within a coal seam are consistent with the distribution of sulfur in modern thick peat deposits. Modern peat deposits frequently show high sulfur at the base of the deposit, for example Staub and Esterle (1994) attribute the high sulfur at the base of a peat deposit on Sarawak, East Malaysia to initial conditions being "mangrove and *Nipa* vegetation" growing on a mudflat under brackish to marine conditions with waters rich in sulfate. This organic rich environment would have near neutral pH and abundant iron, conditions favorable for pyrite formation. Neuzil et al. (1993), likewise found the highest sulfur in the bottom of the peat in the Riau and West Kalimantan provinces of Indonesia. Sulfur values for the basal peat were ~0.3 % (with a high of 0.56 %), whereas the upper peat was less than 0.2 %. The underlying sediments were of marine origin and the authors suggest this may have supplied sulfur to the lowest peat horizons. Esterle and Ferm (1994) looked at thick peat deposits at Sarawak, Malaysia, and Sumatra, Indonesia. Sulfur in the basal one meter of the deposit was 2.4 to 4.5%, and was 0.3% or less above this zone.

It can not be assumed that high sulfur in the upper portion of a coal bed, or high sulfur within a coal bed, are evidence of marine influence. Paleoenvironmental interpretations using sulfur alone, may not be valid. The fact that high sulfur is frequently found at the top and bottom of coal seams, regardless of paleoenvironment, is important from a mining standpoint. The top and bottom of a coal seam are the most likely to be left behind on the mine site as "pit cleanings" because of high sulfur or ash, or as coal that is not recoverable in the mining process. The acid potential from this source must be considered in any evaluation of potential acid-materials problems.

Surface Weathering

All of the discussions so far have involved geologic processes that occurred hundreds of millions of years ago, during the Pennsylvanian. These include the controls that paleoclimate and paleodepositional environment had on overburden mineralogy. This section will deal with a much more recent geologic process, the near surface physical and chemical weathering of rock which has occurred within the past million or so years. The significance of this influence on the distribution of carbonate and sulfide minerals (pyrite) can be as great as those that occurred in the more distant past. The discussion will look at weathering south of the glacial margin and within the glaciated portion of the Appalachian Plateau. Weathering results in the near surface removal of carbonates and sulfide minerals; carbonates by dissolution and sulfides by oxidation. This zone is usually recognizable by the yellow-red hues (indicative of oxidized iron) of the rocks. Generally, in the unglaciated portions of the Appalachian Plateau, the intensely weathered zone extends to 20 to 60 ft (6 to 20 m) below the surface.

Weathering of Bedrock on the Appalachian Plateau

Chemical weathering of bedrock is enhanced by physical factors such as stress-relief fracturing on hill slopes and bedding-plane separations due to unloading. Clark and Ciolkosz (1988) have suggested that periglacial conditions during the Pleistocene contributed to the shattering of near-surface rock. Kirkaldie (1991), in a study of weathering of bedrock on the northern Appalachian Plateau, observed that the maximum thickness of weathered bedrock beneath glacial deposits was similar to the maximum thickness of

weathered bedrock in unglaciated regions. The distribution of thickness of the weathered zone beneath the glacial deposits, however, was different, with less weathered rock typically beneath glaciated areas (Figure 8.57). This is attributed to erosion of much of the weathered surface material by glaciers. The findings of Kirkaldie suggest that (1) the bedrock weathering occurred prior to the last glacial period, or that (2) in the non-glaciated areas the rate of weathering has been balanced by the rate of erosion. No studies of weathering rates have been done for the Appalachian Plateau, so the second theory has not been tested. Whatever the method, and whatever the duration of time, shattering of rock increases surface area and thus provides greater area for contact with water and air, and weathering is accelerated. These processes acting together also increase the permeability of the weathered zone. As discussed in Chapter 10 the ground water associated with the weathered zone is dilute, in terms of dissolved solids, because readily soluble products have been removed by chemical weathering.

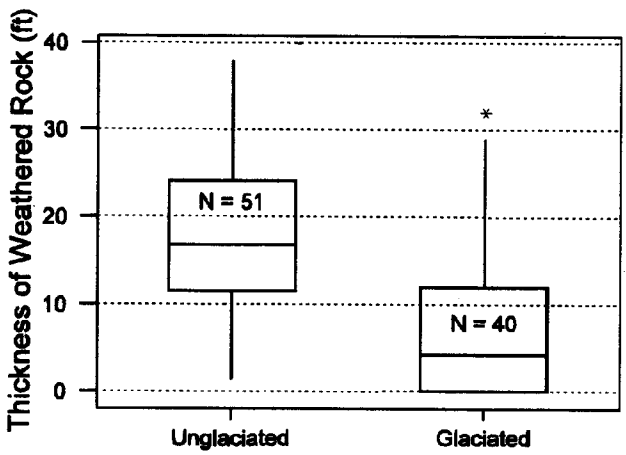


Figure 8.57 Distribution of the thickness of weathered bedrock in glaciated and unglaciated portions of the Appalachian Plateau in Pennsylvania. The large box encloses the 25th and 75th percentiles. The horizontal line within the box is the median, the "whiskers" indicate the range of data. Data are from Kirkaldie (1991).

Chemical weathering is also influenced by lithology. Coarser, more permeable lithologies may allow oxidation to extend to a greater depth. Kirkaldie (1991) measured the depth of the highly weathered zone, noting the type of cover, amount of cover, lithology, and topographic position. In unglaciated terrain, he noted that the maximum thickness of highly weathered rock was 28.9 ft (8.8 m) in sandstone, and only 11 ft (3.3 m) in shale. However, the lithologic difference was not the only variable.

This weathered-rock zone exists throughout the Appalachian Plateau. In spite of this it has been little studied. Smith and colleagues (Grube et al., 1972; Smith et al., 1974; and Singh et al., 1982) investigated the effects of weathering on the Mahoning sandstone in northern West Virginia, and noted a "pyrite-free weathered zone approximating 20 feet (6 m) of depth below the land surface..." (Smith et al., 1974, p. 3). Singh et al. (1982), in addition to noting the pyrite-free zone, also note a loss of "alkaline earth" elements within 20 ft (6 m). This is illustrated for calcium in Figure 8.58. The loss of calcium is best explained by a loss of calcareous minerals (calcite and dolomite). Brady et al. (1988; 1996) in a study of the upper Kittanning and lower Freeport overburden in Fayette County, PA noted a similar loss of calcareous rocks in the near-surface weathered zone to about 7 m depth. Hawkins et al. (1996) noted weathering to depths of 30 to 60 ft (10 to 20 m). The loss of carbonates due to weathering is also discussed in Chapter 10.

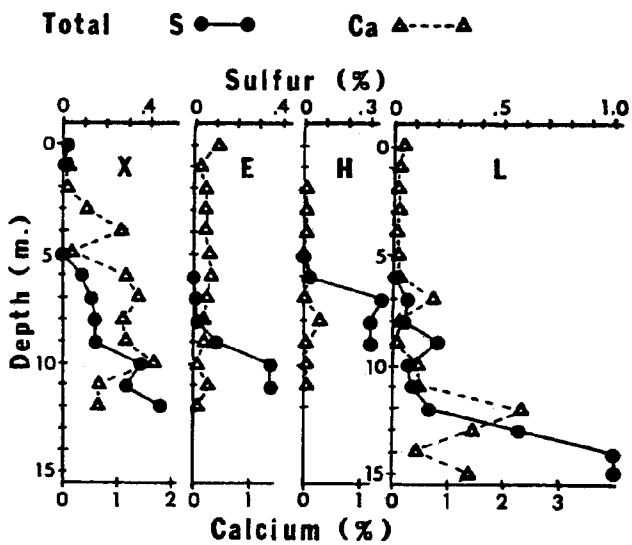


Figure 8.58 Total sulfur and total calcium in sandstone overburden, as a function of depth below the surface, for four sites in Preston County (northern), West Virginia. From Singh et al. (1982).

A weathering profile is evident at the top portion of most drill logs shown in this chapter. It is hard to determine precise rules of thumb for the depth of leaching of carbonates and oxidation of pyrite because these minerals can only occur where they were originally present (before weathering). If no pyrite was ever present within a stratigraphic horizon, its absence is not due to weathering, but to the fact that it was never there in the first place. The same is true for calcareous strata. It is evident from the stratigraphic figures that

rarely do NPs greater than 30 ppt $CaCO_3$ or sulfur greater than 0.5% occur within 20 ft (6 m) of the surface. A good example of this effect is the Blue Lick coal in Figure 8.26. Where the coal is under shallow cover it has less than 0.7 percent sulfur, however, in OB-C where the coal occurs under about 60 ft (20 m) of cover the coal averages over 2 percent sulfur. Most of the exceptions are where a horizon equivalent to a limestone, or strongly calcareous zone lies close to the surface. Some drill holes that encounter this zone at less than 20 ft (6 m) may still contain carbonates. The same is true for very high sulfur zones.

Figure 8.59 shows the effects of weathering on the sulfur content of the upper Freeport coal and the roof rock (shale) in an area of Fayette County. There is a clear loss of sulfur at shallow depth (17 to 20 ft; 5 to 6 m) in both the coal and the shale.

An accurate knowledge of the extent (depth) of the weathered zone is important from an overburden sampling standpoint. Overburden sampling should be done to the extent that it adequately represents the weathered zone and unweathered bedrock. This will entail drilling overburden analysis holes at maximum cover to be mined and at lesser cover. Weathering is also discussed in Chapter 9.

An understanding of the effects of weathering on the distribution of pyrite, sulfate salts, and carbonates is important in (1) accurately defining their distribution within unmined overburden, (2) being able to design a mine plan to prevent postmining problems, and (3) accurately predicting postmining water quality. An understanding of the weathering profile is just as important as understanding the lateral and vertical distribution of strata and their pyrite (sulfur) and carbonate content.

Glacial deposition was discussed earlier. Glaciers not only deposit, but can also erode. Erosion can include previously deposited glacial sediment, bedrock, and soil. Weathered bedrock is easily erodible and tends to be thinner in glaciated regions because of removal by glacial erosion. This is illustrated in Figure 8.57 where the median thickness, as well as the interquartile range of weathered bedrock is lower for areas that have been glaciated than for areas that have not been glaciated.

Weathering of Glacial Sediments in Western Pennsylvania

As with bedrock, the weathering of tills and other glacial sediments results in a change in the geochemistry and therefore in their effect on water quality. Weathering produces a vertical mineralogical gradation within tills. Leighton and MacClintock (1930, 1962) described the weathering of tills by dividing them into five horizons (Figure 8.60). Horizon 5 is unweathered till. It is still its original color (usually a shade of gray in northwestern Pennsylvania) and carbonates are still

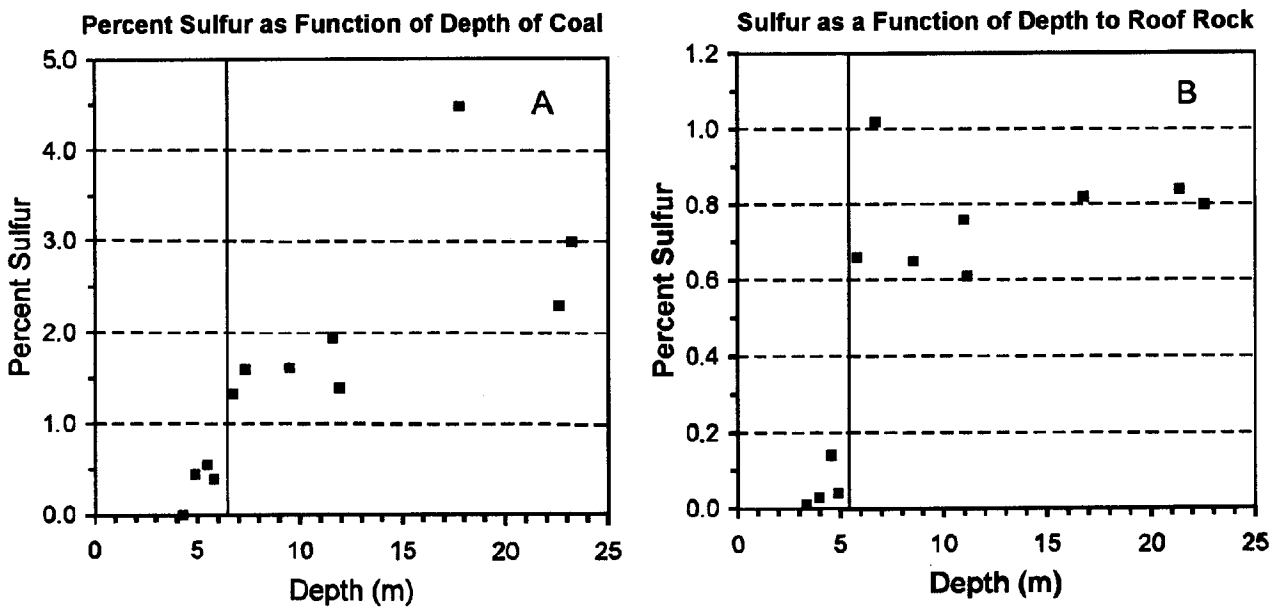


Figure 8.59 Percent sulfur in the upper Freeport coal (figure A) and 5 to 7 ft (1.5 to 2 m) of roof rock (figure B) as a function of depth below the surface. The mine is in Saltlick Township, Fayette County.

present. In horizon 4, pyrite, and other iron minerals, are oxidized. A till's characteristic oxidized color, a shade of yellow, brown, or red, is caused by iron oxide (such as hematite) or hydrous iron oxide (such as goethite and limonite) replacements of iron magnesium silicates and iron sulfides (Hallberg, 1978). Oxidation of manganese minerals (Hallberg, 1978) generally produces a darker brown color. Tills high in carbonate also tend to oxidize to a darker brown compared to low carbonate tills (White, 1982). Carbonate minerals are still present in horizon 4.

In horizons 3, 2, and 1, till is oxidized and totally leached of carbonates. Horizon 2 is chemically decomposed till. Silicates have been degraded. It is still recognizable as till. Horizon 1 is the A and upper B horizons of the soil where major leaching, added organic material, and addition of iron oxide and clay have modified the composition and texture. The parent material is no longer recognizable.

Horizons 4 and 5 are those of benefit in the prevention of acid mine drainage. Carbonate minerals are still present in those horizons, although partial leaching may have occurred. Horizon 4 may be partially leached in the coarse sand fraction (Hallberg, 1978) before leaching is apparent in the clay fraction.

Weathering begins immediately upon deglaciation. A later glacial advance over the existing till may erode

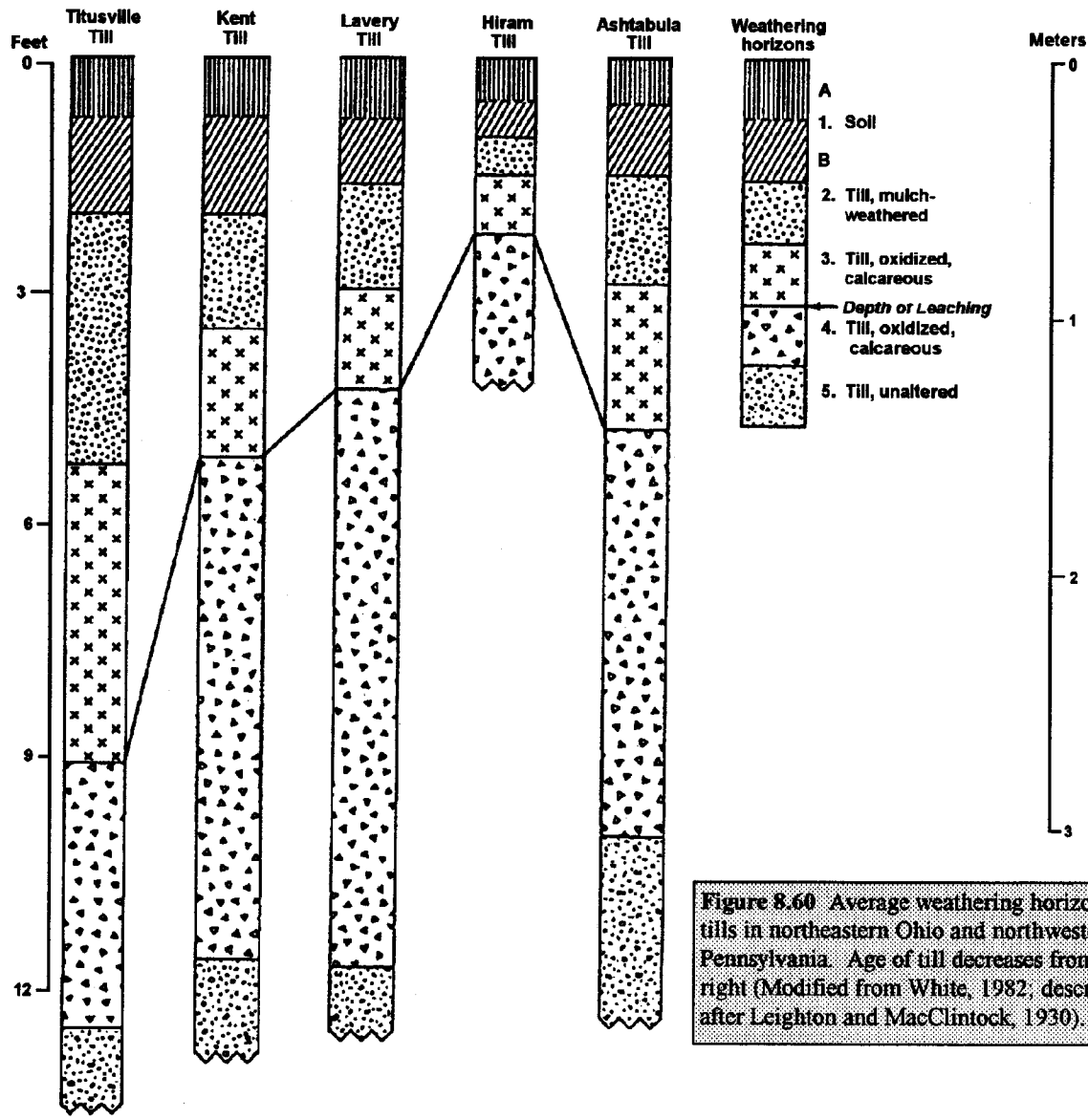


Figure 8.60 Average weathering horizons of tills in northeastern Ohio and northwestern Pennsylvania. Age of till decreases from left to right (Modified from White, 1982; descriptions after Leighton and MacClintock, 1930).

part or all of the weathered horizons of the preexisting till. If multiple tills are encountered during overburden removal, a buried soil or weathered horizon, with carbonate minerals leached, may exist between two calcareous zones. Figure 8.37 illustrates this situation. Unit 6 is a weathered, leached zone between calcareous zones 4 or 5 and 7. Units 10 and 11 are again a leached zone between the calcareous units 9 and 12. In Figure 8.38 and Figure 8.61, the NP distribution with depth at the McCoy and Spagnolo mines show low NP zones between high NP zones. These are partially leached weathering zones at the top of older, buried tills.

Likewise, if a till is thin and overlies another weathered till (a likely scenario in the glaciated coal region), leached zones of both tills may be superimposed, resulting in an excessive depth of leaching. Figure 8.62 illustrates this situation with three tills. Over most of the exposure, calcareous till is not encountered until the third till is reached (unit 6).

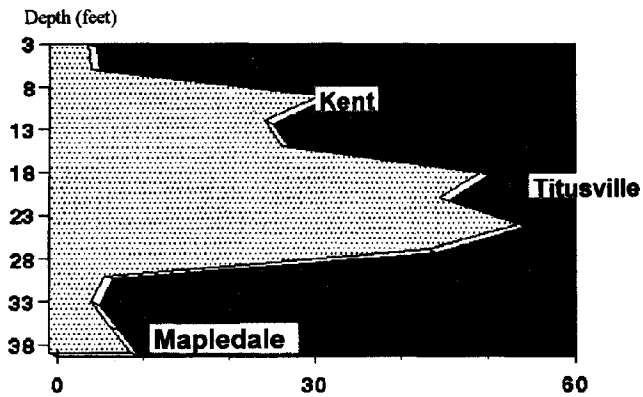


Figure 8.61 Distribution of NP for till stratigraphy at the Spagnola mine, Mill Creek Township, Mercer County. Mine site is at location "B" on Figure 8.36.

Each till has a characteristic average depth of leaching (Figure 8.60), providing no erosion of till has occurred since the beginning of weathering, and no other sediment has been deposited on top to halt the weathering process. The carbonate content of the Mapledale Till is so low that weathering horizon 4 cannot be determined in the field, and the depth of leaching is difficult to determine. The Mapledale Till is oxidized to a depth of 10 to 16 feet (3 to 5 m) (White et al., 1969).

Because a number of factors control the depth of leaching (and other weathering characteristics), the same till may be leached to different depths in different locations. All other factors being equal (which they usually aren't), older tills are leached of carbonates to a greater depth than younger tills. The nature of the parent material affects the rate of weathering. Coarser, more permeable sediments allow greater penetration of weathering agents (Hallberg, 1978). Landscape position can affect runoff vs. infiltration. Also, on steep slopes, erosion may proceed at a rate equal to weathering and a weathering profile may not develop.

Weathering in the Anthracite Region

Many of the weathering processes described above for western Pennsylvania are relevant to the Anthracite Region because the paleoclimate and present climate for both regions were/are essentially the same. The geologic structure of the Anthracite Region, however, as part of the Ridge and Valley Physiographic Province, is dramatically different than the flat-lying rocks

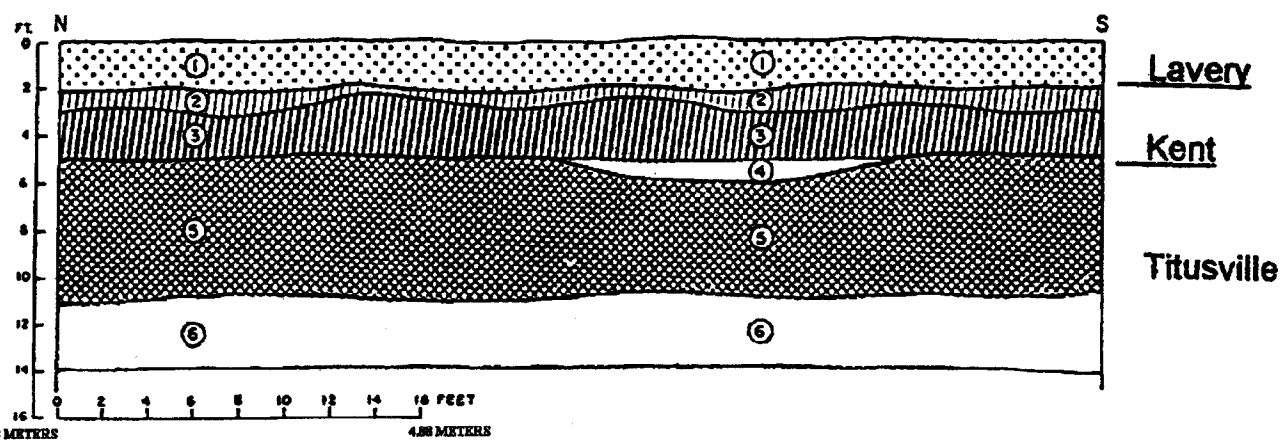


Figure 8.62 Sketch of glacial deposits exposed in an excavation in Mercer County. The tills are essentially devoid of calcareous material above unit 6. Horizon numbers are those used in Figure 8.60. Modified from White et al. (1969). Excavation at location "C" on Figure 8.36.

of the Appalachian Plateau. Due to the combined effects of the folded and faulted geologic structure and the resistance of the sandstone lithologic units to erosion, the weathering processes have formed a different topographic expression in the Anthracite Region.

Classic and recent works on weathering in the Ridge and Valley Province have concentrated on topographic development and glacial and periglacial features. In the first issue of National Geographic, Davis (1888) discussed the geologic structure, erosional history and topography of valleys and ridges of central Pennsylvania and the "dissected plateau further west" (p. 14). A later more detailed discussion of the subject is in Davis (1909). Descriptions of Appalachian slope form development are contained in Hack (1960, 1979). Additional information on weathering in the Ridge and Valley is found in Thornburry (1965, 1969), Clark and Ciolkosz (1988), and Sevon (1989). The four anthracite fields are preserved in synclinal basins that are essentially surrounded and "defended" by sandstone ridges. These ridges are more resistant to erosion than the shales and coals of the Pottsville and Llewellyn Formations. The slope forms of the ridges are typically mature (i.e., convexo-concave), but some free faces occur, such as the Harveys Creek water gap in the Northern Field.

The Pleistocene glaciation and climate left several features that can be observed today. These include till deposited in the Northern Anthracite Field (Hollowell, 1971, and Braun, 1997), and periglacial effects which extend south to the other anthracite fields. Periglacial activity has, in most places, lowered ridge tops as much as a few tens of meters (Braun, 1989). As a result, earlier weathering horizons have been removed, leaving a very small depth of weathered rock. Some of this weathering has resulted in the deposition of colluvium on the lower slopes. Colluvium in the Ridge and Valley province ranges in thickness from one meter on the upper ridge slopes, to 30 meters at the base of the slopes and in valleys. Twenty-seven percent of the soils in the Ridge and Valley province are colluvial, versus only 13 percent in the Plateau (Ciolkosz, 1978). Ridge tops have little or no weathered material. The lower one-half to three-fourths of the ridge slopes are colluvial. Residual soils occupy valley floors (Ciolkosz and others, 1979). In most places in Pennsylvania, at least two ages of colluvium are present, which includes reworked older regolith (Braun, 1989; Sevon, 1989). There is rarely any residual weathered bedrock beneath colluvium or glacial sediments in the Ridge and Valley (W. Sevon, personal communication, 1997), and where present, it is only a few feet thick (Hoover and Ciolkosz, 1988).

Because the bedrock, as far as is known, is low in pyrite and the tills lack carbonates, the effects of weathering in the Anthracite Region on mine drainage is probably not as significant as in the bituminous region.

Lithologic Factors Affecting Postmining Water Quality

Lithology is controlled by geologic factors such as paleoclimate and paleo-depositional environment. Sandstones are deposited in high energy environments, whereas shales and siltstone are deposited in quieter environments. Donaldson et al. (1985a) report the presence of several types of sandstones throughout the Pennsylvanian: lithic, calcareous, and quartz-rich (Figure 8.48). Quartz-rich sandstone is found predominantly in the lower Pennsylvanian Pottsville Group formations, but also occurs in the Allegheny and lower part of the Conemaugh, decreasing in frequency upward (Skema, personal communication, 1998). Lithic sandstones are found throughout the section. Calcareous sandstone is common from the middle of the Conemaugh through the Dunkard. Sandstone can form in a variety of environments, including

Table 8.10 Mean values for select water quality parameters demonstrating differences of water quality with different overburden lithology. "Group" numbers refer to specific lithologic sections shown on Figure 8.63 and Figure 8.64. Data are from Williams et al. (1982).

	Kittanning/Clarion Lithologies						Freeport Lithologies			
Group	**1**	**2**	**3**	**4**	**5**	**6**	**1**	**2**	**3**	**4**
pH	6.2	*3.2	*6.2	3.3	6.9	*6.2	*6.1	2.3	6.2	6.8
Acidity	5	410	*~10	330	*35	*0	*12	1230	26	*10
Sulfate	369	950	132	914	256	19	*25	1987	26	*110
Specific Conductance	*600	*2000	*650	*1500	*480	*65	*800	1455	200	*180

*Estimated from Figures 55, 56, 57, 58, 60, 61, and 62 in Williams et al. (1982). The other values are from the text in Williams et al. (1982).

alluvial and distributary (deltaic) channel sands, and marine barrier-bar sands. Typically sandstone is composed of quartz with varying amounts of feldspar, mica, and organic debris. Frequently they contain a high concentration of quartz because of this mineral's resistance to mechanical and chemical weathering. In this section we will examine the relationship between rock type and water quality. Abundant sandstone relative to finer-grained rock types, such as shale and siltstone, has been linked to acid mine drainage in the Allegheny Group. We will also examine what, if any, relationships exist between rock type and water quality in the other coal-bearing stratigraphic Groups of western Pennsylvania.

Sandstone and Postmining Water Quality

Many published studies of Allegheny Group mines with abundant sandstone overburden attest to a problem with water quality. Examples of Allegheny Group mine sites with sandstone overburden that produced acidic drainage are: Clarion coal (Dugas et al., 1993; Cravotta, 1991; Site 9 in Brady, et al., 1990; Henke, 1985; J.H. Williams et al., in press); lower Kittanning coal (Guo et al., 1994; Durlin and Schaffstall, 1993); upper Kittanning coal (Brady et al., 1988) and upper Freeport coal (Kania et al., 1989).

Williams et al. (1982) did an analysis of the geologic controls on water quality within the lower Allegheny (Kittanning/Clarion "formations") and upper Allegheny (Freeport "formation") for, primarily, the northern portion of the bituminous coal field. Figure 8.63 is the model for the Kittanning/Clarion, showing six different lithologic (overburden) relationships. Table 8.10. Mean values for select water quality parameters demonstrating differences of water quality with different overburden lithology. "Group" numbers refer to specific lithologic sections shown on Figure 8.63 and Figure 8.64. Data are from Williams et al. (1982).

These models, and accompanying water quality as displayed in the above table, show the important influence of marine and freshwater limestones and calcareous rocks on postmining water quality. They also show the effects of predominantly sandstone overburden, especially for the Freeport sites (Model 2) which typically produce acidic drainage. Comparatively, sites with little or no sandstone typically produce alkaline drainage (Models 1, 3, and 4). Williams et al. (1982) found that the "role of sandstone as an acid-producer cannot be determined from this Kittanning study, due to accompaniment of either acid-producing, high-sulfur shale, or limestone" with the sandstone. Kittanning/Clarion models 2 and 4 are both acid producing. Model 2 represents primarily brackish shales in the absence of calcareous strata. Model 4 represents the sandstone overburden, with acid-producing shale below. Model 3 is similar to situations where the marine Vanport limestone overlies the Clarion coal. Models 5 and 6 include freshwater limestone, such as the Johnstown limestone that occurs below the upper Kittanning coal, thus the alkaline water. The non-marine portion of the Kittanning model is very similar to the Freeport model.

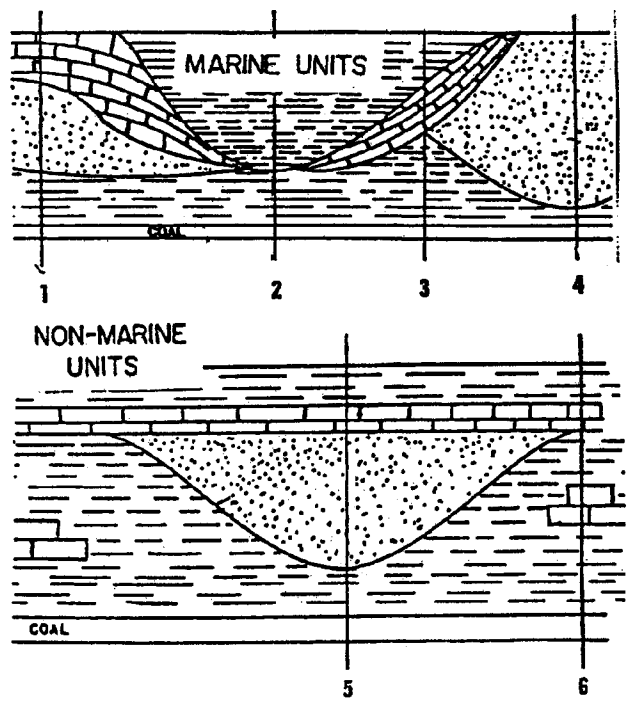


Figure 8.63 Schematic diagram representing the Kittanning/Clarion model of Williams et al. (1982). From Williams et al. (1982).

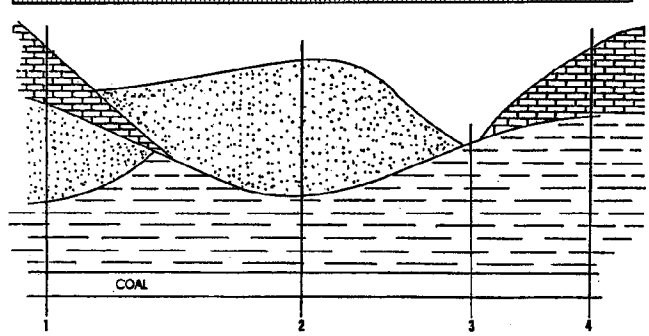


Figure 8.64 Schematic diagram representing the Freeport model of Williams et al. (1982). From Williams et al. (1982).

The work of Brady et al. (1988) is consistent with Williams et al.'s (1982) upper Allegheny "Freeport" model. Brady et al. looked at the overburden above the upper Kittanning coal in the Stony Fork watershed in Fayette Co., PA. Mine sites with predominantly channel sandstone overburden produced acidic drainage. The sandstone lacked calcareous minerals or cements. Overburden in areas away from the sandstone channels contained calcareous shales and muddy limestone, and mining in these areas resulted in alkaline drainage. The mines and resulting water quality in the Stony Fork watershed are discussed in detail in Chapter 9.

Typically sandstone is low in sulfur, even when acid producing. Channel sands can contain eroded material, including ripped up mats of peat (present day "coal spars") and lag deposits consisting of fossilized, and often coalified, logs. Individually these coal inclusions can be high in sulfur, but during typical overburden sampling this high sulfur is diluted by the surrounding inert quartz and other minerals that compose the sandstone. Thus these sandstones may contain acid-forming material (coal spars), but the samples have low overall sulfur concentrations. Occasionally there are pyrite-rich sandstones. Some of these are black and high in organic carbon, still others are light in color, but high in sulfur. The light-colored high-sulfur sandstones seem to occur just above coal or organic-rich shale. An example of this was shown in Figure 8.13, hole A-5.

Within the Allegheny and Pottsville Groups, sandstones generally contain low concentrations of calcareous minerals. There are some (rare?) exceptions to this however. Figure 8.13 shows two drill logs with calcareous sandstone in the lower Kittanning overburden, drill logs A8 and OB-1 from the Kauffman site in Clearfield County. The calcareous minerals are present as cement in the channel bottom deposits. Examination of thin sections reveals that minor amounts of siderite occur with calcite in the interpore cement (V. Skema, 1996, personal communication). Some calcite at the Kauffman site is also associated with fractures. Most of the sandstone at this mine, however, is not calcareous. Sandstones in the Conemaugh, Monongahela, and Dunkard Groups frequently contain calcareous minerals (Figures 8.2, 8.26, 8.31 and 8.34). Some sandstones have lost their carbonates through weathering.

diPretoro (1986) found a relationship between postmining net alkalinity and percent sandstone. All but one mine site within his study area (northern WV) containing greater than 63% sandstone produced negative net alkaline (i.e., acid) drainage. Sixty-seven percent of sites with less than 30% sandstone had positive net alkalinity (Figure 8.65). All but one of the sites with high percent sandstone were Allegheny Group coal mines. All but one of the Dunkard Group (Waynesburg coal) mines were alkaline. Many of the Waynesburg sites were less than 50% sandstone (in contrast to Waynesburg mines in Pennsylvania, where sandstone is the major overburden lithology, Figure 8.2 and Figure 8.34). Figure 8.66 shows a comparison of net alkalinity, for upper Freeport mines in West Virginia, with <50% sandstone and those with >50% sandstone. Median net alkalinity for sites with less than 50% sandstone is 105 mg/L, and for sites with more than 50% sandstone it is -172 mg/L.

An examination of 41 mine sites in western Pennsylvania by the Department of Environmental Protection (DEP) and the Office of Surface Mining (OSM) also shows relationships between percent sandstone and water quality (Figure 8.67). This data is somewhat biased in that, for the most part, it represents sites that were predicted to produce alkaline drainage (in theory acid-producing sites would not have been issued because of regulatory requirements), therefore acidic sites are probably underrepresented. Acidic sites are

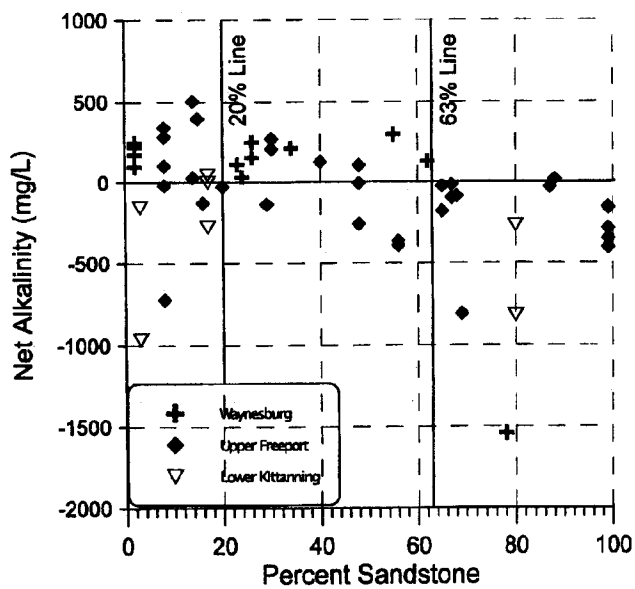


Figure 8.65 Net alkalinity as a function of percent sandstone for surface mines that encountered the Waynesburg, upper Freeport and lower Kittanning coals. Sites are in Preston County (northern), West Virginia. Most sites with greater than 63% sandstone are acidic, and most sites with less than 20% sandstone are alkaline. Data are from diPretoro (1986).

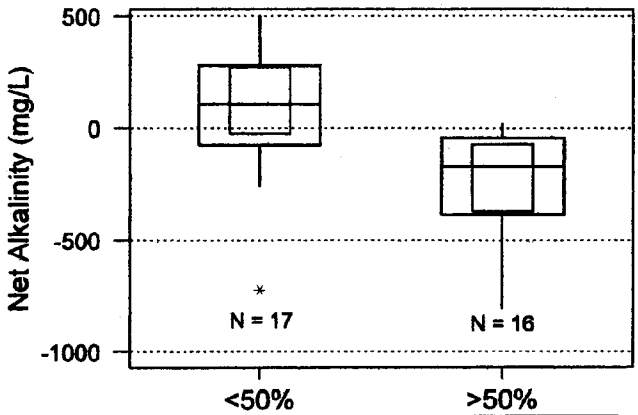


Figure 8.66 Distribution of net alkalinity as a function of percent sandstone for the upper Freeport mines in Preston County, West Virginia. The outer box brackets the 25th and 75th percentiles, the horizontal line is the median, the inner box represents the 95% confidence interval around the median. The two populations are statistically significantly different. Data are from diPretoro (1986).

present however, and make up 36% of the mines studied. Despite this bias toward "good" mines, we feel several observations can be made. Twelve of 13 (93%) mines with less than 20% sandstone are alkaline. Five of 8 mines with greater than 63% sandstone have net alkaline water, which is in contrast with diPretoro's findings where nearly all sites with >63% sandstone produced acidic water. A reason for this difference is that four of the alkaline, high-percent sandstone sites in the DEP/OSM study are in the Monongahela and Dunkard Groups. As Figure 8.2 shows, calcareous sandstones occur in this stratigraphic interval, but are generally lacking in the Allegheny Group. The DEP/OSM data underrepresents high percent sandstone Allegheny Group sites, because experience has shown that they frequently produce acidic drainage, thus the permits were not issued.

The data from the two studies (diPretoro, 1986; and the DEP/OSM study) have not been combined into one data set because they employed different methods of "weighting" to determine percent sandstone. Separation of the studies allows comparison of data from two adjacent, but separate areas. Both studies show that when there is a low percentage of sandstone the mine drainage is generally alkaline (Figure 8.65 and Figure 8.67). Analysis of the DEP/OSM data suggests this is not related to higher NPs in the finer-grained rocks, nor to lower sulfur in these rocks. Some of the low-percent sandstone overburden, in fact, has higher sulfur than the high percent sandstone overburden (Figure 8.68).

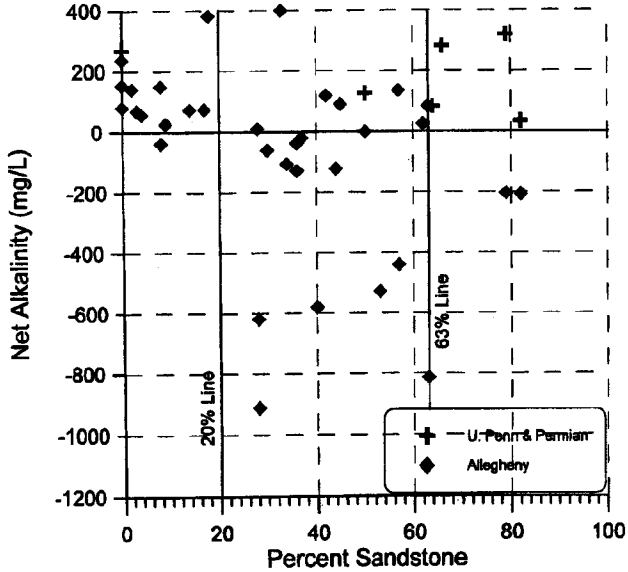


Figure 8.67 Net alkalinity as a function of percent sandstone for 41 surface mines in western Pennsylvania. Mines in the Conemaugh, Monongahela and Dunkard Groups are all alkaline, regardless of percent sandstone. Most sites with less than 20% sandstone are alkaline.

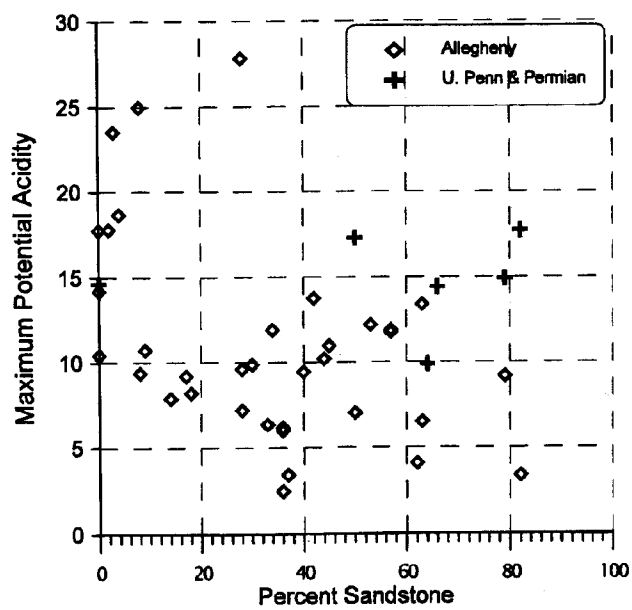


Figure 8.68 Maximum potential acidity as a function of percent sandstone. There is essentially no relationship between the two variables, with the possible exception of higher MPA at low percent sandstone. Data are from 41 surface mines in western Pennsylvania.

Also there is no relationship between net neutralization potential and percent sandstone (Figure 8.69). The finer-grained rocks would contain more clay minerals

than sandstone and these clay minerals may contribute to acid neutralization through silicate weathering, ion exchange, and adsorption of H^+ on negatively charged clay surfaces, thus better quality water.

There are probably several reasons Allegheny Group overburden with a high sandstone content produces acidic drainage. As mentioned, sandstones in the Allegheny group typically do not contain calcareous cements or minerals. This is probably related to paleoenvironmental influences that were not conducive to calcareous mineral deposition. Sandstones, which are composed largely of quartz, lack any appreciable ion exchange capacity and any ability to neutralize acid that would be generated by this process, and thus lack acid-buffering capability. Massive sandstones can have small discrete zones with high pyrite content (such as coal stringers) that may be important in acid mine drainage (AMD) generation. The importance of these zones may be missed in a sulfur analysis of the rock due to dilution of the zone by the surrounding "inert" sandstone. diPretoro (1986) suggested that low pH water generated by sandstones is favorable for AMD catalyzing bacteria, and sandstone, which during mining breaks into large blocks, allows greater permeability to air and water. The greater permeability to air by sandstone overburden is verified by Guo and Cravotta (1996). A site with blocky sandstone had a minimum O_2 in spoil gas of 18 volume percent (vol %). A second site with shale overburden had a minimum O_2 in spoil gas of less than 2 vol %. The minimum values for both sites were measured at ~10 m below the surface. Another way sandstone can affect overburden is where noncalcareous channel sandstones cut out and replace calcareous strata (Brady et al. 1988). As discussed above, the Monongahela and Dunkard Group sandstones are frequently calcareous.

Although there are certain rules of thumb regarding the relationship between sandstone and mine drainage quality, site-specific information is necessary to accurately predict water quality from a particular mine site. For example, sandstone above the lower Kittanning in Clearfield County is normally not calcareous, but some can be on rare occasions; and the sandstone above the Waynesburg coal which though situated in a dominantly calcareous part of the section is not necessarily calcareous. Sandstone and its relationship to mine drainage quality is stratigraphically specific and may be regionally specific. It would be interesting to compare the findings discussed above for the northern Appalachians with other coal-producing regions.

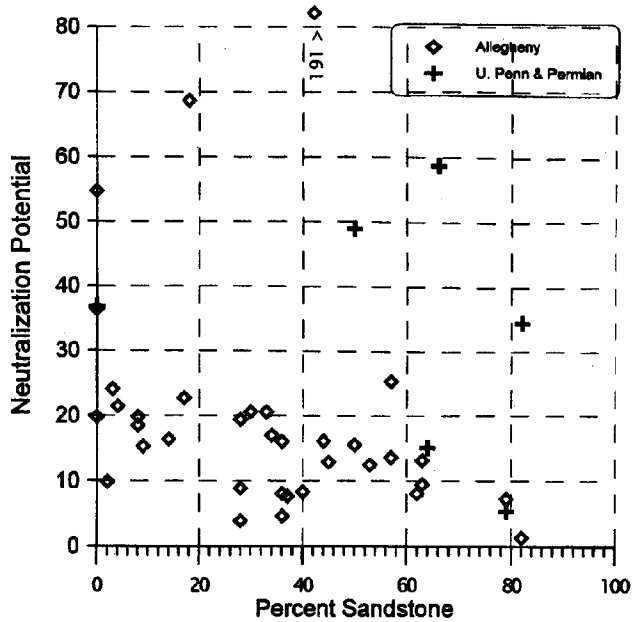


Figure 8.69 Neutralization potential as a function of percent sandstone. Data from 41 surface mines in western Pennsylvania.

Distribution of High-Sulfur Rocks

Frequently the highest sulfur strata are coals, boney coals, and other organic-rich rocks. Typically these organic-rich rocks are immediately above, below, or within a coal seam (e.g., a parting). Figure 8.49 shows sulfur content of roof and floor rocks compared to sulfur in the adjacent coal. Low-sulfur coals, such as those in the Powder River Basin and the southern Appalachians, have low-sulfur roof and floor. High-sulfur coals, such as occur in Pennsylvania and the Illinois Basin, may or may not have high-sulfur roof and floor. The sulfur in the associated rocks in some instances is higher than the sulfur in the coal.

Maksimovic and Mowrey (1993) examined the characteristics of the floor and roof materials from over 450 underground and surface coal mines across the US. The majority of immediate roof rocks were fine-grained sediments, shale, limestone, and fireclay. Sandstone only made up a minor fraction of the immediate roof rock. Sandstone was more significant a component in the main roof, making up 50% of deep mine roofs, but only 29% of surface mines. This difference may possibly be because deep mines are preferentially developed where the roof is sandstone because of more stable roof conditions, whereas surface mines may avoid areas with massive sandstone bodies because of increased mining costs. In all cases, the immediate floor is largely composed of fine-grained

sediments. The fine-grained rocks associated with the coal, whether roof rock, floor rock, or a parting, are often transitional between coal and the rock types above and below the coal. This transitional nature resulted in rocks that are high in organic matter, and probably formed in a higher pH environment than existed in the coal swamp. These conditions, as previously discussed, can be conducive to pyrite formation, since organic matter is a necessary ingredient for sulfate reduction.

The proximal relationships between high-sulfur strata, and coal or rider coal seams can be seen in virtually all the drill logs depicted in this chapter that show sulfur data. An exception to the high sulfur occurring immediately above the coal can be seen in Figure 8.13, where the highest sulfur interval occurs 3 ft (1 m) or more above the low sulfur overburden which overlies the coal. The high-sulfur zone (1.15% in A-8, 0.92% in OB-1, and 4.4% in OB-4) is associated with the brackish fossil *Lingula*. This is consistent with the work of Guber (1972) who found that shales and siltstones overlying the lower Kittanning coal containing the phosphatic brachiopod *Lingula* had higher sulfur than rocks not having *Lingula* (Table 8.11). Morrison (1988) also found on average that brackish shales had higher sulfur (2.40%) than marine (0.95%) or freshwater (0.15%) shales. Our experience confirms that brackish shales are typically high in sulfur.

Table 8.11 Contingency table of observed frequencies of *Lingula*- and non-*Lingula*-bearing rocks by three sulfur classes. The rocks are from the interval above the lower Kittanning coal, Clearfield County. Data are from Guber (1972).

Sulfur Content	Lingula-bearing	Non-Lingula-bearing	Totals
Low 0.0 - 0.5%	11	59	70
Medium 0.5 - 1.5%	49	22	71
High >1.5%	35	2	37
Totals	95	83	178

High-sulfur strata are also associated with marine shales such as the lower Kittanning and Brush Creek overburdens shown in Figures 8.11, 8.12, 8.23 and 8.24. Many of these same shales are calcareous. The top and bottom of some of these shale facies may be brackish. The thickness of high-sulfur zones in marine and brackish environments is often greater than that in the conchostracan-bearing overburden. It is important to accurately account for this high-sulfur material when designing plans to prevent acid drainage problems, and when predicting postmining water quality.

Relationships Among Mineralogy, Stratigraphy, and Regional and Local Variations in Postmining Water Chemistry

Four geologic processes account for overburden mineralogy. Two of these, paleoclimate and paleodepositional environment, date back hundreds of millions of years to the Pennsylvanian Period. The other two, surface weathering and glaciation, are more recent, occurring within the past few million years. Paleoclimate can account for the mineralogy of some terriginous rocks, but probably has little, if anything, to do with the paleodepositional controls that influenced pyrite and carbonate content of marine/brackish sediments. Weathering can reduce the original carbonate and sulfur content of rocks by dissolution and oxidation processes respectively. Glaciation can influence overburden by erosion of weathered bedrock and by the deposition of calcareous tills. The mineralogy of the rocks, particularly the presence of carbonates and pyrite, ultimately influences postmining water quality.

Importance of Carbonates

Earlier discussions argued that the calcareous carbonates are more important in controlling water quality from surface mines than is pyrite. The presence of only 1 to 3% carbonate minerals can influence whether acidic or alkaline drainage is produced (Brady et al., 1994; and Perry and Brady, 1995). The amount of sulfur present is not directly related to acid production except in the absence of calcareous strata.

Despite early recognition of the importance of calcareous strata (Leitch et al., 1932 and Crichton, 1923), most subsequent research has concentrated on studying the reactivity of various forms and features of pyrite. This seemed logical, because pyrite is required for the formation of acid mine drainage. The number of studies on pyrite reactivity is in the hundreds if one includes kinetic (leaching) tests. A few representative examples on relative pyrite activity are Caruccio's studies of pyrite morphology (1970) and trace element content (1972), Hammack et al.'s (1988) studies of pyrite origins (genesis); and Scheetz's (1992) investigations of pyrite molecular structure. Chapter 7 lists hundreds of references for various studies on "kinetic" tests. Few comparable studies have been done on the role of carbonates on mine drainage neutralization and inhibition, despite the clear role they play.

The complexity of carbonate mineralogy, with extensive solid solution substitution, and the role of this variable on resultant mine drainage chemistry is poorly

understood. It is known that the NP test (see Chapters 6 and 11) does not adequately distinguish forms of carbonates (Skousen et al., 1997b). The iron carbonate "siderite" may be temporarily alkalinity producing, but with oxidation and precipitation of the iron component, it is ultimately not alkalinity producing (Cravotta et al., 1990). Possible exceptions are where significant solid solution substitution for the iron, by Mg or Ca occur, or where siderite is mixed with a calcareous carbonate. A revised NP procedure reduces the falsely high readings for NP when siderite is present (Skousen et al., 1997b). The work by Skousen et al. is a follow-up of studies done by Morrison et al. (1990a; 1990b; 1994). The field studies by Brady et al. (1994) and Perry and Brady (1995), as well as references contained therein, suggest that not only do calcareous minerals neutralize mine drainage, but they also inhibit pyrite oxidation. Laboratory studies are consistent with these findings (e.g., Williams et al., 1982). The role of carbonate mineralogy on mine water chemistry is clearly a subject deserving more study.

Others factors, in addition to mineralogy, such as mining methods, mine site hydrology, and controls on spoil pore gas composition can also significantly influence postmining water quality. The role of these variables (and others) is discussed in Chapters 1, 3, 12, 13, 14, 15, 16, and 17.

Stratigraphic Relationships to Water Chemistry

Several studies have examined water quality as it relates to stratigraphic position of coal seams. Most surface mines in Pennsylvania have extracted coals in the Allegheny and Monongahela Groups. Table 8.12 shows comparisons of pH for upper Pennsylvanian (Conemaugh and Monongahela Groups, plus the Permian? Dunkard Group) coal mines, and the upper Allegheny and lower Allegheny Group. Two of these studies looked at water quality from deep mines in Pennsylvania four studies looked at water quality from surface mines in Pennsylvania and West Virginia, and one study included water quality from both surface and deep mines. The last line of Table 8.12 is the mine drainage quality data from Table 8.2 which have been adapted and summarized for comparison with the other studies. Samples of streams and water supply wells have been deleted from our summary.

Deep mines, as discussed in Chapter 9, can produce poorer quality water than surface mines on the same coal seam, if they are "free draining." The deep mines included in these studies are "pre-Act" and mostly updip mines. The study by diPretoro (1986) had the lowest percentage of alkaline sites from the upper Allegheny. This is probably because a high percentage of these sites had predominantly sandstone overburden. The DEP/OSM study and this study have the highest percentage of alkaline sites for the Lower Allegheny mines. This is probably because these studies include a bias toward sites that would produce acceptable water quality, bad permits being denied (and thus no postmining water quality). As a generality, the upper Pennsylvanian and upper Allegheny mines in Pennsylvania produce more alkaline drainage than lower Allegheny mines.

As discussed above, the water quality reflects the geologic processes that have been at work. The upper Pennsylvanian/Permian? strata has freshwater limestones and calcareous shales. The upper Allegheny, with the exception of northern West Virginia, generally has calcareous shales and freshwater limestones. The lower Allegheny is frequently marine or brackish, and

Table 8.12 Median pH from mines in the upper Pennsylvanian (Conemaugh, Monongahela, and Dunkard Groups), upper Allegheny (upper and lower Freeport, and upper Kittanning overburden), and lower Allegheny (middle and lower Kittanning, Clarion/Brookville overburden) Groups in northern West Virginia (WV) and western Pennsylvania (PA). ---- indicates data not provided.

		Upper Penn & Permian			Upper Allegheny Group			Lower Allegheny Group			
Location	Type of Mines	No. of Sites	Median pH	Percent Alkaline	No. of Sites	Median pH	Percent Alkaline	No. of Sites	Median pH	Percent Alkaline	Reference
WV & PA	Deep & Surface	40		52%	20	----	75%	17	----	29%	Bituminous Coal Research (1977)
PA	Deep	0			24	6.2	56%	31	3.3	8%	Hornberger (1985)
PA	Deep	117		30%	347	----	32%	199	----	20%	Emrich and Thompson (1968)
PA	Surface	0			26	5.7	50%	29	4.0	21%	Williams et al. (1982)
PA	Surface	6	7.0	100%	10	6.4	60%	19	6.0	52%	DEP/OSM (unpublished)
WV	Surface	16	7.1	88%	51	3.7	26%	8	2.9	11%	diPretoro (1986)
PA	Surface	18	6.8	72%	13	7.1	85%	21	4.8	52%	This study

often lacks calcareous strata. The Emrich and Thompson (1968) study also tried to look at regional trends in water quality by coal seam. They found that lower Kittanning deep mines in Armstrong and Jefferson Counties frequently produced alkaline drainage. We have found that surface mines in this same area also generally produce alkaline drainage (area of Figure 8.12), and this is discussed in Chapter 9.

A side by side comparison of Figure 8.2 and Table 8.2 (both in pocket at rear of book) shows the relationships between stratigraphic intervals and water quality of the bituminous coal region of Pennsylvania. Table 8.2 can also be compared to total sulfur and NP data of drill holes shown in Figure 8.4 through Figure 8.34, for a more detailed evaluation of the relationships between stratigraphic characteristics of specific surface mine sites and the postmining water quality of those sites. Alkalinity greater than 100 mg/L and acidity greater than 100 mg/L are shown in bold, thus highlighting water samples and stratigraphic intervals with high alkalinity and acidity. The remaining paragraphs of this section describe the relationships from the Waynesburg Formation of the Dunkard Group down to the Pottsville Group, as the data is presented in Table 8.2.

Dunkard Group - The only coal commonly mined in the Dunkard Group is the Waynesburg coal. The postmining water quality from surface mining of the Waynesburg Formation can be highly variable (Table 8.2; in pocket at back of book). The water samples of the Waynesburg interval (Table 8.2) are from D.S. Jones and P. Cestoni (1991, DEP hydrogeologists, personal communication). Samples are from a 2 x 2.5 mile (12.8 km^2) area in Greene County. Most samples were collected at the Susan Ann site, and represent water before, during and after surface mining activities. Surface mining began in 1980 and was completed in 1991. The first two samples, collected prior to mining, have alkalinity of 379 mg/L and 340 mg/L, and are from low flow seeps (<1 gpm; <4 L/min). These emanate from a small abandoned deep mine (DM-2) on the Waynesburg coal. The next two samples (Table 8.2) have acidity of 1500 mg/L and 306 mg/L. These are from low flow seeps adjacent to the sealed entry of DM-2 and were collected during mining. The fifth sample, from the same location, has alkalinity of 92 mg/L, iron of 18 mg/L and manganese of 29.4 mg/L. This sample was collected after backfilling and revegetation in 1991. The next sample in Table 8.2 is from a small underground mine (DM-1). It has an alkalinity of 142.0 mg/L and significantly lower metals concentrations then the preceding sample. The flow was ~5 gpm (~19 L/min.) The two samples labeled "F" in Table 8.2 have high alkalinity, relatively high metals concentrations and emanate from spoil. The remaining Dunkard Group samples are from tributary streams. All have alkalinity greater than 250 mg/L.

The relationship between lithology and water quality of the Waynesburg Formation is evident from a comparison of Table 8.2 to Figure 8.34. Data in Figure 8.34 are from the Susan Ann mine and a nearby site called Fox. There are significant thicknesses of calcareous sandstones, siltstones and shales with NP values greater than 50 ppt. These account for the high alkalinity concentrations in postmining water quality. There are also significant amounts of strata with high sulfur (>0.5%). These include the Cassville shale above the Waynesburg coal (e.g., 1.39% S in Fox # 3) and the high-sulfur sandstone in hole PS-3. These strata account for the high acidity and metals concentrations in some mine discharges.

Monongahela Group - The water quality of the Monongahela Group is shown in Table 8.2. The lithologic and geochemical characteristics of the Group are depicted in Figures 8.2, 8.26, 8.31 and 8.32. Freshwater limestones including the Benwood, Fishpot, and Redstone, and other calcareous strata are abundant in the Monongahela. For example, Figure 8.32 shows drill holes with thick limestones and other high NP strata associated with the Sewickley and Redstone coals. As would be expected from the abundance of carbonate strata, the water quality associated with all but the lowest part of the Pittsburgh Formation is highly alkaline with relatively low metals concentration (Table 8.2). In fact, the sample from Upper Tyrone Township, Fayette County of a spring near the cropline of the Redstone coal has an alkalinity of 626 mg/L, the highest of any samples found in DEP permit files. While the metals concentrations of this sample are relatively low, the sulfate concentration is 1440 mg/L, making it the dominant anion, rather than bicarbonate.

The abundance of carbonate strata in the overburden of the Redstone coal, along with the high alkalinity in natural background water, and the ubiquity of alkaline mine drainage associated with this seam in southwestern Pennsylvania has resulted in overburden analysis rarely being needed to make permit decisions. Thus acid-base accounting data for the Redstone are rare.

Farther east, in Somerset County, the geologic structure and stratigraphic correlations become more complex, and overburden analysis data from the Monongahela Group is more common. For example, the Blue Lick Coal is routinely mined in Somerset County. This is a split or rider of the Pittsburgh seam which is not mineable in counties to the west (Shaulis, 1993). The generally high alkalinity of the Blue Lick 3 and Krause sites (Table 8.2) are representative of the postmining water quality of the Morantown to Sewickley coal overburden in this area. Drill holes OB-A, OB-C, and OB-5 in Figure 8.26 are examples of the overburden for this interval in Somerset County.

Some active and abandoned, surface and underground mining activities on the Pittsburgh coal have produced serious acid mine drainage problems (see water samples from Allegheny and Westmoreland Counties in Table 8.2). This scenario occurs in areas where the Pittsburgh coal is mined alone (see OB-1 and OB-2, Figure 8.31). There are a few calcareous strata in these drill holes, but the high-sulfur (> 1%) shales and sandstones overlying the coal apparently overpower the calcareous strata, thus the production of AMD. This type of AMD scenario also occurs where calcareous Redstone and Sewickley strata are present, but mining does not encounter them. For instance, where deep mines only disturb high-sulfur strata adjacent to the coal, or where a surface mine disturbs only low cover strata that have had the carbonates removed by weathering. A classic example of where a remining operation was able to improve water quality by mining a greater amount of cover and thus encountering calcareous strata, and improve mine drainage quality, is the Solar site discussed in Chapter 9 (and in Skousen et al 1997a). The discharge from a large Pittsburgh deep mine improved from a pH of 2.5 prior to remining to a pH of 7.5 following remining.

Conemaugh Group - The postmining water quality of surface mines within the Conemaugh Group is shown in Table 8.2. The lithology and geochemistry of the overburden are depicted in Figure 8.24 and Figure 8.25. The earlier discussion of Conemaugh stratigraphy documented that this thick sequence of rocks is generally "barren" of mineable coals. Few coals are mined in the Casselman Formation. The only part of the bituminous region where these coals reach mineable thicknesses is in extreme eastern Somerset County. The coals that have been mined are the Morantown (which is actually a split of the Pittsburgh coal and thus in the Monongahela Group), the Wellersburg coal (Figure 8.2 and Figure 8.25), the Barton, and Federal Hill coals. The last two are rarely mineable. Postmining water quality for the Wellersburg overburden is shown on Table 8.2. The alkaline nature of the water is consistent with the calcareous nature of the overburden depicted in Figure 8.25.

The Glenshaw Formation contains several mineable coals and numerous marine and freshwater limestones (Figure 8.2). The principal coals mined are the upper and lower Bakerstown and the Brush Creek, and the water quality associated with surface mines for these coals in Somerset and Fayette Counties are shown in Table 8.2. Drill holes DH-3 and DH-12 in Figure 8.25 are from Southampton Township, Somerset County and water from the same mine is shown in Table 8.2. Three samples of lower Bakerstown pit water and two samples of upper Bakerstown pit water are included in Table 8.2. All have alkalinity greater than acidity (the most alkaline of these is 118 mg/L from a lower Bakerstown pit pool). A postmining discharge from the Stateline site has alkalinity as high as 210 mg/L and a pH of 8.1. This demonstrates that the thick calcareous strata shown above the lower Bakerstown in DH-12 and DH-13 (Figure 8.25) are capable of producing alkaline postmining water quality, despite the presence of some high sulfur coal and shale (e.g. 9.18% in DH-12). Drill holes 5 and 11F in Figure 8.25 are from nearby Brothersvalley Township. The four water samples from the Brothersvalley site are of preexisting discharges with moderate acidity and considerable manganese and aluminum concentrations. These samples were collected prior to the remining operations on the site. These water samples show that acid discharges can occur on some mines where the overburden quality is generally good (Drill Holes 5 and 11F). It is not known whether the water quality following remining improved.

The last six water samples from Conemaugh strata in Table 8.2 are from two sites in Wharton Township, Fayette County where the Brush Creek coal has been surface mined without postmining water quality problems. These samples are from the same site as Drill Holes DH-19 and OB1 in Figure 8.23.

Allegheny Group - The postmining water quality characteristics of surface mine sites in Allegheny Group strata are represented by approximately 100 samples in the bottom half of Table 8.2. The coals of the Allegheny Group are the most extensively mined seams of western Pennsylvania and consequently more is known about the relationships of the stratigraphy,

lithology, mineralogy, and postmining water chemistry of this stratigraphic interval, from published geologic reports and unpublished data in DEP permit files, than any other coal-bearing stratigraphic interval in Pennsylvania.

The areal extent of mining of the upper Freeport and lower Kittanning coals in western Pennsylvania is large. The magnitude of permit file data for this area can be estimated from DEP data bases: (1) mylar map records, (2) a computer system which tracks all permitting, inspection, compliance, and enforcement actions for all mines active since 1985, and (3) an overburden analysis database that contains rock chemistry analyses for permits issued since 1993, plus some historical records. The computer tracking system includes 1594 mines on the upper Freeport coal (from 1985 to November 1997), for a total of 339,018 permitted acres. The lower Kittanning coal was permitted for 1142 mines covering 305,187 acres (M. Klimkos, 1997, DEP, personal communication). The overburden analysis database contains 291 drill logs with chemical data for the upper Freeport overburden and 336 drill logs for lower Kittanning overburden.

The following description of upper and lower Allegheny Group water quality will be brief and broad-brush. Table 8.2 provides details for water samples from specific mine sites. The postmining water quality characteristics of some Allegheny Group surface mines has also been described in detail in Chapters 9, 10, and 18 of this book.

Upper Allegheny - There is a relationship between the stratigraphy and postmining water quality of the upper Allegheny Group (stratigraphy shown in Figures 8.2, 8.17 through 21, and water quality shown in third panel from the bottom of Table 8.2). The three freshwater limestones of the upper Allegheny (Johnstown limestone, lower and upper Freeport limestones) and associated coal, calcareous shales, siltstones, sandstones, and underclays are shown in these drill holes with relatively high NP values. Most of the water samples for this stratigraphic interval in Table 8.2 have alkalinity concentrations greater than 100 mg/L and several samples are greater than 300 mg/L. For example, the Laurel Hill # 1 and # 2 sites in Jackson Township, Cambria County are the same sites as the four drill holes shown in Figures 8.17 and 8.18, and the toe of spoil seep with a pH of 8.1 has an alkalinity of 484 mg/L. The Shero site in West Carroll Township, Cambria County, has postmining water quality with an alkalinity of ~375 mg/L. This site is in close proximity to the Fisanick site shown in Figure 8.19. The Fruithill, Witherow, Beaver # 1, and Fink/Mays surface mine sites from Clearfield County also exhibit relatively high postmining alkalinity for seeps, spoil discharges, and abandoned deep mines that are hydrologically connected to the surface mines, and in headwater tributary samples. The Nashville site in Indiana County and the Schmunk and Rennie sites from Fayette County in Table 8.2 have similar alkalinity and low metal concentrations in postmining seeps, springs, and tributary samples for the upper Allegheny Group strata. However, the Chanin, Morrison, and Stuart sites in Fayette County, particularly in the upper Kittanning coal, exhibit dramatic variations from high alkalinity to high acidity postmining discharge (Table 8.2) corresponding to facies changes where the typically calcareous overburden strata are replaced by thick channel sandstones lacking carbonate minerals. The Morrison and Stuart sites are in the same vicinity of Wharton Township, Fayette County. The dramatic difference is overburden quality is depicted in Figure 8.20 where drill holes BM-OB2F and BM-OB5F from the Morrison site possesses high NP overburden strata, while the drill holes from the Stuart site are generally lacking high NP strata, especially drill holes GBS-DH2, which is entirely sandstone overburden with total sulfur as high as 2.6%.

Lower Allegheny - The relationships between the stratigraphy and postmining water quality of the lower Allegheny Group can be determined by comparing the second panel from the bottom of Table 8.2 with Figures 8.2, 8.7, 8.12, 8.13, 8.15 and 8.39. The lower Allegheny lacks the freshwater limestones and associated calcareous shale which are characteristic of the upper Allegheny; therefore the postmining water quality of the lower Allegheny is often more acidic as displayed in Table 8.2. However, the marine Vanport limestone in the lower Allegheny Group is the thickest and most commercially significant limestone unit in the Pennsylvanian rocks of the state, and in the counties where it is of appreciable thickness (e.g. Armstrong, Butler, Clarion, Lawrence and Mercer, see Figure 8.8), high alkalinity concentrations occur in mine drainage, springs, wells and streams as shown in Table 8.2 (e.g., Graff and Wilson sites).

The water quality associated with the surface mining of the MK coal reflects the transition in stratigraphy from the lower to the upper Allegheny Group (see analyses in Table 8.2). The overburden strata between the MK and UK coals typically includes the Washing-

tonville shale overlying the MK coal which is stratigraphically the highest marine or truly brackish bed in the formation, and the Johnstown limestone underlying the UK coal, which is stratigraphically the lowest freshwater limestone in the formation. In a multiple seam mining operation having a bench for each coal, the MK pit water may have considerable alkalinity because the Johnston limestone is the dominant influence on water quality, overwhelming the acid from the acidic shales and siltstones (Figures 8.13 and 8.15).

Lower Kittanning overburden contains no true limestones. The characteristics of the overburden chemistry and postmining water quality of this stratigraphic interval are quite variable as shown in Figure 8.12 through Figure 8.15 and Table 8.2. More is known about paleoenvironmental and mine drainage quality variations for this interval than for any other coal in Pennsylvania. This is due to the large amounts of data in DEP permit files and numerous geologic studies (e.g., Williams, 1960; Williams and Keith, 1963;, Guber, 1972; Hornberger et al., 1981, 1985; Williams et al., 1982; and Morrison et al., 1990a). In some areas where the lower Kittanning overburden was deposited in a marine environment as shown in Figure 8.12, the mine drainage can exhibit appreciable alkalinity. For example, the Snyder site in Table 8.2 is the same site as drill holes OB-1 and OB-2 in Figure 8.12, and the pit water had an alkalinity of 114 mg/L, despite the presence of sulfur content greater than 1% in several shale strata. (The Snyder site is also featured in Chapter 18 of this book). Additional mine drainage data from a marine environment is contained in Table 8.2 for the Shannon site in Clarion County. The lower Kittanning overburden from brackish environments is generally characterized by black shales overlying the coal. These shales can have very high sulfur content, for example 8.34% in drill hole 560A3 in Figure 8.13. Similar holes were drilled on the Kauffman site in Figure 8.13 (e.g. drill holes OB-1 and OB-4). Comparable acidic postmining water is shown in Table 8.2 for the adjacent Betty site. Water data from the Kauffman site was not used because site reclamation is incorporating imported alkaline material, thus postmining water from it is not necessarily representative of the overburden. Additional postmining discharges with high acidity, metals and sulfate concentrations from brackish environments of the lower Kittanning are shown for the Albert #1 and Kelce sites in Clearfield County. Geologic description and water data for brackish sites in the Luthersburg area of Clearfield County are presented in Chapter 9.

Lower Kittanning overburden from a "freshwater" paleoenvironment (probably marginally brackish) is depicted in drill holes 61-B and 61-C in Figure 8.15. Postmining seeps from the Swiscambria site have moderate acidity and metals concentrations. These LK "freshwater" environment sites (also drill holes OB-1 and OB-2 in Figure 8.15), often have shales with lower sulfur contents than the marine and brackish shales, but these sites still tend to produce water with acidity greater than alkalinity. Finally, some lower Kittanning sites may have overburden strata principally comprised of thick channel sandstones. These often produce drainage with high acidity and metals (e.g., Lawrence site from Fayette County; Table 8.2).

Postmining water quality variations of surface mines on the Clarion coals are probably the most complex of any coal mined in Pennsylvania because three of the four geologic factors that account for overburden mineralogy (i.e., paleoenvironment/stratigraphy, glaciation, and surface weathering) can be operative and significant within the same county (e.g., Clarion County). The result is good and poor quality mine drainage in the same vicinity. Stratigraphic correlations and nomenclature of these lower Allegheny coals can be confusing as discussed earlier.

Often the total sulfur content of the Clarion coals and the overlying shales are high, as shown in drill holes DH23-6 (8.33%) and DH18-1 (5.92%) in Figure 8.7 and drill hole DH-4 (5.16%) in Figure 8.39. Other Clarion coal overburden analyses in DEP files (not included in these figures) commonly have total sulfur greater than 8%. Discharges with >1,000 mg/L acidity related to this type of Clarion overburden strata are common. Examples shown in Table 8.2 are the Old 40 and Zackerl sites in Clarion County, the Orcut site in Jefferson County, and the Philipsburg site in Centre County. Where the Vanport limestone is present, the mine drainage quality can be dramatically different as discussed earlier and shown in Figure 8.10.

The influence of unweathered and weathered glacial tills upon overburden mineralogy and mine drainage quality of Clarion coal surface mines is shown in Figures 8.39 and 8.60 and Tables 8.2 and 8.3. Drill hole OB-2 in Figure 8.39 from the Cousins site in Lawrence County is an example of an unweathered till zone (i.e., zone 5 in Figure 8.60) with NP values > 500 ppt $CaCO_3$. These high values are due to clasts of the Vanport limestone. The pit water sample from the Cousins site on Table 8.2 has an alkalinity concentration of 130 mg/L, while spring samples from the site

(Table 8.2) have higher alkalinity concentrations. Drill hole OB-3 - SPAG (Figure 8.39) is from the Spagnolo site shown in Table 8.3. This drill hole encounters till with several zones of NP greater than 30 ppt. This is indicative of zone 4 (oxidized, calcareous till) in Figure 8.60 and the water quality at the Spagnola site has a pH greater than 6.5 and an alkalinity of approximately 30 mg/L (Table 8.3). Most of the glacial till shown in DH-4 and DH-28 from the Pike Township site in Figure 8.39 appears to be weathered and non-calcareous (see Zones 2 and 3), but the thick Vanport limestone below the till would promote alkaline water at this site without influence from the till.

Pottsville Group - The Pottsville Group coals are generally thin and discontinuous. While generalized columnar sections of the Group show the Sharon, Quakertown and Mercer coals, the only Pottsville Group coal that is mined to any reasonable extent in the bituminous region is the Mercer coal zone. A few surface mines in Somerset County are mining a coal labeled the Quakertown but the correlations are tenuous or doubtful. Recent surface mining of the Mercer coals is largely restricted to an area of northwestern Pennsylvania including portions of Clarion, McKean, Lawrence and Mercer Counties. Since there has been so little mining activity on Pottsville Group coals, very little useful data exists. Consequently the description of the relationships between Pottsville Group overburden chemistry and water quality characteristics has been reduced to a comparison of the drill logs for two proposed mine sites that were not mined, (shown in Figure 8.6), to some background water samples from that area, plus some recent and abandoned mine drainage samples of Pottsville Group mines shown in the bottom panel of Table 8.2.

The five samples of old mine discharges for the Mercer coal site in Norwich Township, McKean County are from the same site as drill holes DH 177-1 and DH 177-9 shown in Figure 8.6. The highest alkalinity for these samples is 7 mg/L, and the highest acidity is 73 mg/L; some of these samples have nearly equal acidity and alkalinity values. The two water samples in Table 8.2 from the Mine #201 site, are from the same site as drill holes DH 201-1, DH 202-2 and DH 201-3 in Figure 8.6. These samples are background (premining) springs off the Mercer coal outcrop and exhibit similar alkalinity, acidity, and sulfate concentrations to the Mine #177 background samples described above. The four pit water samples of the Matthews site on the Mercer Coal in Mahoning Township, Lawrence County, have significant alkalinity concentrations (e.g. 206 mg/L) and relatively low metals concentrations. However, the high alkalinity is chiefly attributed to carbonate minerals in the till overburden.

The mildly acidic to highly alkaline water quality available from the recent Mercer coal sites may tend to deceive some readers because it does not represent the full range of mine drainage quality emanating from the Mercer coal zone in Pennsylvania. Therefore, the abandoned mine discharges from the Horseshoe site in Cambria County were included in Table 8.2 to represent the significant acidity and metals concentrations that are possible from Mercer coal mine discharges. The Louden (MP-29 and MP-22) and Page (MP-65) discharges are from large abandoned underground mine complexes on the Mercer coal near Altoona, PA. The Louden discharge has acidity and iron as high as 1835 mg/L and 194 mg/L respectively. The Quakertown coal pit water sample from an active surface mine in Somerset County, at the bottom of Table 8.2, is the only water sample found in DEP files for this interval.

Regional and Local Variations in Postmining Water Quality

Following is a summary of postmining water quality variations in Pennsylvania attributable to geologic factors. Regional- and local-scale variations in postmining water quality for the bituminous and anthracite mining regions are evident in data from this study and previous studies.

A bimodal distribution of coal mine drainage pH has been observed within both the bituminous and anthracite regions (Figure 8.70a and Figure 1.2, Chapter 1, for bituminous coal mine drainage and Figure 8.70b for anthracite mine drainage). Brady et al. (1997) state: "Although pyrite and carbonate minerals only comprise a few percent (or less) of the rock associated with coal, these acid-forming and acid-neutralizing minerals, respectively, are highly reactive and are mainly responsible for the bimodal distribution.... Depending on the relative abundance of carbonates and pyrite, and the relative weathering rates, the pH will be driven toward one mode or the other." Chapter 1 discusses the pH distribution for the bituminous region.

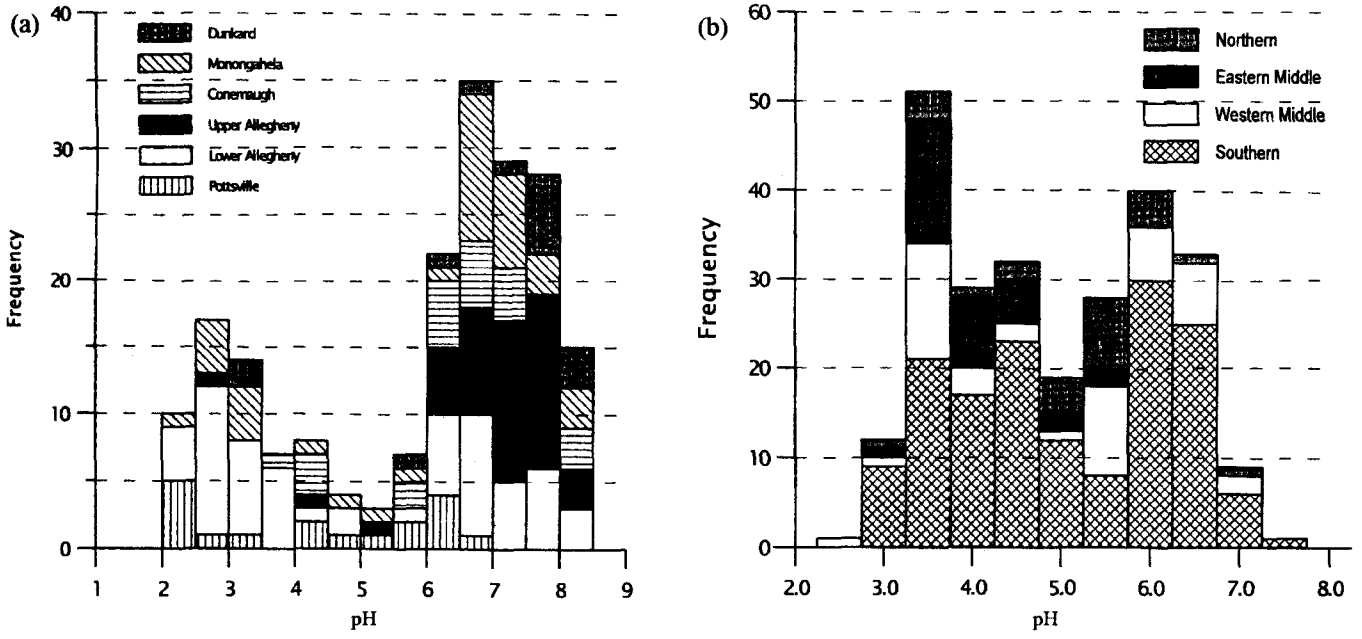


Figure 8.70a and b Bimodal distribution of pH for (a) bituminous mines and (b) anthracite mine discharges in Pennsylvania. Bituminous data are from Table 8.2 and anthracite data are from Growitz et al. (1985). Bituminous data is displayed by stratigraphic group and anthracite data by coal field.

Water Quality in the Bituminous Coal Region - The large-scale variations in water quality within the Bituminous Coal Region are principally related to the outcrop patterns of the Pottsville, Allegheny, Conemaugh, Monongahela and Dunkard Groups, and to paleoenvironmental changes of specific stratigraphic intervals at a regional scale. The large-scale water quality variations are chiefly attributable to the presence or absence of calcareous rocks. A good example of delineating mine drainage quality by outcrop area is the Monongahela Group. Surface mining most Monongahela Group seams results in alkaline drainage (an exception is acid problems from some Pittsburgh deep mines). The alkaline drainage occurs because of the abundance of thick freshwater limestones that are encountered during mining. Good examples of regional-scale paleoenvironmental variations occur within the lower Allegheny Group. Some examples are where: (1) the marine Vanport limestone is thick and overlays the Clarion coals, as opposed to areas where the Vanport limestone is absent; and (2) marine shales overlying the lower Kittanning coal to produce alkaline mine drainage, as opposed to lower Kittanning shales that are of a brackish or "freshwater" environment resulting in acidic drainage.

By comparing Table 8.2 to Figure 8.2 (both in pocket at back of book), relationships between the geology and water quality of the bituminous region can be discerned. The highest alkalinities in Table 8.2 are associated with: (1) the thick freshwater limestone sequences (e.g., the Redstone limestone) of the Pittsburgh Formation in the southwestern corner of Pennsylvania, (2) the thick marine Vanport limestone of the lower Allegheny Group in the central to northwestern area of the bituminous region, and (3) the freshwater limestones of the upper Allegheny Group (i.e., Johnstown, lower and upper Freeport Limestones) in areas where these limestones and associated calcareous shales are abundant, such as portions of Clearfield, Cambria, Indiana, Westmoreland, and Fayette Counties. In addition, significant alkalinity concentrations in Table 8.2 occur in: (1) the Conemaugh Group where the marine Brush Creek and Woods Run limestones are present, and (2) the lower Allegheny Group mines in northwestern Pennsylvania where the overburden includes significant thickness of calcareous glacial till.

The highest acidity concentrations in Table 8.2 are associated with: (1) the Clarion and lower Kittanning coals, particularly where black brackish shales and thick marine shales predominate in the overburden, such as Clarion, Clearfield, and Centre Counties, and (2) in the Pittsburgh coal and Waynesburg coals of the southwestern portion of the bituminous region, in areas where the carbonate strata are absent or lacking appreciable thickness. Significant acidity concentrations are also shown in Table 8.2 where local facies changes occur, such as in the upper Allegheny Group in areas of

Fayette County, where the channel sandstones occur instead of freshwater limestone and calcareous shales.

The medians and ranges of pH, alkalinity, acidity and sulfate concentrations of the major stratigraphic intervals of the bituminous region are shown in Table 8.13. This table has been constructed using data in Table 8.2. Most stream samples were not included from Table 8.2, unless the water reflected drainage from the mine site (e.g., headwater streams during baseflow conditions). Well samples were also deleted, unless they were monitoring wells within mine spoil. Where multiple samples of the same mine discharge point occur in Table 8.2, a median was computed for inclusion in Table 8.13. Unrepresentative premining samples were also deleted. The number of samples (N) shown in Table 8.13, is the number of mine discharge locations used to compute the medians and ranges shown.

Comparison of median pH values in Table 8.13 shows a lower pH for the lower Allegheny Group than for the stratigraphically higher strata. The median pH values for the upper Allegheny, Conemaugh, Monongahela, and Dunkard Groups are within the upper mode of the bimodal frequency distribution for pH shown in Figure 8.70a. These pH values are reflective of the importance of carbonate strata in controlling mine drainage quality. The wide range of pH values and the range of alkalinity and acidity concentrations for the intervals document that some strata within each major interval have the potential to produce alkaline and acidic drainage. The relatively higher median sulfate concentration for the lower Allegheny Group, indicates that this strata has a greater potential for acid production. That is consistent with the extreme acidity and sulfate concentrations in lower Allegheny Group samples in Table 8.2. Many of these samples are also marked by high concentrations of iron, manganese, aluminum, and sulfate.

Anthracite Region Water Quality - Regional variations in mine drainage quality of the Anthracite Region are shown in Table 8.14. The relationships between the postmining water quality and specific stratigraphic intervals of the Anthracite Region are much less well known than those of the Bituminous Region for at least two reasons: (1) the complexity of the geologic structure has impeded the acquisition of stratigraphic data from routine exploration drilling and made correlations of units and associated mine drainage difficult; and (2) a large portion of the mining hydrology of the four anthracite fields is controlled by large-volume, mine pool discharges. The mine drainage from gangways developed in multiple coal beds is commingled in rock tunnels (that crosscut the geologic structure and strata) which interconnect the mine workings. Thus discharges are often a composite water representing multiple coal seams throughout a large mine complex. Despite this, some significant regional variations in mine drainage quality are evident for the anthracite fields (Figure 8.71). These are probably related to mineralogic differences between the fields.

Some Northern Anthracite Field mine waters have significant alkalinity (e.g., Plains Borehole, Table 8.14). This may be attributable to the presence of marine and freshwater limestones and other calcareous rocks in the Northern Field. A few postmining discharges of the Northern Field have low pH and high acidity (Loomis Bank discharge), although high acidity discharges are relatively rare in the anthracite fields. Many large volume discharges of the Northern Field have circumneutral pH with nearly equal concentrations of acidity and alkalinity (e.g., Jermyn Outfall,Table 8.14). Although cirumneutral, some of these discharges have relatively high concentrations of iron, manganese or aluminum, and because of large flows they have high pollution loads.

Table 8.13 Median and range of mine drainage quality of the Bituminous Region of Pennsylvania (adapted from Table 8.2). N = number of samples.

GROUP	N	pH		Alkalinity mg/L		Acidity mg/L		SO_4 mg/L	
		median	range	median	range	median	range	median	range
Dunkard	10	7.75	3.35 - 8.03	251.5	0 - 359	0.0	0 - 903	171.3	124 - 1869
Monongahela	26	6.75	2.45 - 8.30	92.0	0 - 338	0.0	0 - 2851	481.4	39 - 2701
Conemaugh	17	6.40	3.56 - 8.10	24.0	0 - 210	5.1	0 - 168	272.0	22 - 881
Upper Allegheny	31	7.11	2.80 - 8.10	114.8	0 - 484	0.0	0 - 1290	211.0	12 - 1467
Lower Allegheny	41	4.80	2.20 - 8.10	8.0	0 - 310	43.5	0 - 10000	957.5	32 - 14000
Pottsville	15	5.60	2.20 - 7.30	2.0	0 - 206	5.0	0 - 2070	165.0	5 - 3250

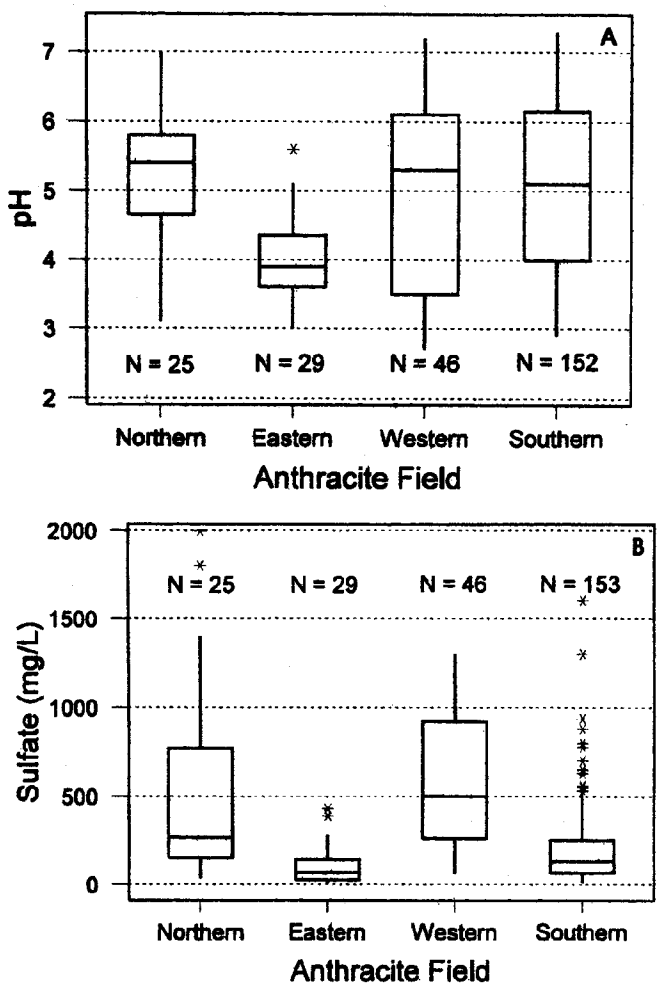


Figure 8.71 Boxplots showing differences in (A) pH and (B) sulfate for discharges from the four anthracite fields in eastern Pennsylvania. The box is bounded by the 25th and 75th percentiles and the median is represented by a horizontal line within the box. "Whiskers" and "*" (outliers) define the range. Data are from Growitz et al. (1985).

There are 14 major discharges in the Eastern Middle Field. Mine drainage from four of these are shown in Table 8.14. There is no significant alkalinity in any of the discharges. As far as is known, there are no limestones or other calcareous strata in this region. The highest alkalinity is 13.8 mg/L and the highest acidity concentration is 194 mg/L. No severe AMD (pH < 3.0, acidity > 1000 mg/L) is known in the Eastern Middle Field. The Eastern Middle Field appears to lack both calcareous rocks and high-sulfur rocks. The Jeddo Tunnel discharge, in the Eastern Middle Field, is the largest mine discharge in the state (Table 8.14), and generally has an acidity concentration >100 mg/L and a flow >50,000 gpm (>190 m^3min^{-1}). Though the acidity concentration is not "high," because of the flow the acid load is large.

The water quality of the postmining discharges of the Western Middle and Southern Anthracite Fields is somewhat more mysterious than that of the Northern and Eastern Middle Fields. Some discharges have significant alkalinity, but no carbonate stratigraphic units have been reported in these fields. The Packer V discharge in the Western Middle Field has alkalinity of 160 mg/L and iron of 20.9 mg/L in Table 8.14. The Richards discharge near Mt. Carmel has a pH of 3.7 and an acidity of 70 mg/L. Other discharges of the Western Middle Field exhibit circumneutral pH, with iron concentrations of 10.6 to 30.5 mg/L in Table 8.14. Because some of these discharges drain large interconnected underground mines spanning square miles, various anthropogenic sources may also contribute to water quality. However the North Franklin and the Doutyville tunnel discharges are located in a mostly rural area.

Several mine discharges of the Southern Anthracite Field have significant alkalinity concentrations, including the Wadesville, Eagle Hill, and Kaska discharges (Table 8.14)). In fact the water pumped from the Wadesville shaft has an alkalinity of 414 mg/L. This is one of the most alkaline mine waters found in Pennsylvania. It is almost certain that a detailed study of stratigraphy in this area would reveal calcareous strata or calcareous secondary mineralization. Several Southern Field discharges have significant acidity concentrations (Bell, Newkirk, Porter Tunnel and Markson discharge, Table 8.14). A study by C.R. Wood (1996) shows that many abandoned underground mine discharges in the anthracite fields have improved in water quality between 1975 and 1991.

A final factor that may affect the relationships between postmining water quality and stratigraphy in the Anthracite Region is the stratification of mine pool water. The mine pools consist of water accumulated in void spaces within abandoned underground mines, and deep pools or lakes in abandoned surface mines that are hydrologically connected to abandoned underground mines. These mine pools typically are chemically stratified into "top water" and "bottom water." The stratification of anthracite mine pools is discussed in Barnes (1964), Erickson et al. (1982) and Ladwig et al. (1984). Additional discussions on the areal extent, volume of impounded water, and interconnections (breeches) between mine pools are contained in a series of studies by Ash (e.g., 1949, 1954).

Table 8.14. Mine drainage quality for the four anthracite fields. N = Northern Field, EM = Eastern Middle Field, WM = Western Middle Field, and S = Southern Field

Site Name	County	Coal Field	Sample Date	pH	Alkalinity mg/L	Acidity mg/L	Iron mg/L	Mn mg/L	Al mg/L	SO_4 mg/L	TSS mg/L	Flow (gpm)
Old Forge Borehole	Lackawanna	N	11/1/85	6.0	80	12	28.0			518		
Duryea Ditch	Lackawanna	N	11/1/85	5.9	90	2	35.2			464		11,670
Jermyn Outfall	Lackawanna	N	3/22/91	6.4	10	4	1.0	0.6	0.1	150	5	8,976
Loomis Bank	Luzerne	N	2/27/95	2.6	0	760	34.0	29.2	94.6	1,975		
Hudson Anthracite	Luzerne	N	4/23/90	2.7	0	1,960	105.0	22.9	242.0	1,782	4	
Plains Borehole	Luzerne	N	3/9/94	6.5	122	0	45.1	3.3	< 0.5	491	< 3	
Alden Strip #2	Luzerne	N	7/28/92	7.1	168	7	0.9	0.3	< 0.5	628	22	
Jeddo Tunnel	Luzerne	EM	10/24/96	4.3	6	104	7.2	4.5	11.1	346	22	50,150
Owl Hole	Luzerne	EM	9/30/96	3.5	0	194	1.3	4.6	30.9	225	12	757
Oneida #3	Schuylkill	EM	12/30/96	4.7	9	26	0.1	0.3	1.1	22	< 2	7,415
Pond Creek	Luzerne	EM	2/15/97	4.7	14	10	0.2	0.5	0.4	33	4	128
Packer V	Schuylkill	WM	7/29/97	6.4	160	0	20.9	7.8	0.1	597	30	Ave= 1,200
Richards	Northumberland	WM	8/19/97	3.7	0	70	7.5	2.5	4.8	82	2	1,672
Scott Overflow	Columbia	WM	8/19/97	5.9	54	68	28.3	4.1	0.3	254	2	4,386
Stirling	Northumberland	WM	6/4/97	6.0	68	52	30.5	3.4	0.3	310	8	4,830
North Franklin	Northumberland	WM	6/10/97	5.6	26	24	10.6	2.4	0.9	287	16	2,097
Doutyville	Northumberland	WM	6/10/97	4.4	6	28	3.0	1.5	2.2	150	20	1,645
Bell	Schuylkill	S	6/18/97	3.9	0	110	11.7	3.0	9.4	294	26	75
Porter Tunnel	Schuylkill	S	12/2/81	2.8	0	802	159.0			1,056		253
Porter Tunnel	Schuylkill	S	4/24/97	3.3	0	98	14.8	3.8	4.3	267	3	4,039
Newkirk	Schuylkill	S	8/12/97	3.6	0	84	4.3	2.4	9.3	97	2	176
Goodspring #1	Schuylkill	S	9/27/95	6.2	66	0	15.2	2.5	0.0	112	6	127
Goodspring #3	Schuylkill	S	9/27/95	6.0	54	32	22.2	3.4	0.0	323	26	516
Markson	Schuylkill	S	9/27/95	3.4	0	82	18.3	5.6	1.6	491	4	844
Kaska	Schuylkill	S	8/12/97	6.3	100	0	18.7	3.0	0.2	194	6	25
Eagle Hill	Schuylkill	S	8/14/97	6.7	268	0	11.7	1.9	0.4	276	24	646
Wadesville	Schuylkill	S	5/19/86	7.1	330	0	1.9	2.6	< 0.50	1,164	14	

The top water discharges are typically of circumneutral pH, although some samples in Table 8.14 may have elevated iron, manganese, or aluminum. Top water is believed to reflect shallow groundwater systems, with relatively short residence times, where most of the flow is confined to the upper part of the mine pool. The bottom water typically has higher concentrations of acidity, metals, and sulfate than the top water of the same mine pool. Bottom waters are indicative of longer residence times, less circulation (and less oxygen). For example, the Markson and Good Spring No. 1 mine pool discharge samples shown in Table 8.14 are from adjacent collieries within the Donaldson Syncline in the Southern Anthracite Field. The mine maps of these two collieries indicate that the coal seams mined, mining engineering factors, and geologic conditions of the collieries are essentially the same; yet the Good Spring No. 1 discharge has a pH of 6.2 (and sulfates of 112 mg/L) and the Markson discharge has a pH of 3.4 (and sulfates of 491 mg/L) (Table 8.14). The Good Spring No. 1 discharge is top water and the Markson discharge is bottom water with a distinct hydrogen sulfide aroma. The samples of the Markson and Good Spring No. 1 mine pool discharges were collected on the same date in relatively low flow conditions and are within a few mg/L of the average sulfate values from five years of monthly samples.

Figure 8.71a depicts variations in the pH of mine discharges for the four anthracite fields. The Eastern Middle Field has the lowest median pH and the least variability in pH, consistent with an absence of carbonate strata. Figure 8.71b shows that the Eastern Middle Field discharges also have the lowest sulfate concentrations and the least variability in concentration. The other fields show a wider range in pH and sulfate, although the Southern Field typically has lower sulfate than the Northern and Western Middle Fields.

Local-Scale Variations in Water Quality of the Bituminous and Anthracite Regions

For purposes of this discussion, local-scale variations in geology and mine drainage quality are those which occur within a single mine site, or between adjacent mine sites, or within a relatively small geographic area. These local-scale variations are much more prevalent and explainable in the Bituminous region, although distinct differences in mine drainage quality have been reported from adjacent active underground

mines in the Anthracite region. There are at least four types of local-scale variations in geology that account for differences in mine drainage quality: (1) abrupt facies changes where freshwater calcareous strata (i.e., from a lacustrine or upper delta plain paleoenvironment) are replaced/cut out by channel sandstones, (2) more subtle facies/depositional environment changes occur where the thickness and purity of carbonate strata or the presence and thickness of high sulfur zones, within the coal seam or overlying shales, can very within a mine site, (3), weathering of bedrock which results in loss of carbonate and sulfur minerals, and (4) variations in the thickness and depth of weathering of glacial tills which result in loss of carbonate minerals.

An example of the effects of abrupt facies changes is shown in Figure 8.20 and reflected in the water quality from the neighboring Morrison and Stuart surface mines (Table 8.2). The mines extracted the upper Kittanning coal in Wharton Township, Fayette County. The calcareous overburden strata of the Morrison site is reflected in the alkaline nature of the seep (pH 7.0, alkalinity 308 mg/L and low metals concentrations). The Stuart site overburden was principally channel sandstones. The postmining seepage from this site is acidic (pH 2.8, acidity 1290 mg/L and high metals concentrations).

The more subtle local variations in facies, carbonate mineral, and sulfur content of overburden strata cannot be readily seen in Table 8.2. However the ranges and medians of acidity, alkalinity, and pH values from Table 8.2, summarized in Table 8.13, demonstrate that low pH and circumneutral pH, and alkaline and highly acidic values occur in all of the major stratigraphic groups in the bituminous region. The high acidity concentrations in generally alkaline stratigraphic sequences may appear anomalous, but they probably represent local variations where significant pyrite is present and carbonate minerals are lacking.

Geologic variability in portions of Lawrence, Venango, and Mercer Counties illustrate some of the reasons for local variations in mine drainage quality. The water quality differences result from differences in thickness and weathering depth of tills, and abundance of carbonate and sulfide minerals in till and bedrock. Mine drainage quality in Table 8.2 for the Cousins site on the Clarion coal in Hickory Township, Lawrence County show the influence of calcareous till (alkalinity of 130 mg/L in pit water), as does the Mathews site on the Mercer coal in Mahoning Township, Lawrence County (pit water alkalinity as high as 206 mg/L). This is consistent with the alkaline nature of till on the Cousins site (with NP > 500 ppt). Drill hole OB3-SPAG in Figure 8.39 from the Spagnola site in Millcreek Township, Mercer County contains a few zones with NP > 50 ppt. This calcareous overburden resulted in alkaline drainage. By contrast, the Oddfellow site in Pine Township, Mercer County, with a lack of calcareous rock, produced acidic drainage. Drill hole DH-28 from the Oddfellow mine shows thick till (and essentially no bedrock) overlying the Clarion coal, with only one zone with NP greater than 50 ppt; while DH-4 exhibits equally thick till with no zones of NP greater than 30 ppt, but the till is underlain by ~15 ft (5 m) of Vanport limestone with NP values from 920 to 956 ppt. A surface mine on the Clarion/Brookville coal with no evidence of thick till or Vanport limestone in the overburden, is the old Riddle site from Mineral Township, Venango County. An unnamed tributary to Sulphur Run receiving water from the Riddle site has a pH of 3.0 and an acidity of 240 mg/L (Table 8.2).

Worst case examples of acidity, metals, and sulfate concentrations that can be produced from Clarion coal overburden, without the benefits of Vanport limestone or calcareous tills on site, are the Old 40 and Zacherl sites in Table 8.2, located a short distance to the southeast in Clarion County. These two sites have the highest acidity concentrations of the any stratigraphic interval shown in Table 8.2. Thus, the importance of carbonates in controlling mine drainage quality is evident in both local and regional water quality for the bituminous and anthracite fields of Pennsylvania.

APPENDIX

Fossil Fauna and Paleosalinity

This Appendix proposes a revision of Williams (1960) "Environmental Faunal Classification" by reexamining the paleoecology of conchostracans, a fossil used by Williams (1960) to define freshwater depositional environments, and by adding an additional faunal group.

Williams (1960) pioneered the use of fossil fauna as a paleosalinity indicator in the Pennsylvanian of Pennsylvania. Table 8.15 is a list of faunal facies. Faunal Groups 1 through 4 are from Williams. Faunal Group 5 has been added by the authors. Faunal Group 4 was interpreted as "Fresh-water" by Williams. A reexamination of what is known about the most abundant fossil Order in Faunal Group 4, conchostracans, suggests

that this group lived in a marginally brackish, not freshwater, environment. This is important from an overburden chemistry standpoint. As discussed in the body of the text, ocean water is high in sulfate and freshwater contains very small amounts of sulfate. Sulfate, through reduction, supplies the sulfur that forms pyrite. Where sulfate is low it can limit the amount of pyrite that is formed. Thus salinity can control the amount of sulfur available for the formation of pyrite.

Faunal Groups 1 through 3 retain the same interpretations that Williams gave them. Faunal Group 1, which is often associated with limestone, was probably deposited in deeper water than Faunal Group 2. Crinoids, which are stenohaline (i.e., not tolerant of brackish conditions or variable salinity) have been added to Faunal Group 1.

Tasch (1969) has an extensive discussion on "Ecology and Paleoecology" of conchostracans. Most modern conchostracans live in "small, temporary, alkaline, inland ponds," although they have also been reported "on coastal salt flats" and "(s)ome living species are known from both fresh and brackish water environments" (Tasch, p. R146-R147). Tasch goes on to say "...living conchostracans can withstand brackish water and it is in zones of brackish-water deposits that the mixture of the fresh-water and marine [fossil] forms in question probably occurred" (p. R149). Tasch adds that "(p)resent evidence suggests transition from an original marine to a fresh water environment during the Carboniferous" (p. R149). Thus, at a minimum, Pennsylvanian conchostracans are not conclusively representative of a freshwater depositional environment, and in fact during the Pennsylvanian they most likely lived in a marginally-brackish environment.

The marginally brackish environment may have been "paralic." Paralic is defined as "pertaining to intertongued marine and continental deposits laid down on the landward side of a coast or in shallow water subject to marine invasion, and to the environments (such as lagoonal or littoral) of the marine borders" (Bates and Jackson, 1987). Skema (1997, personal communication) has suggested the term "marginally-brackish" because it infers salinity (of interest to overburden chemistry), whereas paralic infers geographic position. The evidence for conchostracans occupying a marginally-brackish environment during the Pennsylvanian, in addition to the comments by Tasch, include the following:

(1) Progressions from one paleoenvironment to another, such as those found in the rocks above the lower and middle Kittanning coals, are completely transitional. The transition is from truly marine conditions such as Williams' Faunal Group 1, which has a wide variety of marine fauna, to a more restricted fauna in Faunal Group 2, to the brackish fauna of Group 3, to the conchostracan-bearing Group 4. This transition can be lateral or vertical. The paleoenvironmental maps (Figure 8.11 and Figure 8.16) show this lateral transition. Skema (1997, personal communication) has seen conchostracan-bearing strata grade vertically into *Lingula*-bearing strata, and back to conchostracan-bearing strata.

(2) The faunal groups can interfinger laterally. An excellent illustration of this is the cross-sections in Plate 2 of Glass et al. (1977). The cross-sections show conchostracans and *Lingula* occurring at the same stratigraphic horizon above the middle Kittanning coal only a few miles (km) apart.

(3) Many of the rocks and coals associated with conchostracan fossils are high in sulfur (>0.5%). The sulfur content of the upper Kittanning, lower and upper Freeport coals and overlying strata are higher than typical for freshwater coals and sediments. This is consistent with some marine influence.

Table 8.15 Faunal groups showing typical fossils for specific depositional environments. Salinity increases downward in the table. Also shown are the carbonates that are typically associated with the rocks from these faunal groups.

Faunal Group	Index Fossils	Depositional Environment	Most Common Carbonates
5	Ostracods, *Spirorbis*, fish remains	Freshwater Lakes	Calcite, Dolomite
4	Conchostracans	Paralic with marginally brackish water	Siderite?
3	Phosphatic brachiopods (*Lingula*), and pectenids (*Dunbarella*, *Aviculopecten*), and *Orbiculoidea*	Marginal marine with brackish water	Siderite
2	Calcareous brachiopods (*Chonetes*, *Marginifera*, *Composita*)	Shallow marine with sea water	Calcite, Siderite
1	Calcareous brachiopods (greater diversity than in Faunal Group 2), cephalopods, crinoids, bivalves, gastropods	Deeper marine, with sea water and stenohaline organisms	Calcite

(4) Conchostracan-bearing rocks occur at the same stratigraphic positions as known marine horizons. This is true from at least the lowest Allegheny marine/brackish zone to the Skelly horizon of the Casselman Formation (Skema, 1997, personal communication). The Freeport roof rocks, which are entirely within Faunal Group 4 in Pennsylvania, grade laterally into marine or brackish rocks in Ohio (Sturgeon and Hoare, 1968).

(5) Convincingly freshwater deposits, such as the freshwater limestones that occur in the upper Allegheny and younger strata, have a very different suite of fossils composed of Faunal Group 5. Also, these strata can not be followed laterally into marine or brackish zones.

With the inclusion of marginally brackish environments, some marine influence is present in Pennsylvanian Period rocks in Pennsylvania from the Pottsville Group through at least the Skelly horizon of the Glenshaw Formation. The importance of this reinterpretation of Faunal Group 4 is that the higher than freshwater salinity that influenced the faunal facies would also influence the amount of sulfate available for pyrite formation. The marine influence present for Faunal Group 4 was less than that of brackish or truly marine sediments. This is reflected in the generally thinner sequences of high-sulfur strata associated with conchostracan-bearing rocks. Marginally brackish facies would be exposed to marine influence for less time, from transgressive to regressive portions of a cycle, than more fully marine sequences, and the shallower depths of water allowed for less sediment deposition. Thus the thinner zone of high sulfur rock.

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Chapter 9

GROUNDWATER CHEMISTRY FROM PREVIOUSLY MINED AREAS AS A MINE DRAINAGE QUALITY PREDICTION TOOL

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Introduction

The groundwater quality emanating from adjacent abandoned or reclaimed mine sites has proven a very useful tool for predicting water quality characteristics of proposed mine sites. The assumption is that if the same coal and overburden are being mined and the mining conditions are similar, hydrogeologic conditions will be sufficiently alike so that the groundwater quality from the proposed mine will approximate that of the previously mined area. Frequently, this is the case. Groundwater chemistry from previous mining, when available and used properly, is the best prediction tool in the tool kit. In fact, there are times when the requirement for acid-base accounting is waived because water quality from previous mining has affirmatively demonstrated that mining can occur without pollution. Groundwater chemistry from previously mined areas has the advantage of providing concentrations of water quality parameters that resulted from actual mining. Interpretation, however, requires an understanding of the limitations of this method.

Water quality from prior mining has been used as a prediction tool since at least the early part of the twentieth century. The deleterious effects of previous mining were used in the early 1900's as an argument by the Pennsylvania Railroad while trying to prevent additional mining within the Indian Creek watershed in Fayette County (Crichton, 1923; Collins, 1923). The Pennsylvania Railroad and public water supply companies were using a reservoir that was in danger of being degraded by additional deep mining. The Crichton and Collins studies showed that most deep mines in Pennsylvania were producing acid mine drainage. During these investigations, Leitch et al. (1932) found that the water from the "Thick Freeport Coal" deep mines in an area northeast of Pittsburgh was alkaline; so it has been long recognized that not all mines and coal seams produce the same quality water.

A publication entitled "Factors Involved in estimating Quality and Quantity of Mine Drainage" (PA Department of Health, 1966) pointed out that "nearby abandoned and operating coal mines can yield significant information about the quality and quantity of mine drainage to be expected from new mining operations." This publication also points to several things pertinent to interpreting adjacent mine information, such as whether mining was to the dip or rise, the size of area mined, the type of mining, and the "completion" practices (i.e., reclamation). In January, 1975 a surface mine permit application from Harmon Coal Company was denied because of the potential pollution of the stream which served as Brookville's water supply. This denial, perhaps the earliest for environmental reasons, used previous mining within the area of the proposed mine site as a mine drainage quality prediction tool.

Brady and Hornberger (1990) discussed the use of postmining water quality as a prediction tool for surface mines. They listed limitations to this method as:

> "(1) stratigraphic or chemical changes occur between sites (i.e., overburden on adjacent site may not be similar to the proposed site, or differing depths of mining are responsible for the chemical and stratigraphic changes), (2) mining practices, such as disposal of high sulfur coal refuse, may have adversely affected water quality, (3) multiple seam mining has occurred on adjacent sites and the observed water quality cannot necessarily be tied to any one particular coal seam and overburden, and (4) hydrologic complications make it difficult to relate water quality to previous mining (such as the absence of discharges, dilution of discharges by water unaffected by mining, interference from other pollution sources, neutralization from unaffected strata, and so forth)."

The examination of mine drainage from previously mined lands is the best predictor of mine drainage quality, when adequate data is available and interpretation of that data is done properly. The major advantage of looking at the quality of preexisting mine

drainage is that it is the result of a full-scale weathering (leaching) test, which has incorporated into it climatic, mining, and other variables. Climatic variables include: site specific precipitation, and field temperatures, including any seasonal variations. Field conditions also include infiltration and runoff factors. The mining variables include the strata (lithologies) encountered by mining, including its variability within the site, and the redistribution of these rocks in the spoil. Other variables include spoil pore gas chemistry, including vertical variations, and real world scale (i.e., rock particle size, ratios of rock volume to water volume). These are factors that are only approximately simulated, if at all, in laboratory leaching tests. Studies of previous mining also provide information on actual concentrations of mine drainage constituents, including pH, alkalinity, acidity, iron, manganese, aluminum, and sulfate. Previous mining water quality is, with some limitations, "the proof of the pudding." As with any prediction technique, interpretations must be considered in the light of information provided by other prediction tools.

Factors to Consider

Four factors must be considered when interpreting water quality from previously mined areas. Each of these, if not properly taken into account can lead to improper predictions of water quality for the proposed mine. These factors are: the proposed mining is on different coals and overburden, mining on same seam(s) but with significant differences in stratigraphy or in amount of area disturbed, hydrologic complications, and differences in mining practices.

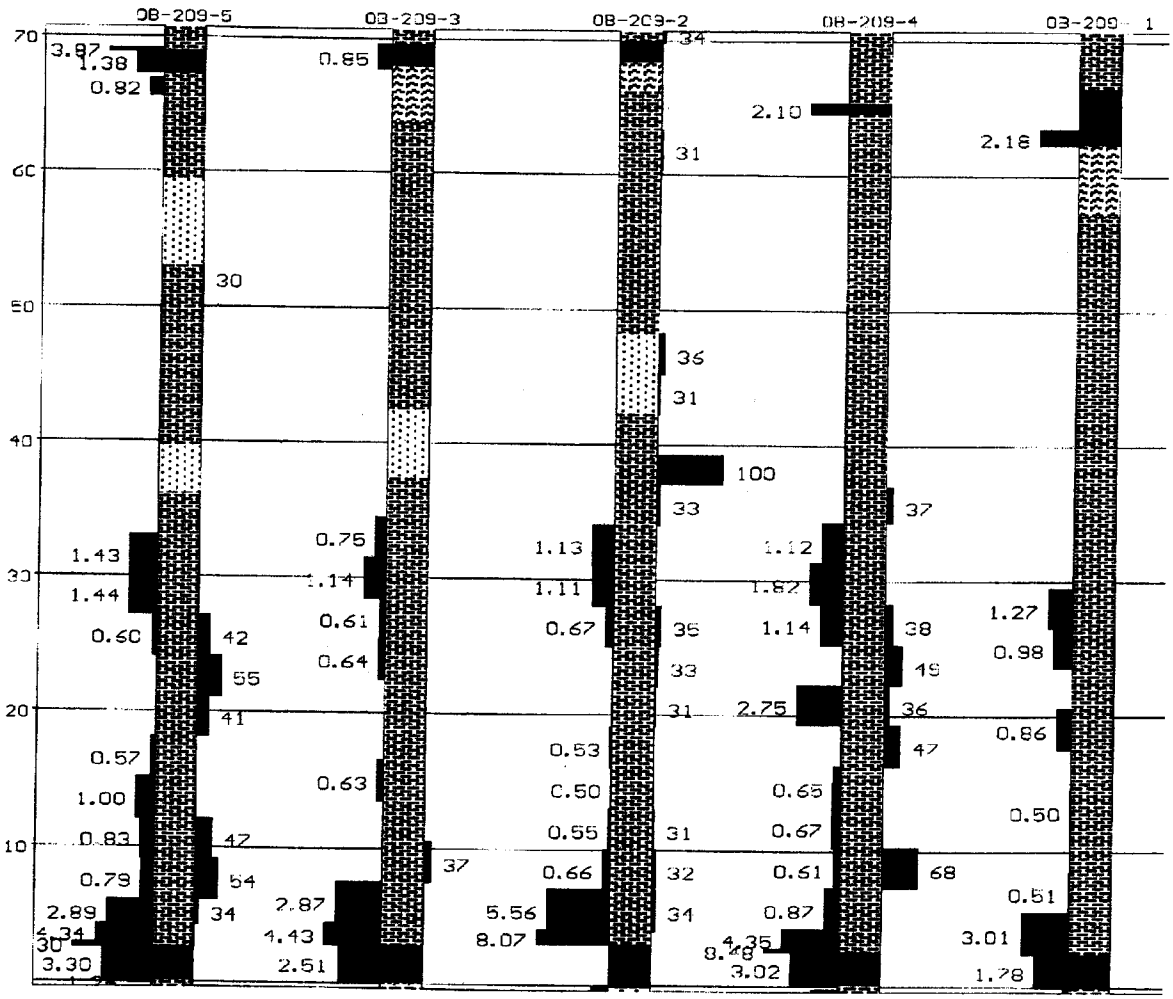


Figure 9.1 Overburden from the lower Kittanning coal to just above the middle Kittanning coal showing percent sulfur (left of columns) and neutralization potential (NP) (right of columns). The site is located in Redbank Township, Clarion County. Only sulfur values greater than 0.5% and NP greater than 30 ppt $CaCO_3$ are shown.

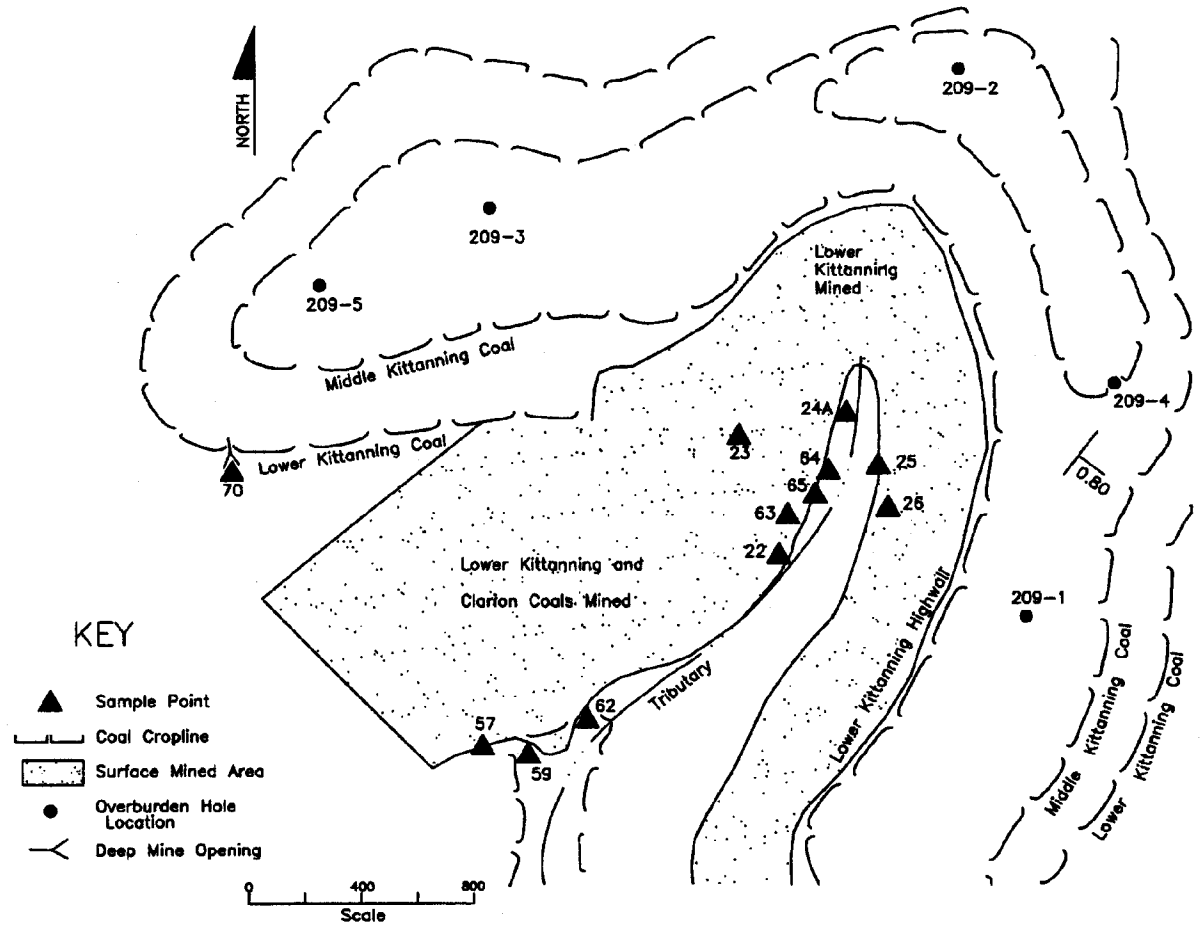


Figure 9.2 Site map showing mined areas, coal outcrops, water sample points and location of overburden drill holes. The drill logs are shown in Figure 9.1. Net alkalinity of water is shown next to water sample points (diamonds). The site is located in Redbank Township, Clarion County.

The Proposed Mining is on Different Coals and Overburden

Obviously, if no mining has occurred on a particular coal seam in the area of interest, previous mining's water quality cannot be used as a predictive tool, because it does not exist. Also, predictions of water quality can only be made if the same coal seam(s) and strata are being considered. Accurate geologic maps, showing coal croplines and structure are an extremely helpful aid in assuring correct correlations of coal seams. Numerous excellent studies by the Pennsylvania Geological Survey, in particular since the early 1970s, have helped resolve stratigraphic correlation problems around the state. Local geologic reports should be consulted for stratigraphic correlations, locations of coal outcrops, and structure. Site specific and nearby permit drilling information should also be consulted to confirm correlations.

Some examples will illustrate the importance of knowing which coal seams were mined. The first example involves the Clarion and lower Kittanning coals in Redbank Township, Clarion County, PA. Water quality associated with the lower Kittanning is typically acidic, which is consistent with results of acid-base accounting, which shows up to 30 ft (10 m) of strata with percent sulfur frequently being 0.5 to 7.5 percent (Figure 9.1). Neutralization potentials (NP) within this same stratigraphic interval are generally less than 40 ppt $CaCO_3$. Drill holes 1, 2, and 3 were analyzed by a different laboratory than holes 4 and 5. It is interesting to note that only holes 4 and 5 show NP's greater than 40. Differences between laboratories for NP's in this range have been frequently noted when siderite is the dominant carbonate. Siderite is not an effective acid neutralizer.

The marine Vanport limestone occurs stratigraphically between the Clarion and the lower Kittanning coals. Although no acid-base accounting was performed on the Vanport in this vicinity, it typically has greater than 80% calcium carbonate (see Chapter 8). In the area of the mine site the limestone is about 6 ft (2 m) thick. The Figure 9.2 map shows areas where the Clarion and lower Kittanning coals were mined, and the associated mine discharges. Table 9.1 shows the associated water quality. Where the spoil is predominately Clarion coal overburden, the drainage is net-alkaline (e.g., sample points 57, 59, 62). Discharges associated with mining that was predominantly on the lower Kittanning coal are net-acidic (e.g., 23, 24A, 25, and 26). Discharges that are a mixture of Clarion and lower Kittanning spoil range from net-alkaline (e.g., 63) to net-acidic (e.g., 22, 64, 65). The mixed spoil, even when acidic, is less acidic than water from areas where just the lower Kittanning coal was mined. Thus, the overburden from the two coals produces different water qualities.

Table 9.1 Median water quality values for sample points shown in Figure 9.2. LK indicates water associated with the lower Kittanning coal, CL identifies water associated with the Clarion coal, and "mix" is water from both seams.

Sample Point	Coal Seam	N	pH	Conductance (µS/cm)	Net Alkalinity (mg/L)	Fe (mg/L)	Mn (mg/L)	Sulfate (mg/L)
23	LK	5	4.8	1557	-38	1.96	40.0	1050
24A	LK	3	5.8	2110	-84	0.32	60.2	1690
25	LK	2	3.5	1570	-99	3.39	39.2	1185
26	LK	3	4.3	1663	-52	0.08	35.0	1220
70*	LK	1	4.7	130	-13	1.35	0.3	35
22	MIX	2	4.2	1398	-19	0.21	27.1	1047
57	CL	2	6.6	1181	+42	3.48	24.6	760
59	CL	2	7.8	1462	+83	2.90	12.8	931
62	CL	1	8.1	1369	+121	1.32	6.4	832
63	MIX	3	8.0	948	+189	0.28	0.0	272
64	MIX	3	6.8	1657	-10	0.05	47.5	1070
65	MIX	1	5.7	1798	-39	2.28	51.9	1375

*Sample point 70 is from a small "country bank" mine. All other samples are surface mine discharges.

The importance of knowing which coals were mined in an area is also illustrated by a study near Luthersburg in Clearfield County, PA (David Bisko, DEP hydrogeologist, personal communication, 1991). The lower Kittanning through upper Kittanning coals were mined. The lower Kittanning and middle Kittanning coals, if surface mined by themselves, produce acidic drainage. If these coals are mined in conjunction with sufficient calcareous strata associated with the upper Kittanning coal, the water quality is usually alkaline. Most mines in the area did multiple seam mining, although the combination of seams mined varied from site to site. Figure 9.3 is a map of the area showing

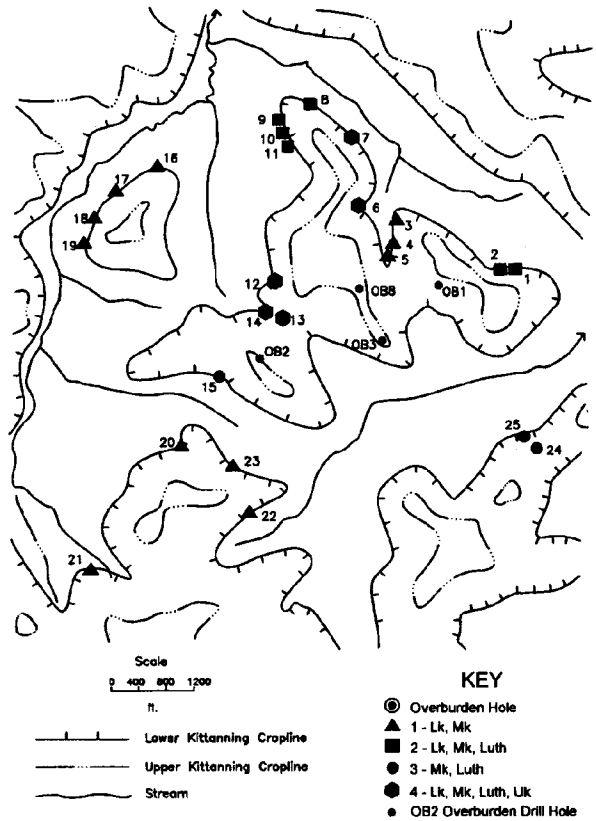


Figure 9.3 Map of an area within the Luthersburg Quadrangle, Clearfield County. Map shows coal croplines and mine discharge sample point locations discussed in text and shown in Table 9.2. The different symbols used at water sample locations indicate which coal seams and associated overburden were mined upgradient from the discharge point.

locations of water samples and overburden drill holes. Figure 9.4 shows representative examples of overburden percent sulfur and neutralization potential for intervals from the lower Kittanning coal through the upper Kittanning coal overburden. Note that overburden above the lower and middle Kittanning coals is high in sulfur (up to 2.7%), but low in NP (< 40 ppt CaCO3). The highest NP's (as high as 327 ppt CaCO3) are associated with the "Johnstown limestone" which occurs below the upper Kittanning coal.

Table 9.2 shows water quality analyses for the discharge points shown on the Figure 9.3 map. Boxplots comparing pH and net alkalinity for various combinations of coal seams mined are shown in Figure 9.5. It is clear from the pH and net alkalinity values that the coal overburden combinations of the lower Kittanning and middle Kittanning, and the LK, MK and Luthersburg result in water that is acidic. Mining of the MK

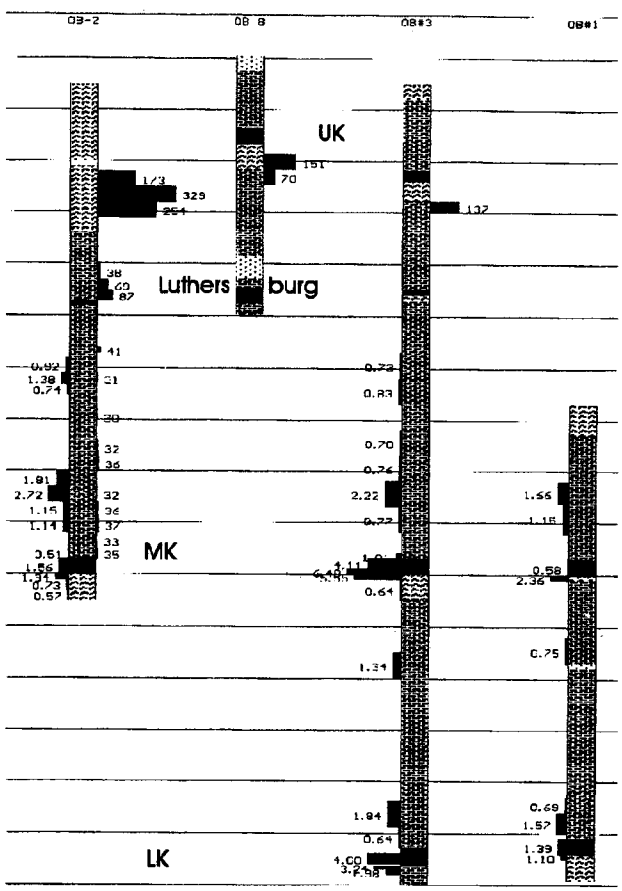


Figure 9.4 Overburden chemistry of the interval from the lower Kittanning through the upper Kittanning coals. The location of the drill holes is shown on Figure 9.3. Total percent sulfur values are displayed to the left and NP to the right of the drill log. Only sulfur values greater than 0.5% and neutralization potential values greater than 30 ppt $CaCO_3$ are shown. Gridlines are at 10 ft (3m) intervals.

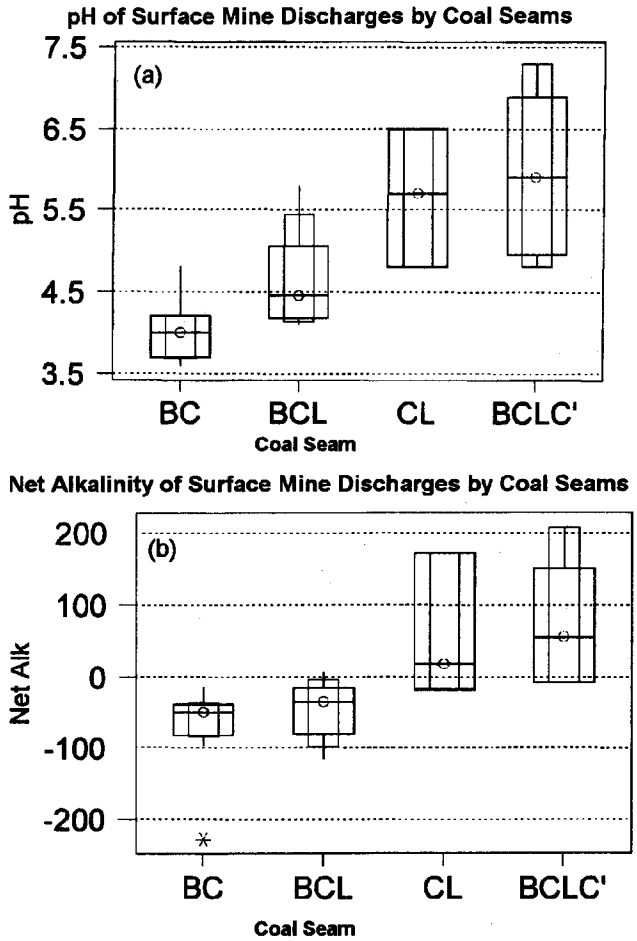


Figure 9.5 a and b Boxplots showing the distribution of (a) pH and (b) net alkalinity for discharges representing different combinations of coal seams that were surface mined. Wide "box" shows interquartile range (i.e., contains 50% of data). Horizontal line with circle is the median. Narrow box shows the 95% confidence interval around the median. Letters on x-axis indicate the coal seams that were mined. BC = lower Kittanning and middle Kittanning coals; BCL = lower Kittanning, middle Kittanning, and Luthersburg coals; CL = middle Kittanning and Luthersburg coals; BCLC' = lower Kittanning, middle Kittanning, Luthersburg, and upper Kittanning coals. The letters used are those that are frequently used in Pennsylvania's bituminous coal fields to indicate the designated coal seam (with the exception of the Luthersburg coal, which is rare in other areas of the coal field). Water quality data is from Table 9.2.

and Luthersburg coals, and the LK, MK, Lutherburg, and upper Kittanning coals typically results in net-alkaline drainage. (The Luthersburg coal occurs between the MK and UK coals, and occurs in minable thickness in the area of Luthersburg, Clearfield County.) The differences in pH and net alkalinity of mines that disturbed only the overburden of the stratigraphically lower coals (LK and MK coals), compared to mines that disturbed higher strata (LK through UK overburden), are statistically significantly different. The mines that encountered the higher strata, in particular sufficient amounts of Johnstown limestone, produced alkaline drainage. The mines that encountered only the lower strata produced acidic drainage.

The point of the above examples is that apples must be compared to apples. Mines having similar geology can be compared with meaningful results. However, mines involving different coal seams or different sections of strata should not be compared. Water quality

prediction requires knowing the stratigraphic relationships of the coal seams that were mined.

Table 9.2 Water quality data for sample points shown on Figure 9.3. Distributions for pH and net alkalinity are shown on Figure 9.5 for the four groups of coal overburden. LK is lower Kittanning, MK is middle Kittanning, Luth is Luthersburg, and UK is upper Kittanning.

Sample No.	Coal Seam Mined	pH	Net Alkalinity (mg/L)	Mn (mg/L)	Sulfate (mg/L)
1	LK, MK, Luth	4.1	-116	57.9	1807
2	LK, MK, Luth	4.6	-68	45.9	1330
3	LK, MK	4.8	-14	5.8	738
4	LK, MK	4.1	-47	16.3	678
5	LK, MK	4.0	-68	15.7	588
6	LK, MK, Luth, UK	4.8	-6	4.2	780
7	LK, MK, Luth, UK	5.1	-8	1.4	654
8	LK, MK, Luth	5.8	+6	23.5	1578
9	LK, MK, Luth	4.3	-22	14.1	1500
10	LK, MK, Luth	4.8	-38	9.5	414
11	LK, MK, Luth	4.2	-32	15.6	768
12	LK, MK, Luth, UK	6.5	+94	12.0	852
13	LK, MK, Luth, UK	5.9	+56	13.6	1680
14	LK, MK, Luth, UK	7.3	+208	.4	1710
15	MK, Luth	6.5	+172	18.2	572
16	LK, MK	3.9	-98	36.7	1428
17	LK, MK	4.3	-23	14.2	732
18	LK, MK	4.1	-82	52.0	1692
19	LK, MK	3.7	-42	16.4	462
20	LK, MK	4.2	-38	4.6	850
21	LK, MK	3.6	-50	36.7	937
22	LK, MK	3.6	-74	8.5	294
23	LK, MK	3.7	-228	18.6	978
24	MK, Luth	5.7	+18	37.2	1470
25	MK, Luth	4.8	-18	21.5	792

As a rule of thumb, the closer the previously mined area is to the proposed mine site, the better it can serve as a prediction tool. At what distance a mine fails to serve as an accurate prediction tool will vary depending on the similarity of the geology between the area previously mined and the proposed mine site. Where significant facies changes occur over short distances, immediately adjacent mines may not be representative. This limitation is discussed below in more detail.

Mining on Same Seam(s) but with Significant Differences in Stratigraphy or in Amount of Area Disturbed

Mining may be proposed on the same seam, but if there are significant stratigraphic changes between the previously mined area and the proposed area, comparisons may be inappropriate. The two most common factors related to stratigraphic changes are geologic facies differences from one mine to the next, and the mining of differing amounts of cover. Higher cover will encounter additional strata. An additional factor that will be discussed is the role that differing amounts of disturbed area can have on water chemistry.

Facies Relationships - An example of the role of facies changes can be illustrated by five mines studied in the Stony Fork watershed in Fayette County (Brady et al., 1988). All mines in this area extracted the upper Kittanning coal seam. The mines with predominately sandstone overburden are producing acidic drainage, whereas mines with calcareous shales and limestones are producing alkaline drainage. The mine sites (A through F) are shown in relation to the depositional environment interpreted from strata at 25 ft. (7.6 m) and 50 ft (15.2 m) above the coal (Figures 9.6 a and b). Since the time of the Brady et al. study, several additional mine permit applications have been received for this watershed, and consequently more data have been obtained. Since publication of the Brady et al. (1988) paper, two permit applications have been received for the area between mine sites A and B. Both mine sites occur in the area having calcareous shales and limestones. One of these has been mined and reclaimed and is producing alkaline drainage (site F, Figures 9.6 a) and b)). Another application was received for the area just north of site D. Its overburden was essentially identical to site D (i.e., predominantly sandstone overburden), and the permit was denied.

The mines developed in the area interpreted to have been deposited in a high energy depositional environment, have sandstone and siltstone overburden. Mine sites A, D, and E occur within this depositional environment. The area interpreted as a lower energy depositional environment contains mines B, C, and F. The sandstone and siltstone units are not calcareous, whereas the low energy deposits contain calcareous shale and freshwater limestones. Mining in the area containing the calcareous strata results in alkaline drainage. Table 9.3 shows water quality chemistry for the six reclaimed mine sites.

Paleoenvironmental maps, such as those constructed for the Stony Fork drainage basin, may help predict the distribution of facies, however, studies of this type are rare. Even if good paleoenvironmental maps exist, facies changes can be abrupt, and detailed drilling is typically necessary in areas of facies transition. Paleoenvironmental maps probably are best used as a tool for designing an overburden sampling plan. In the Fayette County study, mine site A is both within the high energy and low energy depositional environments. Inspection of the active highwall revealed an

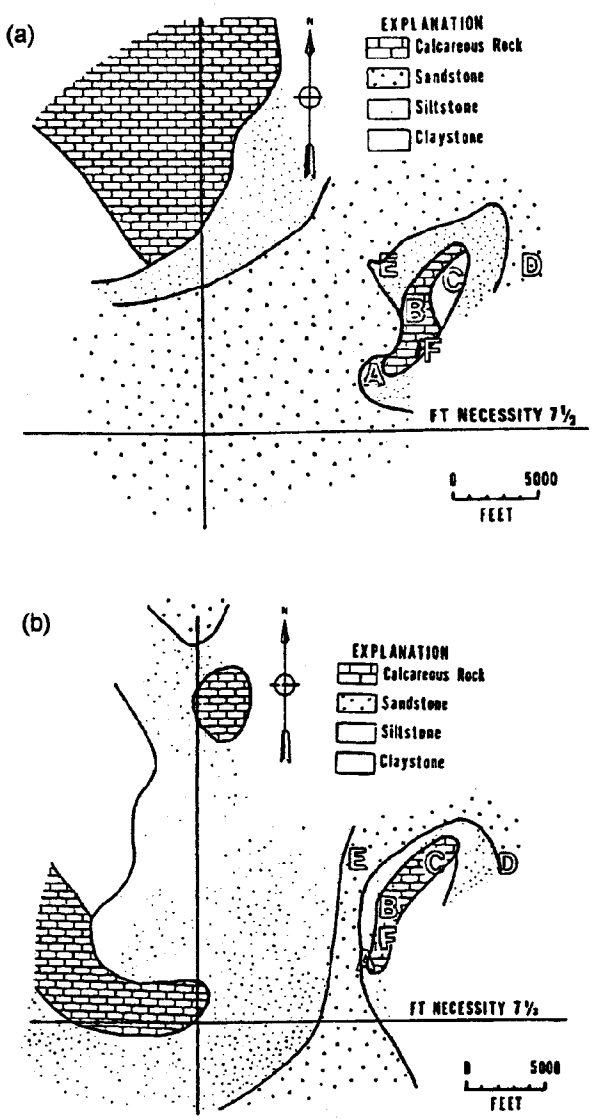


Figure 9.6 a) Facies map of lithologies at 25 feet above the upper Kittanning coal in the vicinity of the Stony Fork watershed, Fayette County, PA. b) Facies map of lithologies at 50 feet above the upper Kittanning coal in the vicinity of the Stony Fork watershed, Fayette County. Figures from Brady et al. (1988). The letters show the locations of mine sites discussed in the text and correspond with water quality data shown in Table 9.3.

area where the limestone was eroded and replaced by a channel deposit. All the overburden drill holes were located within the low energy portion of the mine, thus overestimating the calcareous nature of this site. This permit was issued prior to an understanding of the lateral distribution of depositional facies. If the true nature of the site had been known, either the permit would have been denied or the mining plan would have been modified to compensate for the acid potential. Sandstone overburden within the Allegheny group, as illustrated in the above example, can be acid producing. This subject is dealt with in detail in Chapter 8.

Table 9.3 Median postmining water quality for mine sites in Stony Fork watershed.

Mine Site	pH	Net Alkalinity (mg/L)	Fe (mg/L)	Mn (mg/L)	SO_4 (mg/L)
A	3.2	-185	25	22	1434
B	5.6	+6	0	0	<43
C	7.6	+382	5	5	744
D	2.9	-814	51	29	981
E	3.1	-361	52	31	432
F	7.4	+237	0	1	32

Amount of Cover - Different amounts of cover mined on the same coal seam can result in different water quality. Because of mining equipment limitations, old pre-act mining from the 1940s and 1950s seldom exceeded 40 ft (12 m) of cover. Improvements in mining technology have allowed many of these sites to be remined to greater cover heights. Mining of additional cover can have both positive and negative influences. Figure 9.7 illustrates a situation where low cover mining ~40 ft (12 m) or less would encounter high sulfur strata, but no appreciable calcareous strata. A mine would not encounter calcareous strata until a highwall height of 40 ft (12 m) or more is mined. The reason for this is a combination of the stratigraphic position of the calcareous strata and the dissolution of carbonates by surface weathering, at shallow <20 ft (6 m) cover.

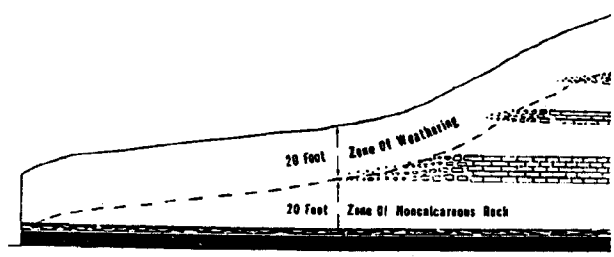


Figure 9.7 Schematic cross-section showing relative positions of high-sulfur strata and calcareous strata (brick pattern). In this example 40 ft (12 m) or more cover must be mined in order to encounter the alkaline material.

Shallow mining <40 ft (12 m) would probably result in acidic drainage, whereas mining to a cover height of 85 ft (26 m) should encounter enough calcareous rock to result in alkaline drainage.

An example of water quality differences between old mining, that encountered shallow cover and occurred over a limited area, compared with more extensive and deeper mining is illustrated by a mine site in Cambria County. The original shallow-cover <30 ft (10 m) mining occurred in the 1950s, and only a few tens of acres were affected. No water quality data is available from this early period. The earliest water quality data available is from 1978, over 20 years later (Figure 9.8). In the intervening years some natural amelioration may have taken place. It is doubtful, however, that the mining in the 1950s ever had a significant impact on the water quality, because the overburden was mostly weathered shallow-cover material and the area of disturbance was small. Modern mining methods were first used at this site in November 1980.

Figure 9.8 shows plots of various water quality parameters at a spring down-gradient from the mine in Cambria County. The initial water quality in 1978 through 1981 represents conditions from pre-modern mining methods. The water had low concentrations of sulfate, acidity, manganese, and aluminum, and little variation in their concentrations. Specific conductance was also low (~100 µS/cm). Figure 9.8 shows water quality through time for acidity, manganese, and sulfate. The mining that occurred from November, 1980 through September, 1985 took a maximum of 80 ft (24 m) of overburden and affected approximately 175 acres (71 hectares). Mining-related increases in acidity, manganese and sulfate are apparent from Figure 9.8. Other parameters that increased are aluminum and specific conductivity.

Figure 9.9 shows the acid-base accounting data for the coal and overburden from three drill holes at the Cambria County mine site. The coal and overlying strata have the potential to produce acid (% S > 0.5%), and have little, if any, neutralization potential. Thus, additional mining exposed unweathered rock that had acid potential, but no neutralization potential.

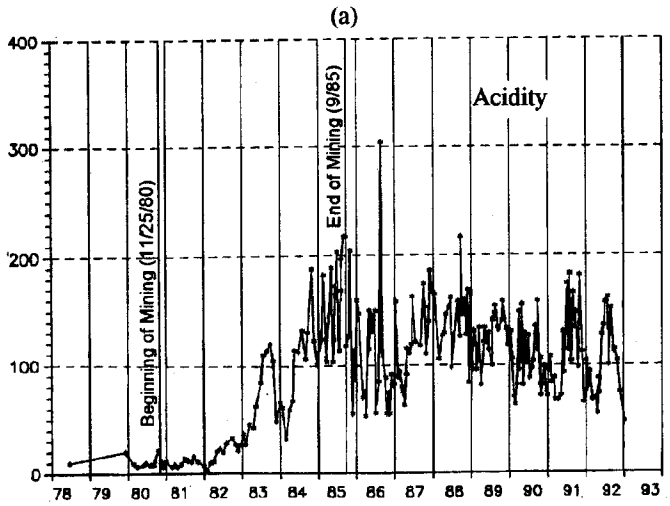
Water from the previously mined area of the 1950s did not reflect the water quality that was produced by the mining conditions in the 1980s. Mining on this site was concurrent, done according to permit plans, and is now reclaimed with lush vegetation. Mining in accordance with permit conditions does not assure successful water quality on a site that has acid-producing potential and lacks calcareous strata.

Increased Area of Disturbance - The affect of an increased area of disturbance and the mining of additional cover is illustrated in Figure 9.10. This is the same Cambria County site that is discussed in the above paragraphs. Two conservative water quality parameters, sulfate and manganese, show increases in concentration that are directly related to the amount of area affected. Sulfate compared to acres mined is shown in Figure 9.10. When mining was progressing quickly, as in early 1982, there was a sharp increase in manganese and sulfate a year later. When mining was progressing more slowly, as during the second half of 1982 through the middle of 1983, there was a corresponding leveling off of water quality from the middle of 1983 to the middle of 1984. The larger the area affected by mining, the higher the concentration of water quality parameters.

Figure 9.10 suggests that discharge quality can be a function of the area disturbed. In this case, the stopping of mining in mid-course would have reduced the amount of acid and metal formation. Alternatively, monitoring results could have been heeded and mine drainage prevention methods could have been incorporated into the mine plan. As can be seen from Figure 9.10, the downgradient discharge point that was being monitored showed delayed effects from mining of about one year. There are two factors that could account for this delay, one being the rate of acid formation and the other being the rate of transport (flow rate) of acid weathering products. If the delay was due to flow rate, the length of time it took for water from the mine site to discharge at the surface water monitoring point, a quicker monitoring warning system might have been achieved by installing monitoring wells in the spoil.

Hydrologic Complications

There are several hydrologic complications that can affect the use of water quality from adjacent mines as a prediction tool. The most obvious of these is the situation where there is no water discharging from the previously mined area; the old adage "it's a dry site." This can be falsely assumed to mean mining "success", because there are no "pollutional discharges." There is no such thing as a "dry site" in Pennsylvania. The absence of discharges does not mean that there is no water associated with or flowing from the mined area. Pennsylvania has a humid climate, where precipitation exceeds evapotranspiration on a yearly basis. Thus, there is groundwater recharge, and this groundwater recharging through the mine spoil is flowing somewhere. It may not discharge as seeps or springs, but may be entering



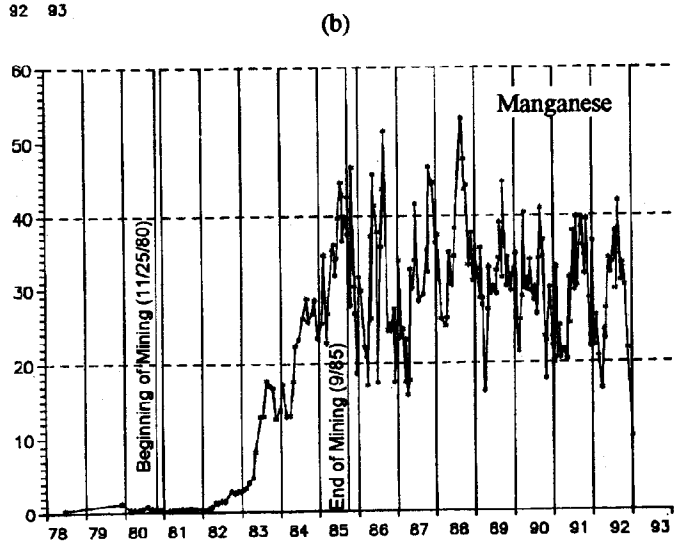
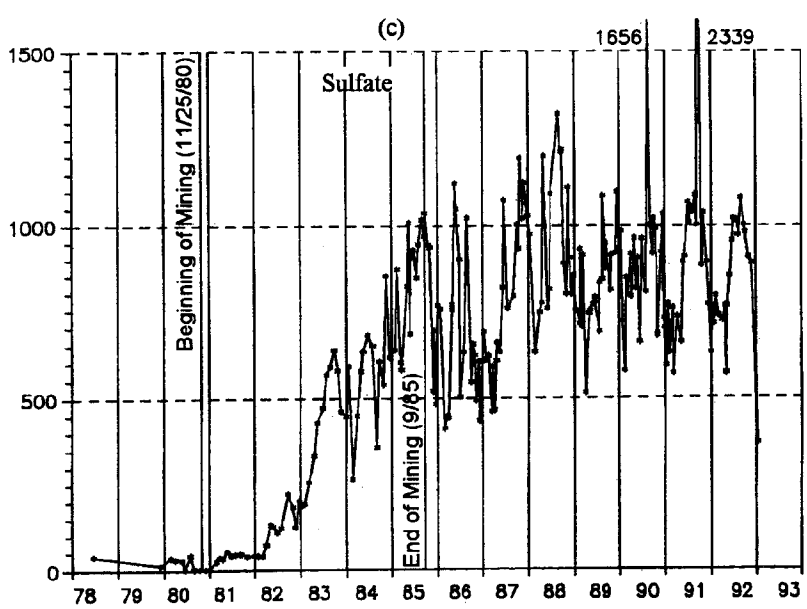


Figure 9.8 Graphs of (a) acidity, (b) manganese and (c) sulfate through time for a mine site in northeastern Cambria County. Y-axis unit is mg/L. Conditions prior to impact by modern mining are represented by data from 1978 through 1981. Postmining conditions are those samples collected after the end of mining in September 1985.



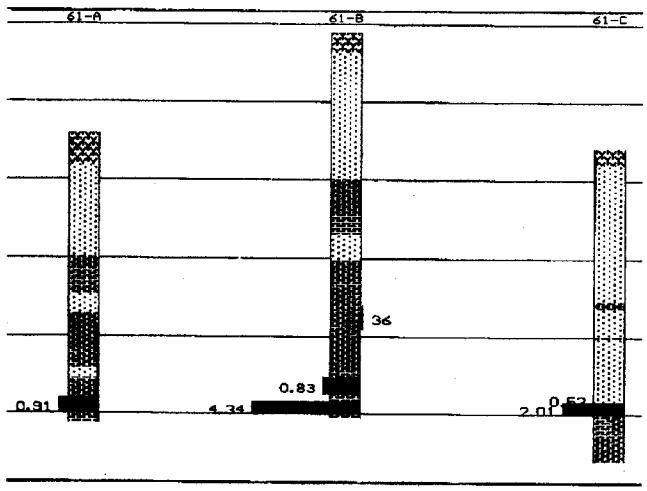


Figure 9.9 Overburden data for drill holes from the same mine as the water sample data shown in Figure 9.9. Total percent sulfur is shown to the left of the drill logs and NP is shown to the right. Only sulfur values greater than 0.5% and neutralization potential values greater than 30 ppt $CaCO_3$ are shown. Gridlines are spaced at 10 ft (3m).

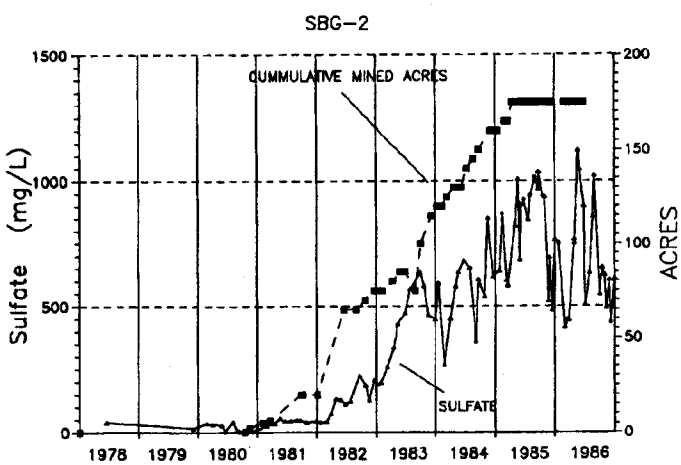


Figure 9.10 Graph showing the relationships between acres mined and water quality changes for sulfate. All acreages are estimates by one mine inspector, with the exception of the one "decrease" in acreage (late 1983), which was an estimate by a different mine inspector.

a deeper groundwater flow system which will ultimately discharge as base flow to a stream or as a discharge from a lower stratigraphic interval. Groundwater and surface water will be discussed separately because of the many different factors that influence their chemistry.

Groundwater - Adjacent mining as a prediction tool only works where there is representative groundwater (from springs or wells) that can be sampled and analyzed. If existing groundwater sample points are inadequate, monitoring wells or piezometers can often be installed into previously mined spoil, or into an underlying aquifer, to ascertain the postmining water quality. Groundwater chemistry is rarely uniform through time or through space. The discussion that follows will illustrate water quality variability.

Climatic influences on discharge quality. When using water quality data as a prediction tool, it must be kept in mind that water quality, even at the same sample point, is not normally a constant, but will vary for a variety of climatic reasons such as seasonal influences and precipitation/infiltration events. In some instances, not only water quality, but also water quantity must be considered. Flow can affect concentration. Concentration times flow is "load," which has units of mass (or weight) per period of time. Load is significant if determining the amount of reagent necessary to treat a mine drainage problem, and load is used to determine water quality changes, pre- and post-remining, on remining sites (see Chapter 17).

Flow can be greatly influenced by infiltration, which is dependent on various processes, such as rainfall, runoff, evapotranspiration, and snow-melt. Not all mines respond similarly. Smith (1988), in discussing flow, concentration, and load, points to three types of discharges. A forth type of discharge is also discussed below based on observations of the author and other sources. The four types of discharges are:

1. High flow - low concentration / low flow - high concentration response, where the flow rate varies inversely with concentration and variability is generally very great;
2. Steady or damped response discharges which exhibit relatively minor or delayed response in flow rate with minor changes in chemical characteristics;
3. "Slugger" response, whereby dramatic increases in discharge are accompanied by little change in concentrations, resulting in large increases in loading; and
4. "Slammer" response, whereby dramatic increases in discharge are accompanied by increases in concentration. This will result in significant increases in loading during these "slammer" events.

Figure 9.11 illustrates an example of a Type 1 discharge at the Arnot No. 1 deep mine in Tioga County. This figure shows the relationships between flow,

acidity concentration, and acidity load. The data represents the averaging of approximately four years of monthly data. Figure 9.11 shows an inverse relationship between flow and concentration and the seasonal influences on both. During the spring months (March, April and May) flow is high and concentrations are low due to dilution. Load is most influenced by flow. Smith (1988) concludes that "the majority of preexisting discharges fall into this category. This usually occurs with non-point surface mine discharges where the capacity for ground water storage is relatively small and groundwater flow paths are short." Type 4 discharges are probably the second most common from surface mines.

The Type 2 discharge "shows no systematic trend in acidity concentration with increasing discharge, presumably due to the large ground water storage reservoir and its ability to dampen changes in water quality" (Smith, 1988). The example given in Smith is a discharge from a large anthracite deep mine with a huge mine pool. The Type 3 discharge described by Smith is represented by a discharge from a coal refuse pile in Indiana County. "This type of discharge exhibits large variations in discharge rate with relatively minor, if any, change in acidity concentrations. Consequently, rapid increases in flow result in similarly large increases in acid loading rates or acid "slugs." Types 2 and 3 are probably less common with surface mine discharges.

Type 4 discharges often have a dramatic increase in acidity (and other mine drainage parameters) following substantial rainfall and infiltration. Brady et al. (1990) observed a surface mine discharge (Mine Site 10) in Venango County that had net alkalinity ranging from -225 mg/L to +225 mg/L $CaCO_3$ and pH from 4.5 to 6.8. The acid conditions followed precipitation events. This site had an abundance of both calcareous and pyritic strata. McCommons and Shaw (1986), DEP hy-

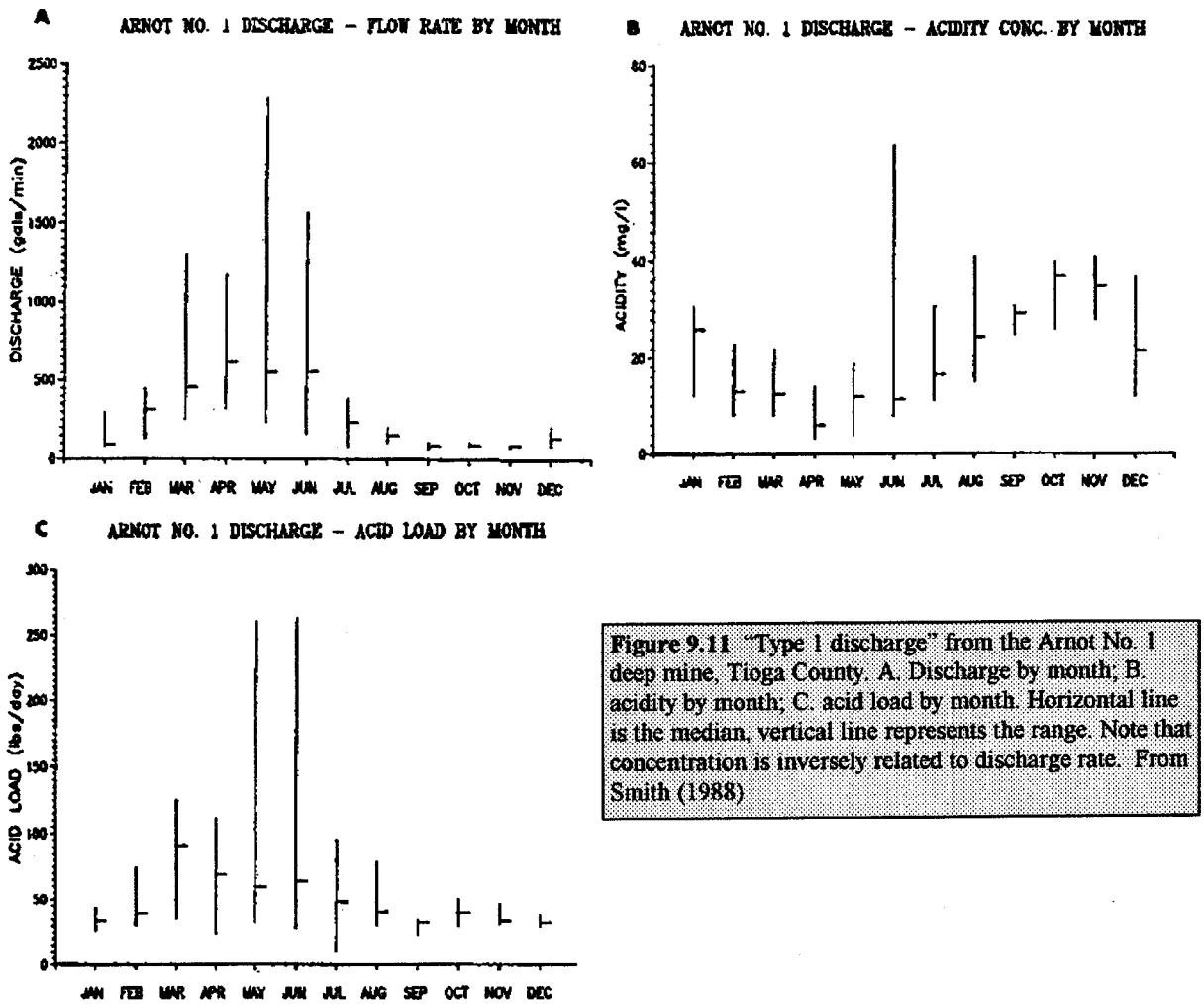


Figure 9.11 "Type 1 discharge" from the Arnot No. 1 deep mine, Tioga County. A. Discharge by month; B. acidity by month; C. acid load by month. Horizontal line is the median, vertical line represents the range. Note that concentration is inversely related to discharge rate. From Smith (1988)

drogeologist and aquatic biologist respectively, observed increased sulfate following significant rain events at a deep mine discharge in northern Cambria County. This discharge had been impacted by surface mining of overlying coal seams. McCommons and Shaw compared fluctuations in sulfate concentration with the occurrence of rainfall events. Table 9.4 summarizes significant precipitation events that preceded peak sulfate concentrations (>1000 mg/L). "In each case, observed rainfall for the 15 days prior to the sample date exceeded expected accumulations for that time interval. Each sulfate peak, resulting from a precipitation event, was followed by a considerable drop in sulfate concentration as the hydrologic system returned to near base flow conditions. The rainfall observed during the 15 days preceding these low readings was less than or near normal accumulations."

The "slams" of sulfate and acid following rain events is apparently due to several processes. First, during dry periods, there is a buildup of pyrite weathering products, soluble sulfate salts, in the unsaturated mine spoil. These salts are essentially stored mine drainage. Second, infiltrating waters from rainfall or snowmelt dissolve these salts, and flush them into the saturated groundwater zone. A third process that influences the variable water quality involves unequal rates of acid production (from pyrite oxidation and flushing of these weathering products) and dissolution of calcareous minerals.

It is obvious from the above examples and discussion that to accurately characterize mine discharge chemistry, it is necessary to have multiple samples which represent seasonal variation and variation due to various other climatic events such as rainfall and snowmelt. With only one sample it may be impossible to tell whether or not a sample is representative of seasonal and other climatic influences that affect the water chemistry.

Lateral variability in water quality within a mine site. Another complication in interpretation of mine site water quality is that water chemistry can vary within a mine, and some mines produce both alkaline and acid water. Sites with alkaline and acid water seem to be the exception rather than the rule in Pennsylvania, but these types of sites do exist (e.g., Brady et al., 1990, Mine Site 6; and examples cited below). Erickson and Hedin (1988) in their study of 32 mines in Pennsylvania, West Virginia, Maryland, Illinois, and Kentucky looked at some sites that had both alkaline and acid discharges. Which states these sites occurred in is not stated, but about half of the sites studied were in Pennsylvania.

Three mine sites with multiple sample points in mine spoil will be examined. Two of these sites also had postmining discharges. These sites were chosen to show mines with alkaline spoil water, acidic spoil water, and both alkaline and acidic spoil water. The first site (Table 9.5) represents spoil with predominantly alkaline water. The coal seam was the lower Kittanning and the depositional environment above the coal was marine. The mass-weighted net neutralization potential for the area of the wells was 2.92 ppt $CaCO_3$, with MPA being 18.67 and NP being 21.59 ppt $CaCO_3$. The three spoil wells and one bedrock well (N-1) shown in the table were drilled in an area of less than 15 acres (6 hectares). More details on this site, including locations of wells and overburden chemistry, are contained in Cravotta et al. (1994a; 1994b). This study was partially funded by the Department of Environmental Resources (DER) (now the Department of Environmental Protection (DEP)).

The second site, the John A. Thompson site in Clearfield County, illustrates water chemistry variation across a mine that has acidic water (Table 9.6). The lower Kittanning coal was mined on this site. Brackish shales overlie the coal, and fluvial sandstones overlie the brackish shales. The mass-weighted net neutralization potential for the site is 1.71 ppt $CaCO_3$ (NP = 13.59, MPA = 11.88). Most of the carbonate at this site is probably siderite. All spoil wells and discharges have acidic water. Detailed information on this site is presented in Cravotta (1998). This study was also partially funded by the DER. Another example of a mine site with acidic water is the Fran mine site in Clinton County. This mine is discussed below in the section on "Differences in Mining Practices," along with representative water quality data. The water quality at this site varies from very poor to extremely poor. The worst water quality is associated with "coal cleanings" (Schueck, 1996).

The third mine site has extremely variable spoil water quality. Figure 9.12 shows locations of wells and a mine discharge and the water quality from these sample locations. This mine is located in Springfield Township, Fayette County, and the lower Kittanning seam was mined. The information on this mine was provided by DEP hydrogeologist Richard Beam. The overburden was primarily sandstone. One overburden hole was drilled, but only percent sulfur was determined. The analyses showed the 2 ft (0.6 m) coal had

Table 9.4 Variations in sulfate concentration at a mine discharge in Cambria County as a result of precipitation and snow melt. Precipitation is reported in cm (1 cm = 0.394 inches). Climatological data from Carrolltown, approximately 5 miles (8 km) south of the discharge. Table adapted from McCommons and Shaw (1986).

Sample Date	SO_4 (mg/L)	observed[1] (cm)	expected[2] (cm)	observed - expected	Preceding Days (15 days unless otherwise indicated)[3]
2/22/84	1002	7.29 (2.0)	4.37	+2.92	2/8 to 2/22/1984
3/22/84	510	4.04 (2.0)	4.37	-0.33	3/8 to 3/22/1984
8/22/84	1320	10.26	4.95	+5.31	8/8 to 8/24/1984 (17 days)
9/27/84	822	3.18	4.37	-1.19	9/12 to 9/26/1984
2/28/85	1320	7.16 (3.8)	4.67	+2.49	1/13 to 1/28/1985 (16 days)
3/6/85	624	4.27 (3.0)	4.37	-0.10	2/22 to 3/6/1985
9/10/85	1041	8.05	4.95	+3.10	8/25 to 9/10/1985 (17 days)
10/16/85	799	3.71	4.37	-0.66	10/2 to 10/16/1985

[1]Parentheses values in this column represent proportion of the observed cm as rain equivalent of depth of snowpack that melted during observation period. It is realized that actual snow/rain ratios are variable, being dependent on environmental conditions. For this study a snow/rain ratio of 10:1 was used.
[2]Expected rainfall values represent the daily average times days of observation period. The average annual rainfall measured at Carrolltown, 106.4 cm (41.88 inches), is based on a 30 year period (1951 to 1980). The daily average = 106.4 cm / 365 = .291 cm / day (x 15) = 4.37 cm = 15 days expected accumulation. 4.37 cm = 1.72 inches.
[3]The 16 and 17 day exceptions to the preceding 15 day time interval were made to include abnormally high rainfall events commencing just before the 15 day period started.

Table 9.5 Water quality from four wells in surface mine spoil, Clarion County. Chemical analyses are from samples collected December, 1992. Data from Cravotta et al. (1994b).

Well No.	pH	Fe (mg/L)	SO_4 (mg/L)	Alkalinity (mg/L)
N1-1	6.7	0.6	570	130
N2-1	6.1	30.0	2200	120
N3-1	6.1	2.0	680	170
N4-1	5.5	3.3	1150	51

8.4 percent sulfur (% S), a one ft (0.3 m) sand stone/shale stratum above the coal had 1.12 % S, and the coal/mudstone stratum below the coal had 4.45 % S. The highest sulfur in the overlying 53 ft (16 m) of sandstone is 0.19 %. Although neutralization potential of this overburden is unknown, it would appear from some of the more alkaline spoil water that some calcareous strata were present. All surface discharges emanating from this site are acidic. As can be seen on Figure 9.12, pH ranges from 2.9 to 6.4, and net alkalinity from -504 to +100. Acid and alkaline water occurs in wells only 200 ft (60 m) apart. This is the most variable spoil water known to the author.

The overburden of the Waynesburg coal (Dunkard Group), is notorious for producing both alkaline and acidic discharges, commonly on the same permit area (D. Scott Jones, DEP hydrogeologist, personal communication, 1991). As discussed in Chapter 8, water quality from the Waynesburg seam is among the most difficult to predict.

Fortunately, from a mine drainage prediction standpoint, most mines on other coal seams produce either alkaline or acidic water, not both. The point to be made here is that a single sample point may not reflect the true character of water being produced by a mine site.

Table 9.6 Water quality from the John A. Thompson mine in Boggs Township, Clearfield County. Net alkalinity is alkalinity minus acidity. Samples collected December 1991. Data from Durlin and Schaffstall (1993).

Sample Point	pH	Fe (mg/L)	SO_4 (mg/L)	Net Alkalinity (mg/L)
Well 2	4.0	120.0	880	-173
Well 3	4.3	36.0	1000	-150
Well 4	3.7	50.0	1600	-418
Well 5	3.4	72.0	1300	-364
Well 6	3.4	120.0	4600	-1140
Well 7	3.6	8.8	1300	-1000
Well 8	3.5	84.0	2300	-2000
Well 9	4.1	52.0	860	-710
Discharge N-1	3.3	48.0	2300	-380
Discharge S-1	3.3	0.7	990	-162

Chemistry changes along flow path. Something that must be kept in mind about groundwater is that its chemistry can change along the flow path. Dissolution or precipitation of minerals can alter the original chemistry of the mine drainage. When conditions allow for oxidation of iron, spoil water within the subsurface may be high in iron, and have a higher pH, than a surface discharge from the "toe" of the spoil. Table 9.7 illustrates the differences in water quality that can result from oxidation and precipitation of iron. Spoil water from the well is compared to water quality from two downgradient seeps. The spoil well has high iron (49.7 mg/L), whereas the discharges have low iron (<1.0 mg/L). The pH in the backfill is relatively high (5.5), whereas the seeps have pH from 3.8 to 4.1. It should also be noted that all of the iron in the spoil is in the reduced form, Fe^{2+}. Under reduced conditions, high iron water can have a relatively high pH. With precipitation of the iron, as has occurred between the spoil well and the discharges, the pH is lowered. Another factor that has occurred between the spoil well and the discharges is dilution. The Mn, SO_4, Ca, and Mg are

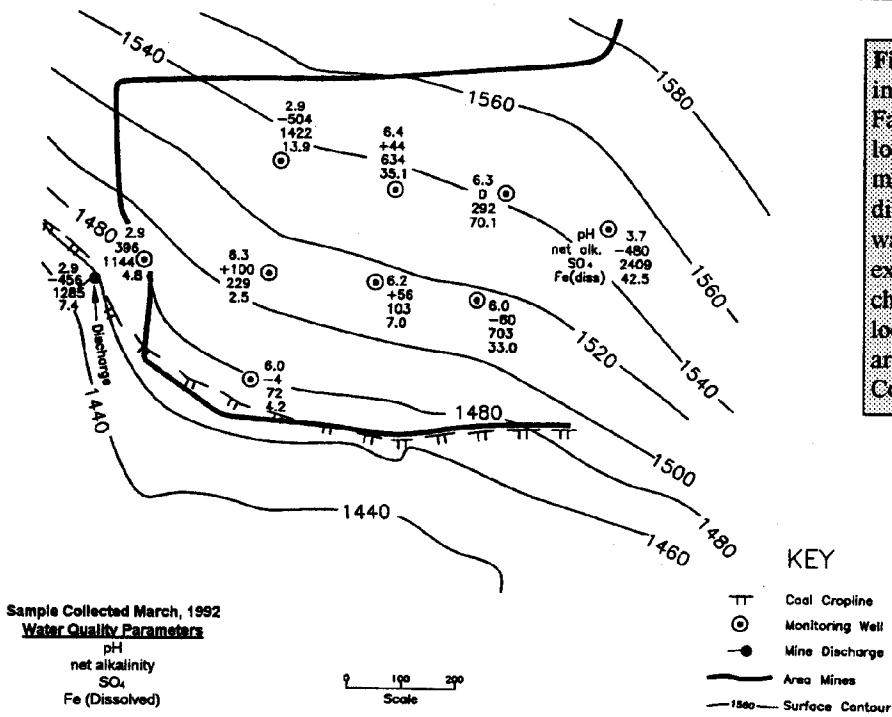


Figure 9.12 Map of mine site in Springfield Township, Fayette County, showing locations of wells drilled in mine spoil and a mine discharge, and associated water chemistry. Note the extreme variation in water chemistry among sample locations. Water quality units are mg/L, except for pH. Contours are in feet.

Table 9.7 Water quality from spoil and discharges at a mine in northern Cambria County.

Sample Point	pH	Net Alkalinity (mg/L)	Tot. Fe (mg/L)	Fe^{2+} (mg/L)
Spoil Well	5.5	-106	49.70	49.7
Discharge	4.1	-45	0.96	0.2
Discharge	3.8	-54	0.62	–

Sample Point	Mn (mg/L)	Al (mg/L)	SO_4 (mg/L)	Ca (mg/L)	Mg (mg/L)
Spoil Well	35	1	1327	192	172
Discharge	10	4	370	47	46
Discharge	8	4	277	30	32

four to five times higher in the spoil subsurface water than at the seeps.

If an acid pollution plume travels through calcareous rocks, some attenuation of the mine drainage quality should occur. Also, groundwater samples may be a mixture of water from mined and unmined (or mined on a different seam) sources.

Interference from other pollutional sources can also complicate interpretation. Mine drainage from coal mines is typically distinct enough in chemistry that other sources can be readily identified. For example, mine drainage is notorious for containing elevated sulfate, but surface mines normally have low chloride concentrations. Gas and oil well brine waters, on the other hand, have low sulfate in comparison to the high chloride concentrations. The differences between coal surface mine drainage and well brines are so distinct that they cannot be confused. Sometimes water from brines and mine drainage can commingle producing a mixed chemistry of the two waters. The interpretation of groundwater chemistry also requires an understanding of baseline water quality and the site's location within the groundwater flow system. Groundwater flow and hydrochemical zones are discussed in Chapter 2, and spoil hydrology is discussed in Chapter 3. Poth (1973) and Rose and Dresel (1990) identify three hydrochemical zones above the brine/freshwater interface (see Chapter 2). Most surface mines occur within the upper, most shallow, zone which has a Ca-HCO_3 baseline signature (see Chapter 10). Same deep mines occur in the deeper Na-HCO_3 zone (see Chapter 2).

Another factor that could possibly result in water quality differences between deep mines, especially flooded mines, and surface mines is differences in iron concentrations due to oxidation and the subsequent precipitation of iron. Iron from flooded deep mines may stay in solution as it travels from the mine to the surface discharge point. Surface mine spoil water, on the other hand, often will be oxygenated enough in the shallow subsurface such that substantial iron will have precipitated within the spoil; thus, the discharge may be low in iron.

The bottom line is that caution must be exercised when interpreting groundwater chemistry from previ-

ously mined areas. Multiple sample locations and an understanding of the groundwater hydrology is invaluable and will contribute to accurate interpretations of the data.

Surface Water - This chapter emphasizes the role of groundwater in water quality prediction, however, it is necessary to make a few comments about surface water chemistry. Surface water is much less desirable as a prediction tool than groundwater for a multitude of reasons. Interpretation of groundwater chemistry is not without its problems as discussed above. Surface water, however, is even more complicated in this regard. Hydrologic factors that can complicate the interpretation of surface water quality from previously mined areas are: dilution of mine drainage by surface runoff, mixing of waters from tributaries that are not impacted by mining, groundwater baseflow from areas unaffected by mining, flow of ground or surface waters affected by mining on a different seam of coal, and chemical alteration of the water by oxidation and precipitation of metals.

Stream water chemistry can change in the downstream direction because of the precipitation of metals, particularly iron. Figure 9.13 shows the concentrations and loads for iron, manganese, and sulfate at various points in a stream in northeastern Cambria County. Significant quantities of mine drainage enter the stream at three different points. Concentrations vary along the flow path for all parameters, but especially so for iron. Concentrations can be affected by dilution, load is not. The graph of constituent load shows that the conservative parameter sulfate is essentially cumulative along the downstream course. Manganese, for a metal, is comparatively conservative (i.e., does not precipitate readily from solution), and likewise its load increases or only slightly decreases downstream. There is some precipitation of manganese along the flow path, but it is minor compared with iron, which is not conservative. The iron load is high at locations just below mine drainage entry points, but it quickly precipitates out of solution and by the time the water reaches the mouth of the stream, the iron has been mostly removed from the water through precipitation onto the stream bed.

Stream water quality can be useful in presenting a "broad-brush" view of mining related problems over a large area. As illustrated above, it is most useful for conservative parameters. Surface water quality studies such as Wetzel and Hoffman (1983, 1989) can show broad regional trends in water quality (see Chapter 8).

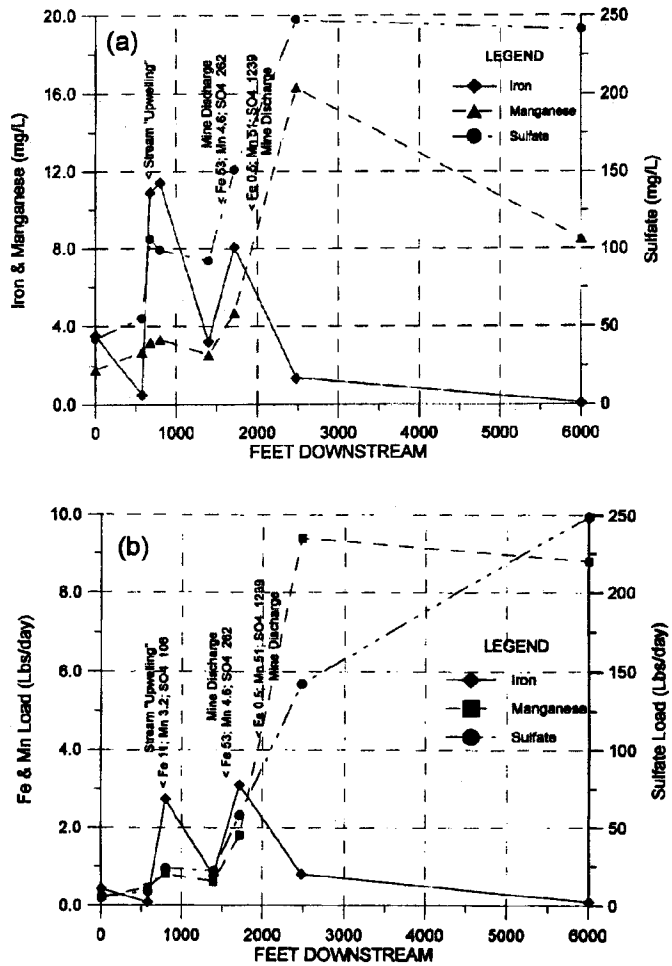


Figure 9.13 Graphs of (a) concentrations and (b) loads for iron, manganese and sulfate in a stream in northeastern Cambria Co. (a). Changes in stream concentration in response to entry of mine drainage discharges along stream reach. (b). Iron, manganese and sulfate load in response to entry of mine drainage discharges along stream reach. Unpublished data from H.S. Baker, Jr., DEP aquatic biologist.

However, unless more detailed information is available, such as what seams were mined, what percentage of the watershed was mined, and what mining practices were used (deep mining, surface mining, refuse disposal, type of reclamation practices, etc.), this information is not generally useful for the prediction of water quality for a proposed mine site.

Differences in Mining Practices

Differences in mining practices must be considered when predicting water quality from previous mining. Different mining practices can significantly influence the water quality produced from a mine. Deep mine

water quality may differ significantly from surface mine water quality on the same coal seam. There have been recent advances in surface mining practices that have the potential to favorably affect water quality. Examples are concurrent reclamation, alkaline addition, special handling, and engineering water movement through or around the backfill. Mine sites that clearly employed adverse practices may be producing water of poorer quality than what a proposed mine site would produce employing favorable mining practices. Mining practices that can adversely affect surface mine water quality include disposal of "tipple refuse" (i.e., rejected material from a coal processing plant), auger mining, improper disposal of acidic strata, and non-concurrent reclamation. Other mining practices that may influence postmining water quality are the type of mining equipment used (dragline vs. trucks and loaders vs. bulldozers), and the length of time a pit remains open and exposed to weathering.

Surface Mine vs. Deep Mine Water Quality - As a general rule of thumb, if a deep mine on a particular coal seam is making alkaline drainage, a surface mine on that same seam will also produce alkaline drainage. The inverse, however, is not necessarily true. If a deep mine is discharging poor quality water, it should not be assumed that a surface mine on the same seam will also produce poor quality water.

The following example of daylighting a deep mine by stripping is an extreme case of water quality improvements. A company named "Solar" deep mined approximately 760 acres of Pittsburgh coal in Findlay Township, Allegheny County, during the early 1900s. Water was sampled from this mine in 1974 for an Operation Scarlift report (Department of Environmental Resources, 1976). Aloe Coal Company began daylighting the deep mine in about the mid-1970s. They daylighted approximately 60 percent of the mine (John Davidson, 1996, DEP mine inspector, personal communication). Aloe mined up to 250 ft (87 m) of cover, which is not normally economical; however, this was a "cost-plus" operation (the coal buyer paid costs, plus a profit). Figure 9.14 is a general geologic column showing the stratigraphy above the Pittsburgh coal in this area. There are several freshwater limestone units that were encountered by surface mining, the thickest being the Benwood, which is frequently 50 ft (15 m) thick. Figure 9.15 illustrates the improvement in pH before deep mine daylighting (1974) and after daylighting (1995). The improvement in water quality after daylighting is dramatic and obvious. Most deep mine daylighting will not encounter as much calcareous strata as in the above example and the water quality improvements would not be as spectacular; however, when calcareous materials are encountered during daylighting operations, water quality does generally improve.

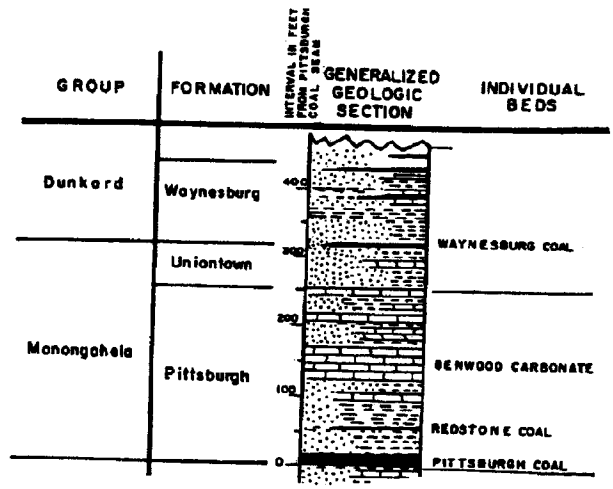


Figure 9.14 Generalized geologic section of the stratigraphy in the vicinity of the Solar/Aloe site. Note the thick Benwood Limestone and other thinner limestones.

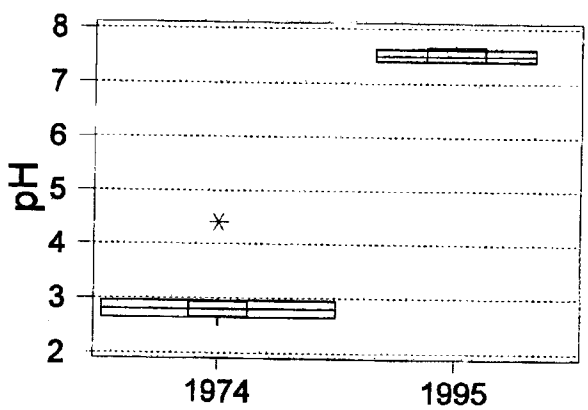


Figure 9.15 Boxplots showing the distribution of pH before (1974) and after (1995) daylighting of the Pittsburgh deep mine.

The reason for poorer water quality from deep mines relative to surface mines is that the strata with the maximum disturbance and exposure to weathering is the coal, roof rock and floor rock. This rock frequently has the greatest amount of pyrite in the overburden. Postmining caving and rubblization of the mine roof and crushing of coal pillars increases the surface area of these pyritic rocks. Water and air flowing through the mine will cause pyrite in the rock to oxidize. A second factor that can contribute to better

water quality being produced from surface mines than from deep mines is that surface mines can disturb and utilize stratigraphically higher overburden rock. If this rock is calcareous, alkalinity generated by this rock can neutralize acid and inhibit pyrite oxidation. Thus, postmining water quality from a surface mine can be alkaline, whereas that from a nearby deep mine on the same coal seam is acidic. These factors are illustrated in the example below.

Discharges from surface and deep mines on the same coal seam (middle Kittanning) in Saltlick Township, Fayette County, show marked differences in water quality (Lighty et al., 1995; and personal communication, 1997). Table 9.8 compares discharge water quality from three surface mines and three deep mine discharges. Figure 9.16 shows the distribution of net alkalinity for each of the mine discharges. The deep mine water is markedly poorer quality than the surface mine water. Figure 9.17 shows acid-base accounting data for three drill holes from one of the surface mines. When the middle Kittanning coal is surface mined, the thick interval of high NP strata below the upper Kittanning coal is encountered and incorporated into the backfill. Water in the deep mine, however, is primarily influenced by the chemistry of the roof rock, coal pillars, floor rock, and any coal waste that was left in the mine. Some of this material, especially the floor rock, has high sulfur content. The rock 10 ft. (3 m) above the mine roof has NP's in the 15 to 60 ppt $CaCO_3$ range. Low NP's at this stratigraphic position (i.e., immediately above the middle Kittanning coal), and the lack of alkalinity in the deep mine water suggest that the NP is from siderite rather than a calcareous carbonate.

Mining Practices - Mining practices that can positively affect water quality are addressed in several other chapters. These practices include special handling, alkaline addition, and water management. A site that includes these pollution prevention measures may produce different quality water from sites that did not include these measures. Examples are given in each of those chapters illustrating the effectiveness of these methods.

An example of poor special handling practices that resulted in extremely poor water quality can be illustrated by the Fran site studied by DEP hydrogeologist Joe Schueck (e.g., Schueck et al., 1996). This site had fairly shallow overburden (average around 30 ft (10 m)) with high sulfur content and little to no neutralization potential. Mining occurred in the 1970s. The operator "special handled" the coal cleanings by placing them in piles. In addition, the operator returned several loads of tipple refuse to the site which was also placed in piles. However, the operator failed to insure that these high-sulfur materials were placed in piles, failed to insure that these materials were placed well above the pit floor, and no attempt was made to cover these materials with an impervious cap.

Table 9.8 Comparison of median water quality from middle Kittanning surface and deep mines in Saltlick Township, Fayette County. Net alkalinity is alkalinity minus acidity. Sample points S 1 through S 3 are from surface mines and D 1 through D 3 are from deep mines. All units, with the exception of pH are mg/L. Data from Lighty (1997, personal communication).

Sample No.	S 1	S 2	S 3	D 1	D 2	D 3
No. of Samples	15	6	5	6	17	7
pH	6.3	6.5	7.2	3.2	3.2	3.1
Net Alkalinity	92	163	194	-235	-284	-216
Fe	13.7	2.2	0.2	52.4	65.9	66.8
Mn	3.3	2.3	0.5	2.5	2.3	2.4
Al	0.2	0.1	0.2	14.0	12.7	5.2
SO_4	180	156	356	529	570	418

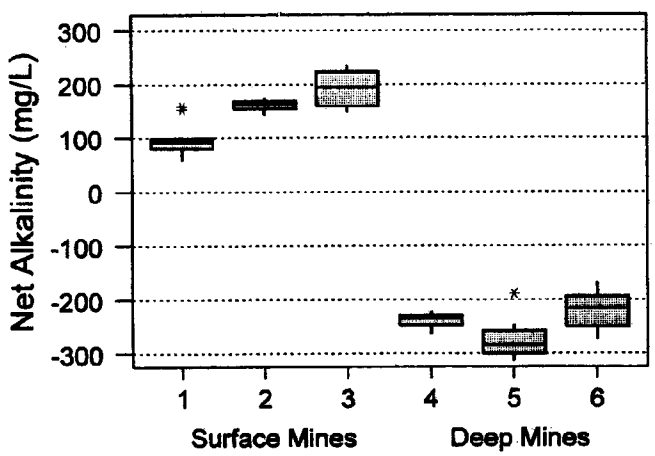


Figure 9.16 Distribution of net alkalinity for three surface and three deep mine discharges from the middle Kittanning coal seam, Saltlick Township, Fayette County, PA.

Table 9.9 shows representative water quality from selected monitoring wells located on the site which clearly demonstrate the impact that tipple refuse and coal cleanings can have on water quality when not properly handled. Well L44 represents the poor water quality resulting from the overburden alone. This well is not influenced by the piles of coal cleanings and tipple refuse on the site. Well K23 is located in a pile of improperly handled, buried tipple refuse. Both infiltrating precipitation and water migrating along the pit floor contacts this acid forming material. Concentrations of the mine drainage parameters in this "acid

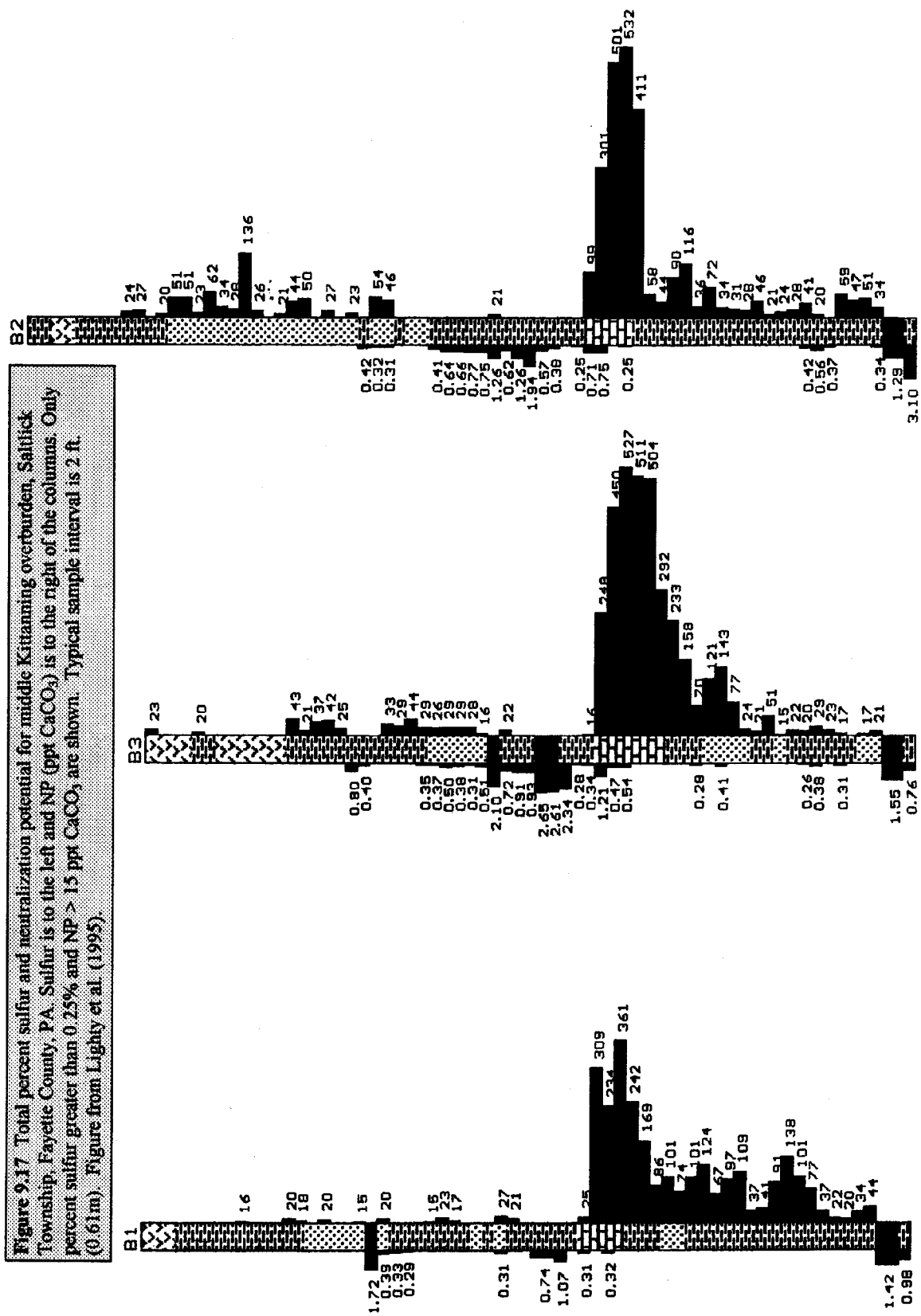


Figure 9.17 Total percent sulfur and neutralization potential for middle Kittanning overburden, Saltlick Township, Fayette County, PA. Sulfur is to the left and NP (ppt $CaCO_3$) is to the right of the columns. Only percent sulfur greater than 0.25% and NP > 15 ppt $CaCO_3$ are shown. Typical sample interval is 2 ft. (0.61m). Figure from Lighty et al. (1995).

factory" are more than 5 times higher than in well L44. As the mine drainage migrates from this location toward the discharge points, it becomes diluted by the poor quality AMD generated elsewhere on the site. The resulting water quality is represented by well X48, located downgradient from the K23 well. The quality of the water which ultimately discharges from the site is shown in well FF62. This well taps a perched aquifer located below the coal seam which was mined. The water discharging from this portion of the site migrates to the regional water table and discharges into the receiving stream as base flow, some 250 ft (76 m) lower in elevation (Schueck, personal communication, 1997).

Department experience has shown that long-term cessations on mine sites with low NP overburden can result in poor postmining water quality. During the cessation the acidic spoil is left exposed to the elements to weather and form acid products. When comparing mines on the same coal seam that were mined concurrently with mines that had long-term cessations, the area mined with the cessation frequently had poorer water quality.

Table 9.9 Representative water quality from a mine in Clinton County, PA. Values are means. Data from Schueck (1996).

No. of Samples	pH	Acidity (mg/L)	Fe (mg/L)	Al (mg/L)	Mn (mg/L)	Sulfate (mg/L)	Sample ID & Description of Sample Point
16	2.5	2995	321	268	48.3	2571	D3, toe-of-spoil seep
15	2.3	4088	876	256	39.2	3477	FF62, spoil well
21	2.5	3828	747	236	48.1	2958	L44, spoil well
13	2.1	21315	5437	1515	60.5	15639	K23, spoil well
14	2.4	7470	1707	492	72.8	6991	X48, spoil well

Discussion

When the geology, hydrology, mining practices, and reclamation practices are similar between a previously mined area and a proposed mining area, and this tool is used properly, no other single prediction tool is better or more useful than the examination of water quality from a previously mined area. Previously mined sites can demonstrate water chemistry generated by rock weathering under actual mining and field (hydrologic, climatic) conditions. Important mining conditions include: the strata encountered by mining, including its variability within the site; the distribution of these rocks within the spoil; weathering of the rocks at the actual scale (rock sizes) that were produced by mining; and influences from various mining methods. Important field conditions include: site specific precipitation, infiltration and runoff; field temperatures, including seasonal variations; pore gas chemistry, including vertical variations; and real world scale of rock to water ratios. These are factors that are only approximately simulated, if at all, in laboratory tests. The examination of water quality from areas previously mined also provides information on actual concentrations of mine drainage constituents, including pH, alkalinity, acidity, iron, manganese, aluminum and sulfate. Previous mining water quality is "the proof of the pudding."

The most confident predictions of postmining water quality will always be those made using a variety of prediction tools, especially if each tool points toward the same conclusion. Much more often than not (although there are exceptions) if postmining water quality is good the acid-base accounting will likewise show calcareous overburden and premining water quality will be alkaline. If postmining water quality is good, but the acid-base accounting data suggest that acid will be produced, a couple of possibilities exist (in addition to the various factors discussed above). First, sampling may not be representative. Additional sampling may reveal calcareous strata that was missed in the initial sampling. Second, the carbonate mineralogy of the overburden may need to be better defined (e.g., siderite masquerading as neutralization potential).

Adjacent mining is often given precedence when prediction tools are conflicting. An example of this is an area where the lower Kittanning coal was mined in northeastern Armstrong County and southwestern Jefferson County. Figure 9.18 shows acid-base accounting data for two overburden drill logs from a lower Kittanning mine site in Redbank Township, Armstrong County. The overburden is clearly high sulfur. The weighted-average NP for the site is 24.08 ppt $CaCO_3$ and the MPA is 23.51 ppt. Thus, the NNP is a mere 0.57 ppt. With "thresholds" (see chapters on acid-base accounting for discussion of thresholds) the NP is 9.16 ppt and the MPA is 21.27, giving an NNP of -12.11. This site would normally be interpreted to indicate an acid-producing site. The site is actually producing alkaline drainage. The following water quality shown below is the average of ten samples from a representative postmining discharge. Values (except for pH) are in mg/L.

pH	Alkalinity	Acidity	Fe	Mn	Al	SO_4
6.7	68	0	0.23	0.25	<0.5	267

The lower Kittanning mines in this area of Armstrong and Jefferson Counties, despite having high sulfur overburden, produce alkaline drainage. Permits in this area of Armstrong and Jefferson Counties have

been issued routinely based on adjacent mining water quality.

A problem with interpreting neutralization potentials in the range shown in Figure 9.18 is not knowing what carbonate minerals are present. The common iron-carbonate mineral siderite frequently produces NPs in this range. Siderite, as discussed in other chapters, is not alkalinity generating. X-ray diffraction analyses for the Armstrong County site discussed above did not detect siderite. The NP is from calcite

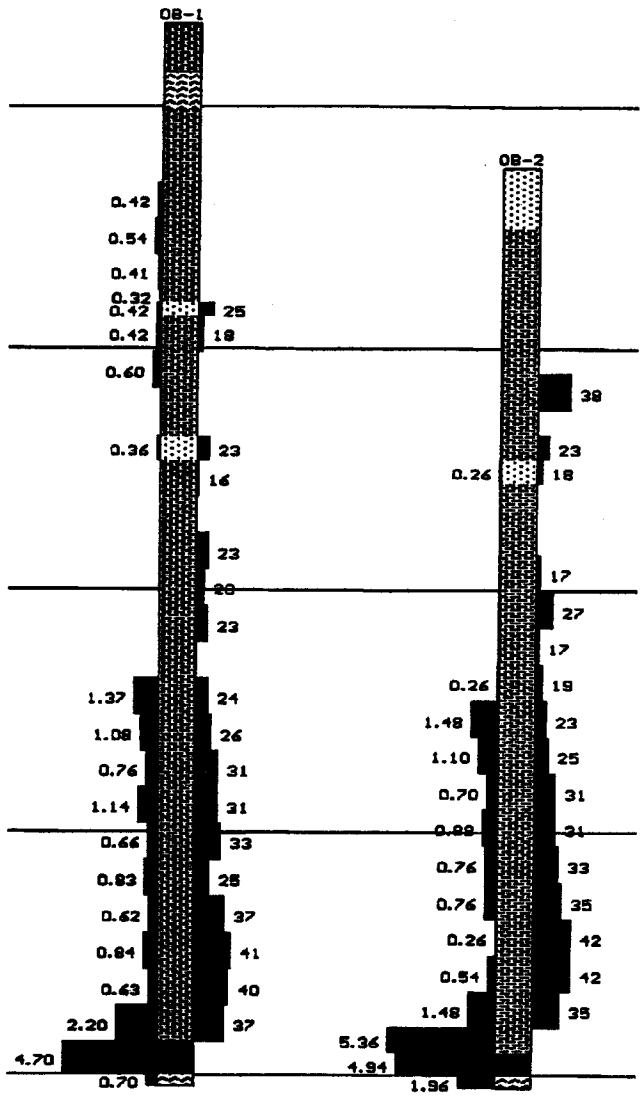


Figure 9.18 Acid-base accounting results for two drill holes penetrating down to the lower Kittanning coal seam in Redbank Township, Armstrong County. Total percent sulfur is shown on the left and neutralization potential (ppt $CaCO_3$) is shown on the right. Only percent sulfur values greater than 0.25% and NP values greater than 15 ppt $CaCO_3$ are shown. Grid lines are at 20 ft (6 m) spacing.

(R. Smith, PA Geological Survey, personal communication, 1996). The intimate association of the calcite with the pyrite may inhibit some pyrite oxidation.

Conclusions

Groundwater quality from previously mined areas, when available and if used properly, can be the best mine drainage quality prediction tool in the tool box. Accurate predictions of water quality for a proposed mine require that apples be compared with apples (i.e., mines and mining conditions be alike). It is therefore important that it can be demonstrated that the same coal seam(s) is being mined, the geology is similar, the amount of area disturbed is similar, there are no complicating factors such as mixing of water from other sources or chemical changes along flow paths, and that there are no significant differences in mining practices. When these conditions are met, adjacent mining is an accurate forecaster of postmining conditions. Previous mining provides real-world field data with actual chemical concentrations of, among other parameters, alkalinity, acidity, metals, and sulfate.

Acknowledgments

Reviews by Tim Kania (DEP), Roger Hornberger (DEP), Robin Lighty (DEP), Rocky Parsons (WV DEP), and a group from the Pennsylvania Mining Professionals/Pennsylvania Coal Association helped to improve this chapter. Many of the examples and data cited in this chapter were brought to my attention by DEP scientists. I have tried to acknowledge their contributions in the text and references. I apologize to anyone I have failed to acknowledge.

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Chapter 10

NATURAL GROUNDWATER QUALITY FROM UNMINED AREAS AS A MINE DRAINAGE QUALITY PREDICTION TOOL

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Introduction

Premining water quality has been used as a mine drainage prediction tool in Pennsylvania since at least the mid-1980s (Brady and Hornberger 1990). Brady et al. (1996) and Hawkins et al. (1996) have provided an in-depth examination of the physical and chemical characteristics of shallow groundwater in unmined regions of the northern Appalachian Plateau.

The bituminous coal field of Pennsylvania lies within the Appalachian Plateau physiographic province. The unglaciated portions of the Appalachian Plateau vary from moderate to high relief (300 > 1000 ft; 90 > 300 m) in the east and northeast, to low to moderate relief (100 to 600 ft; 30 to 180 m) in the western portion of the state. The higher relief areas are marked by deep, V-shaped valleys, and the lower relief areas are marked by a smooth, undulating surface with numerous narrow, relatively shallow valleys (Berg et al., 1989). The rock strata consist of sandstone, shale, siltstone, claystone, limestone and coal, which is horizontal to slightly dipping. This chapter will address only the unglaciated portions of the plateau.

Natural water quality in shallow groundwater flow systems of the Appalachian Plateau results from the influences of three factors: the chemistry/mineralogy of the rock the water contacts, flow path and water contact time.

Of the many solutes in groundwater, we will concentrate in this chapter on bicarbonate alkalinity because it can be compared to overburden neutralization potential (an estimate of carbonate content), and because it can be used as a mine drainage quality predictor. Other water quality parameters will be addressed where appropriate. The water quality can be evaluated from springs and wells.

The recharge area for most springs is the weathered/leached regolith or highly fractured and weathered bedrock (Figure 10.1). The depth of weathering is enhanced by horizontal bedding-plane separations, caused by unloading, and vertical fractures, caused by stress-relief (Hawkins, et al. 1996). The weathered zone is typically 20 to 40 ft (6 to 12 m) thick, but can extend deeper along fractures and is characterized by a red, yellow, or brown color resulting from iron oxidation. The weathered regolith and bedrock has been depleted of the most readily leachable (e.g., carbonate) and oxidizable (e.g., pyrite) minerals. Water flowing through the weathered zone has a short residence time because it is near the surface, has limited thickness, and has higher permeability which is induced by physical (fracturing) and chemical (leaching and oxidation) weathering. Hawkins et al. (1996) have estimated the residence time as days to weeks. Both the scarcity of readily weatherable minerals and short residence time result in spring water quality that is typically dilute.

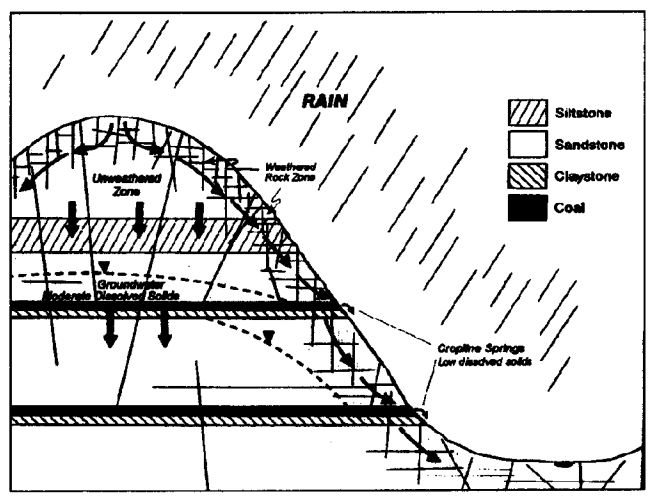

Figure 10.1 Schematic cross section showing conceptual shallow groundwater flow model, which includes the near-surface weathered-rock zone and the deeper unweathered-rock zone (modified from Hawkins, et al., 1996).

Below the weathered regolith is a zone of largely unweathered bedrock (Figure 10.1). Weathering is restricted to some fractures and bedding-plane separations. Unweathered rock can contain readily soluble minerals, in particular carbonates, if they are part of

the rock composition. The water flowing through the rock has a longer residence time because of lower permeabilities, and the slower flow rate allows longer contact with soluble minerals. The permeability is orders of magnitude less than that for the weathered zone and the residence time is in the order of years (Hawkins et al., 1996). Groundwater in passing through unweathered rock will typically have higher dissolved solids than water emanating from the weathered-rock/regolith zone.

To illustrate the relationship between rock chemistry and water chemistry, several specific sites will be discussed. The locations of these sites are shown on Figure 10.2.

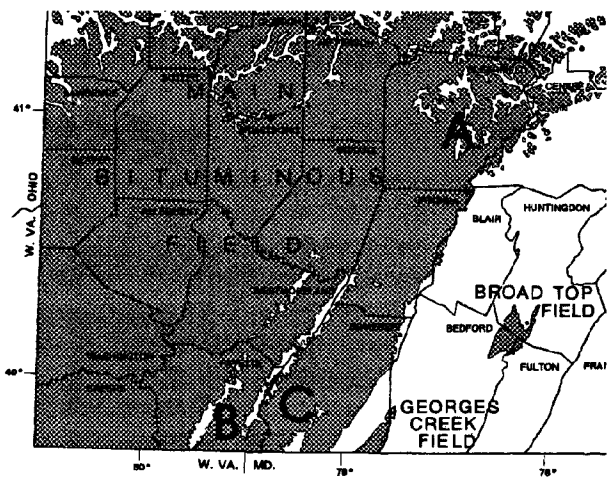

Figure 10.2 Map of southwestern Pennsylvania showing location of sites discussed in text.

The quality of groundwater from both weathered rock/regolith systems and unweathered rock systems can help to identify the presence or absence of carbonates within the area to be mined. Water chemistry can also shed light on the groundwater flow system (see Chapter 2).

Methods

The three study areas discussed in this chapter were selected because they had:

1. water chemistry data from coal cropline springs;
2. water quality data from wells completed down to the same coal seam as the cropline springs; and,
3. acid-base accounting (ABA) data.

Additionally, the sites were selected because they are isolated hill tops where the only recharge is from precipitation.

The acid-base accounting variables "neutralization potential" (NP) and "maximum potential acidity" (MPA) and their derivative "net neutralization potential" (NNP) are discussed in chapters 6 and 11. Units are traditionally reported as tons $CaCO_3$ /1000 tons of material (e.g., equivalent to parts per thousand, ppt, $CaCO_3$). Average NPs and MPAs were determined for each overburden drill-hole by using thickness weighting and assuming each hole represented a column of constant diameter, following the methods described in Smith and Brady (1990).

All water quality sample locations were represented by multiple samples. Medians were determined for pH. Other water quality parameters discussed in this paper, unless specified otherwise, are mean concentrations.

Mine A: "Kauffman Site", Boggs Township, Clearfield County

Mine A is the Kauffman mine where various research studies have been and are being conducted (e.g., Abate, 1993; Evans, 1994; Rose et al., 1995; Hawkins et al., 1996). Mine site topography, locations of drill holes and water-sample points for this mine are shown on Figure 10.3. This map also shows alkalinity and specific conductivity of wells and springs associated with the lower Kittanning (LK) coal seam, plus a few springs flowing from the Clarion #2 cropline. All the wells are completed as 10-cm-diameter piezometers that are open for 1.5 m at the interval of the lower Kittanning (LK) coal. Figure 10.3 also shows summaries of acid-base accounting data for overburden drill holes completed to the lower Kittanning coal.

Figure 10.3 clearly indicates that spring water quality is significantly lower in alkalinity and specific conductance than well water. Alkalinity of springs is typically less than 5 mg/L and conductivity less than 50 µS/cm. In contrast, wells in the western portion of the hill typically have much higher alkalinity (> 70 mg/L) and specific conductivity (~ 200 µS/cm). It is also apparent that there is a regional distribution of well water alkalinity. Wells on the eastern portion of the area have lower alkalinity than those for the western portion. This pattern is consistent with the higher NPs reflected in the overburden data on the western portion of the site (Figure 10.3). Piezometers completed within the hill of the Kauffman site indicate a steep downward flow gradient at the horizon of the LK coal. Between the lower permeability of the unweathered rock zone and the downward component of much of the flow, little water from the unweathered rock

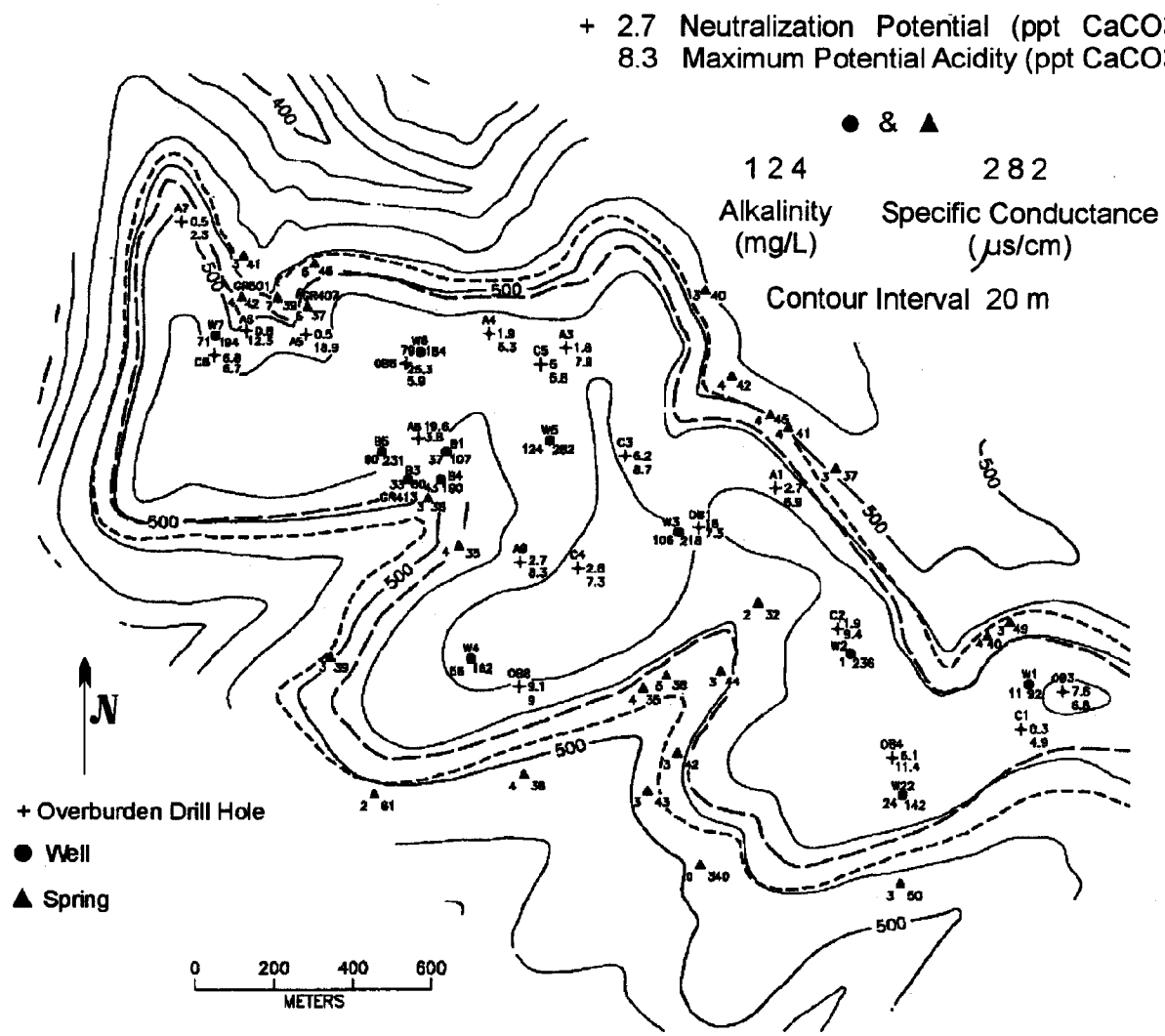

Figure 10.3 Locations of coal croplines, water sample points, overburden drill holes, and piezometers on mine site A (Kauffman site). Values for select water quality parameters and overburden analysis summary numbers are portrayed next to the sample point.

zone is contributed to the springs. The groundwater quality is related to overburden NP along the flow path.

The geologic controls on distribution of calcareous units are complex on this site. Observations of highwalls show that the calcareous material occurs as calcite and minor siderite as cement between sandstone grains in trough bottoms of some channel sandstones (V. Skema, 1995, personal communication). These calcareous trough deposits are laterally discontinuous and occur only in the basal portion (bottom 3 to 5 m) of a thick (18 to 24 m) channel-sandstone unit. Observations of drill cores also suggest that some of the calcareous cement in sandstone is associated with vertical and bedding plane fractures. However, most fractures are not associated with calcareous minerals.

Overburden holes and wells 470 ft (140 m) or less apart were paired for comparisons of alkalinity of groundwater with overburden NP. These two parameters show a strong positive relationship (Table 10.1; Figure 10.4), with alkalinity (mg/L) being four times the NP value (tons/1000 tons). A similar relationship is seen between specific conductance and NP (Figure 10.5). As would be expected, specific conductance and alkalinity show a strong positive relationship ($r = 0.94$). These relationships imply that dissolution of calcareous minerals, where present, has a significant impact on groundwater chemistry.

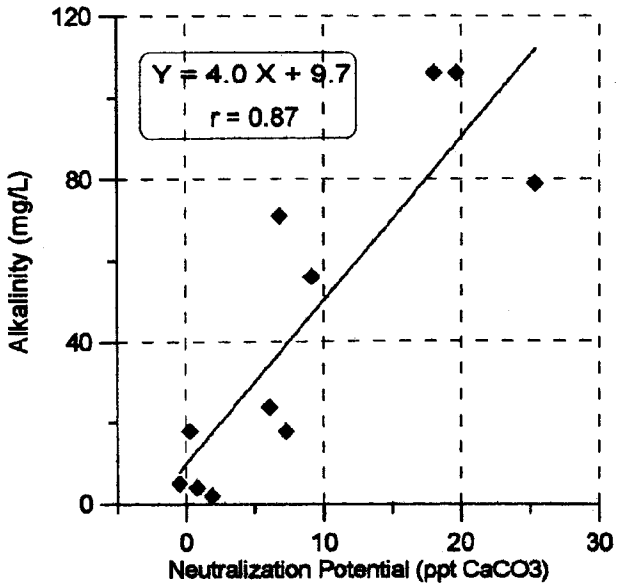

Figure 10.4 Alkalinity of groundwater associated with the Lower Kittanning coal seam as a function of neutralization potential at mine site A.

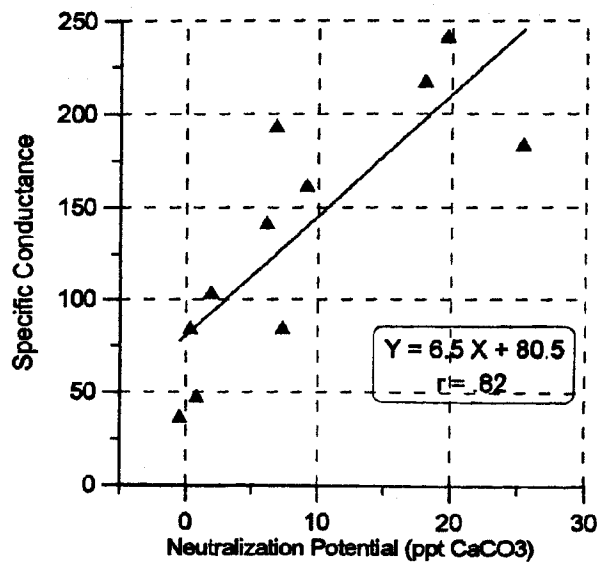

Figure 10.5 Specific conductance of groundwater associated with the Lower Kittanning coal seam as a function of neutralization potential at mine site A.

Table 10.1 Groundwater chemistry and acid-base accounting rock chemistry data for 11 pairs of water sample points and overburden sample points.

OBA #	WATER SAMPLE POINT	DISTANCE BTWN OBA & H_2O ft (m)	WATER CHEMISTRY ALK. mg/L	WATER CHEMISTRY SO_4 mg/L	WATER CHEMISTRY Mean SC	OVERBURDEN CHEMISTRY Tons NP/ 1000 tons	OVERBURDEN CHEMISTRY Tons mpa/ 1000 tons
A6	GR501	250 (75)	4.5	8.5	48	1.24	12.23
A5	GR407	250 (75)	4.7	12.0	37	-0.58	18.47
OB6	W6	80 (25)	79.0	14.6	184	24.30	5.98
OB1	W3	130 (40)	106.2	8.8	218	17.85	7.61
C2	W2	180 (55)	2.0	132.0	104	1.82	9.56
OB3	W1	280 (85)	17.5	8.6	85	7.55	6.79
OB8	W4	470 (140)	56.4	26.6	162	9.05	9/97
OB4	W22	330 (100)	24.0	33.6	142	6.34	11.67
A8	B5	370 (110)	106.0	24.0	242	19.41	5.27
C1	W1	370 (110)	17.5	8.6	85	0.28	4.86
C6	W7	170 (50)	70.6	19.6	194	6.72	6.94

Sulfate, a conservative aqueous ion, is a weathering product of pyrite. Therefore, a comparison was made between MPA and sulfate (Figure 10.6). MPA was also compared with specific conductance (Figure 10.7). MPA shows no relation to sulfate in nearby groundwater and has, if anything, an inverse relation to specific conductance. With one exception, sulfate was generally less than 35 mg/L. The exception is the result of anthropogenic influences. The inverse relationship of sulfate with specific conductance is an artifact of the site data. Specific conductance is strongly related to alkalinity, and alkalinity to NP. And at this site the high NP overburden holes tend to have low MPA,

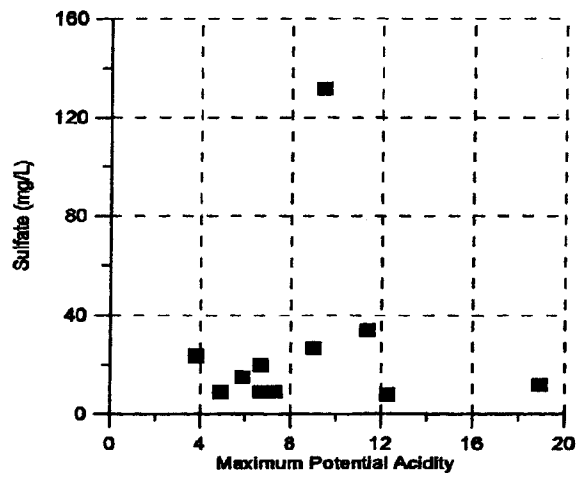

Figure 10.6 Sulfate of groundwater associated with the lower Kittanning coal seam as a function of maximum potential acidity at mine site A.

whereas high MPA holes tend to have low NP (Figure 10.8).

Brady et al. (1996) provide a detailed study of one of the springs, GR-413 (Figure 10.3). A hydrograph of this spring (Figure 10.9) illustrates the relationship between rainfall and spring flow. Almost immediately after rainfall there is a sharp peak in flow resulting from surface runoff. This is followed a few days later by a broader peak that is interpreted to result from flow through the shallow weathered zone. The hydro-

graph illustrates the rapid flow-through time for groundwater in the shallow weathered-rock zone. The broad peak in flow occurs 3 to 4 days after rainfall, and continues to tail off for a week or so. The spring flows year-round, thus storage must exist in this shallow zone to account for the year-round flow. The spring water is similar in chemistry to the other coal-cropline springs.

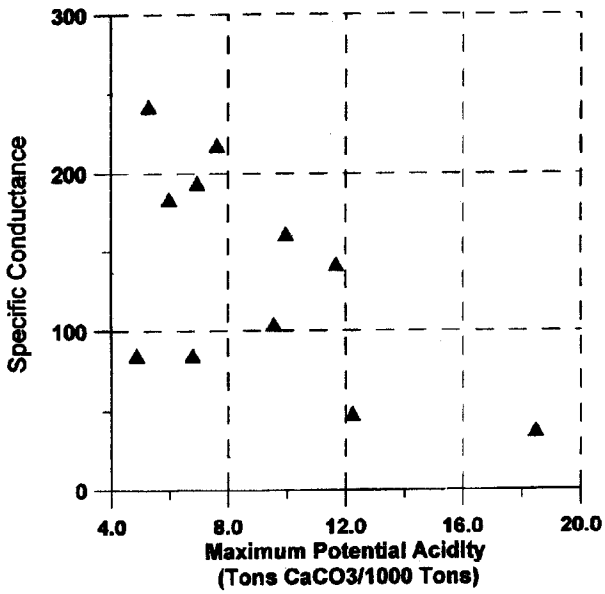

Figure 10.7 Specific conductance of groundwater associated with the lower Kittanning coal seam as a function of maximum potential acidity at mine site A.

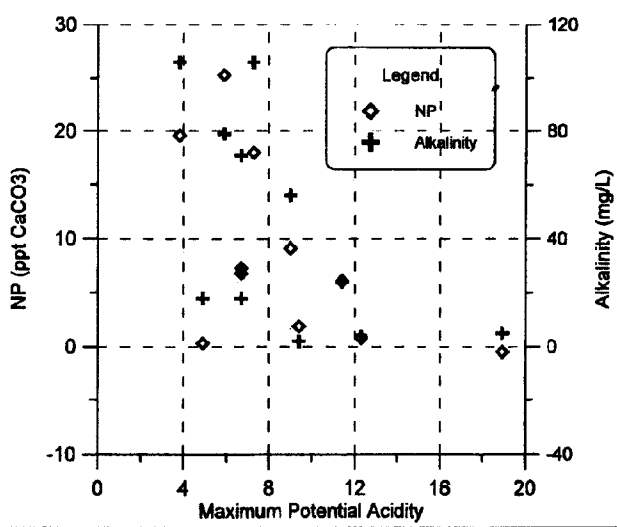

Figure 10.8 Comparisons between neutralization potential, alkalinity, and maximum potential acidity at mine site A.

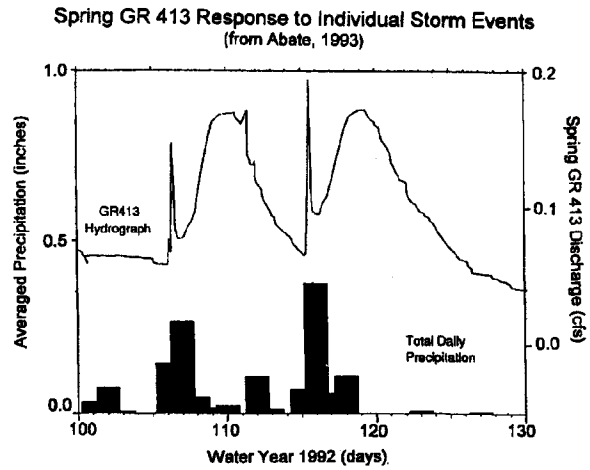

Figure 10.9 Spring GR-413 response to individual storm events. See Figure 10.3 for location of spring. The initial spikes are from surface runoff (from Abate, 1993).

Mine B: Wharton Township, Fayette County

The principal coal seam that was mined is the upper Kittanning (UK). Field pH and specific conductance were measured prior to mining in several uncased drill holes which were completed down to the UK seam. Additionally numerous UK cropline springs were sampled during collection of background data. Figure 10.10 is a map showing the Upper Kittanning coal cropline and water sample points.

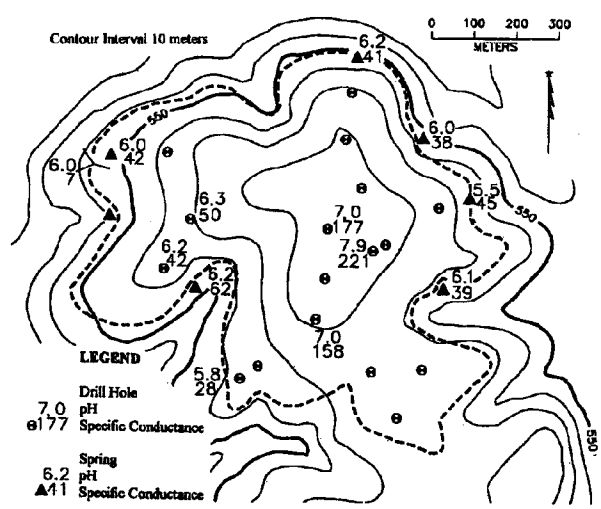

Figure 10.10 Location of coal cropline, drill holes and water sample points, and water quality data at mine site B.

The specific conductivity of the crop springs and shallow (near crop) wells have lower values (38 to 62 µS/cm) than the drill holes located toward the middle of the hill where depth to coal is greatest (158 to 221

µS/cm). The pH of the springs is also lower than the pH of the wells. NP is negligible in areas with less than 9 to 12 m of cover, evidently because of weathering (Figure 10.11). The higher pH and conductance increase are both coincident with an increase in NP (Figures 10.11 and 10.12). The water in deeper drill holes exhibits higher dissolved solids (reflected as specific conductance) than in cropline springs and holes with shallow cover, due to the increasing abundance of calcareous minerals with increasing overburden. The high NP strata are freshwater limestones and calcareous shales. The geology of this area is addressed in Brady et al. (1988), where the mine site is referred to as area "C."

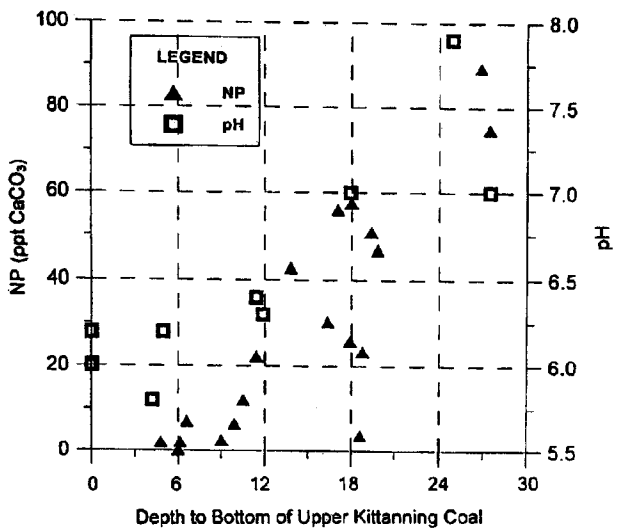

Figure 10.11 NP and pH as a function of depth from the surface to the bottom of the upper Kittanning coal seam for overburden holes (NP), and drill holes and springs (pH). Site is located in Fayette County. The scale of the x-axis is in meters.

Crop springs have alkalinity between 1 and 9 mg/L. Unfortunately alkalinity was not sampled in the drill holes, but it is a near certainty that the alkalinities were higher, judging from elevated pH and conductance. This hill top has been mined and the mine is producing drainage with an average alkalinity of 380 mg/L.

Mine Site C: Lower Turkeyfoot Township, Somerset County

Mine Site C (Figure 10.13) is an example of a site where there is no significant calcareous overburden rock within the proposed mine area. This deficiency is shown by the low NPs of the two overburden holes (OB-A and OB-C), and by the low alkalinity of cropline springs, small country bank mines, and water collected from the two overburden holes which were uncased down to the coal. Near the actual area mined, the highest alkalinity is 11 mg/L from cropline spring SP-14. Two of the springs below the coal cropline have alkalinity as high as 31 mg/L. Apparently calcareous strata exist below the coal.

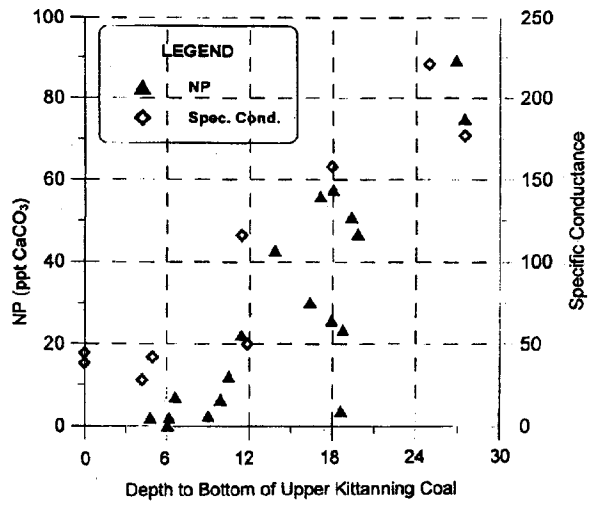

Figure 10.12 NP and specific conductance (µS/cm) as a function of depth from the surface to the bottom of the upper Kittanning coal seam for overburden holes (NP), and drill holes and springs (specific conductance). Site is located in Fayette County. The scale of the x-axis is in meters.

The two overburden holes encountered predominately sandstone, with coal at 54 ft (16 m) and 77 ft (23 m) for OB-A and OB-C respectively. The highest neutralization potential in OB-A is 19 ppt $CaCO_3$, the highest in OB-C is 15 ppt $CaCO_3$. The highest percent sulfur (excluding the coal) in OB-A was a 1 ft (0.3 m) binder within the coal bed that had 2.0 percent sulfur (% S). A 3 ft-thick (one m-thick) shale overlying the coal contained 0.5 % S. The highest percent sulfur in OB-C was the shale below the coal, which had 1.7% S. The next highest sulfur in the overburden is only 0.2%. The overburden shows the presence of acid-producing strata, but lacks alkalinity-producing strata.

Table 10.2 compares rock chemistry and water chemistry in the two overburden drill holes. The low alkalinity of the water agrees with the low NP of the overburden data. Because of the lack of naturally occurring calcareous rocks, an average of 45 T $CaCO_3$/ac (1 x 10^5 kg/ha) was brought to the site. Additionally, the material with percent sulfur greater than

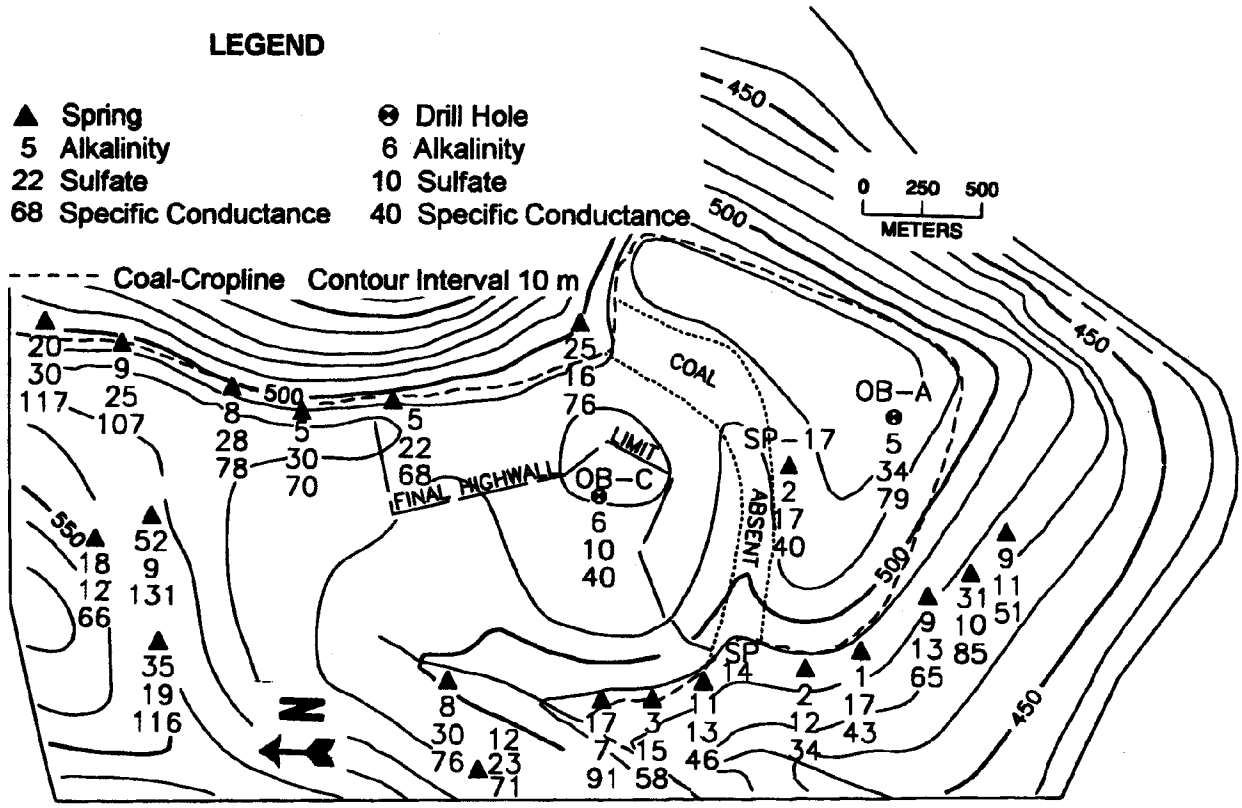

Figure 10.13 Location of coal cropline, water sample points, select water quality parameters and overburden holes for mine site C.

0.5 % was selectively placed in "pods" that were located such that they would be above the postmining water table. Twenty tons/acre of the alkaline material was placed on the pit floor, with most of the remainder mixed into the high-sulfur spoil pods. Indications are that the amount of alkaline material added was inadequate and the site is producing acidic drainage. Table 10.3 shows water quality from one of the postmining discharges from this mine.

Table 10.2 Overburden and water quality comparisons for drill holes OB A and OB B at mine site C.

		NP	ALK	NPA	SO_4	NNP
OB A	w/out thresholds	3.47		4.45		-0.98
	with thresholds	0.0		2.44		-2.44
	water quality		5.5		34	
OB B	w/out thresholds	4.48		2.78		+1.69
	with thresholds	0.0		0.98		-0.98
	water quality		6.5		10	

Notes: NP, MPA, and NNp are in units of tons $CaCO_3$/1000 tons.
All MPA's calculated as %S x 31.25.
Alkalinity and Sulfate are in mg/L and are mean values.
Acid-base accounting values are calculated form column weighting
w/out thresholds refers to traditional means of computing ABA data, where all NP and %S values are used.
With thresholds refers to the computation method where all NP's <30 and %S's < 0.5 are assigned a value of zero.

Table 10.3 Postmining water quality at CD4A.

DATE	pH	Alk.	Acid.	Fe	Mn	Al	SO_4
12/29/97	4.2	18	1070	1.9	81	148	3003
4/24/97	4.0	9	2110	0.4	110	229	4643

Figure 10.13 includes water quality for some springs, up slope and to the north of the mine site, that have higher alkalinity (35 to 52 mg/L) than cropline springs. The recharge of these springs is stratigraphically and topographically higher than the upper Freeport coal. The Glenshaw Formation, which is the unit from which these springs arise, is known to contain several calcareous marine zones (Flint, 1973). These higher alkalinities may indicate that there is some calcareous material preserved within the shallow flow system or the springs may be receiving some water form a deeper source. Although no deeper well data exists for the Glenshaw Formation in the immediate area of the mine site, a 130-ft (40-m) deep well 2 miles (3 km) north-northeast of the site, which penetrates the lower portion of the Glenshaw Formation, has alkalinity of 106 mg/L, specific conductance of 260 µS/cm, and sulfate of 9 mg/L (Tom McElroy, 1996 personal

communication). These data are consistent with the findings of McElroy (in preparation), that wells within the Glenshaw Formation have higher alkalinity than springs associated with the same strata.

All sulfate concentrations shown on Figure 10.13, whether from a well or a spring, and regardless of stratigraphic or topographic position, are less than 40 mg/L.

Comparison with Other Parts of the Appalachian Plateau

Climate in the Appalachian Basin from Pennsylvania to Alabama is fairly similar. Average annual temperature in the north is about 50° F (~10° C) and above 60° F (>15° C) in the south. Precipitation also increases from north to south, with rainfall averaging 35 inches (90 cm) in northern Pennsylvania to more than 55 inches (140 cm) in Alabama (Weeks et al., 1968). Annually the infiltration rate of water is sufficient that groundwater is continually flushed through the rock strata from recharge to discharge points. This flow tends to leach out the soluble products of the more weatherable minerals.

Geology throughout the Appalachian Plateau is also similar in many respects. The rocks are predominately flat-lying, consisting of sandstone, conglomerate, siltstone, shale, claystone, limestone and coal (Miller et al., 1968). Hills have been subjected to stress-relief and unloading forces which have intensified fracturing and bedding-plane separations, and subsequently, weathering of the rocks. This physical weathering, coupled with chemical weathering, has resulted in higher permeabilities within the weathered zone (Hawkins et al., 1996). These geologic and climatologic factors result in similar groundwater hydrologic characteristics throughout the plateau.

Numerous studies have investigated the groundwater hydrologic characteristics on the Appalachian Plateau, but very few studies have related the hydrology, groundwater chemistry and rock chemistry. Powell and Larson (1985) investigated water quality in an unmined watershed in a coal-producing region of the Appalachian Plateau of southwestern Virginia. The rock strata are in the Pennsylvanian Norton Formation. The most common carbonate present was siderite, following by calcite and dolomite. Minor amounts of pyrite were generally associated with coal and adjacent rocks. They observed that water from springs typically had lower concentrations of alkalinity and dissolved solids than water from dug and drilled wells Figure 10.14 is a plot of alkalinity as a function of bottom depth of sample point. The springs typically have lower alkalinity than dug wells, which have lower alkalinity than drilled wells. With one exception sulfate was less than 40 mg/L, for springs, dug wells and drilled wells. In fact only 6 of 32 sample points had sulfate above 20 mg/L. This is consistent with observations of sulfate for groundwater not impacted by mining in Pennsylvania.

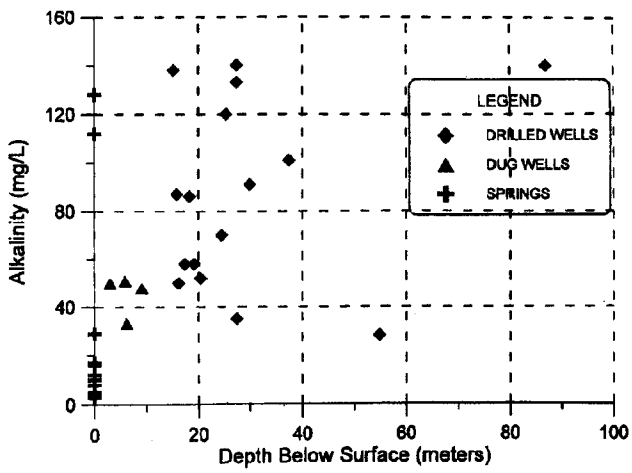

Figure 10.14 Alkalinity as a function of depth of groundwater sample source in Buchanan Co., VA. Springs are shown at zero depth. Data from Powell and Larson (1985).

Recent studies in Somerset (McElroy, in preparation) and Indiana (Williams and McElroy, 1997) Counties, Pennsylvania show spring water to be routinely more dilute than well water. This is true throughout the Pennsylvanian Period strata in these counties.

Powell and Larson (1985) envision two groundwater flow systems, one of which "moves under and through the weathered rock or soil layer along the surface of the consolidated rock." The other system "flows through rock fractures and provides the main source of domestic supply" (most domestic supplies were drilled wells). Water in the shallow flow system flows relatively rapidly through rocks thoroughly leached of calcareous minerals. A few of the springs, and many of the deeper wells have high alkalinity (>100 mg/L) (Figure 10.14). The two springs with highest alkalinity occur in stream valleys, and they probably issue from deeper flow systems. The spring with the highest alkalinity occurs at the lowest elevation of any of the sample points. Springs with high alkalinity are the exception rather than the rule, indicat-

ing that most springs are from shallow groundwater sources.

Singh et al. (1982) in a study of the Mahoning Sandstone in Preston Co., WV, found a weathered zone of about 20 ft (6 m) deep which was low in sulfur and "exchangeable bases" (i.e., Ca and Mg). This indicates that both pyrite and calcareous minerals were removed by weathering within this zone. Brady et al. (1988), in a study that included the area of Mine C of this study also documented the loss of calcareous minerals within ~20 ft (6 m) of the surface. These findings on surface rock weathering are consistent with the current study.

The literature review presented by Hawkins et al. (1996) demonstrates the consistency of groundwater hydrologic properties throughout the Appalachian Plateau. Although less research has been done on rock and water chemistry, that which has been done shows results similar to those in PA. It appears that the principals observed in Pennsylvania are applicable to much of the Appalachian Plateau.

Discussion

The combined observations of Powell and Larson (1985), Singh et al. (1982), Brady et al. (1988) and this study provide an explanation for the differences in water quality often observed between wells and springs from the same stratigraphic horizon. There are two separate shallow flow systems; a near-surface zone that is chemically and physically weathered, and a deeper unweathered-rock zone. Figure 10.1 is the conceptual model of these groundwater flow zones.

Surface mining in Pennsylvania generally occurs within one hundred feet (30 m) or less of the surface and most mines are in groundwater recharge areas (e.g., hilltops). A common misconception has been that water quality from cropline springs in unmined areas is typical of water associated with the coal seam. As illustrated at Mine Sites A and B, water associated with coal-cropline springs can be much more dilute than water from the same coal seam under deeper overburden cover. The cropline springs and shallow wells represent water flowing through the near-surface weathered-rock zone. This weathered-rock zone is quite permeable due to chemical and physical weathering. Typically calcareous rocks are absent or negligible within this weathered zone. The rapid flow-through time for the water along with the leached nature of the weathered rock results in water that lacks alkalinity and contains low dissolved solids.

Wells penetrating deeper overburden are completed in unweathered or less weathered rock with lower permeability. Groundwater flow is primarily along fractures and bedding planes. The combination of calcareous minerals, and longer residence time for the groundwater, results in significant dissolution of calcareous minerals forming bicarbonate alkalinity. Downward flow and substantially lower hydraulic conductivities probably result in little of this water reaching the cropline springs.

Mine Site C is an example of a site that lacks significant calcareous rocks. This situation persists at shallow cover and at deep cover (maximum overburden that would be mined). The lack of calcareous rocks is confirmed by the chemistry of the two overburden test holes and water quality associated with springs, country bank mines and the overburden drill holes. Wells penetrating strata that lack calcareous minerals will exhibit low alkalinity.

From Mine Sites A and B there appears to be a direct relationship between the amount of calcareous material preserved in the overburden and the alkalinity, conductivity, and pH of the groundwater. Whether the relationships observed in Figures 10.4, 10.5, 10.11, and 10.12 are site specific or more universal is not known. More sites were NP and alkalinity comparisons can be made must be investigated. The general rule of thumb, however, that alkalinity is higher in areas with calcareous rocks compared to areas without calcareous rocks is certainly true.

No relationship seems to exist between MPA (i.e., percent sulfur) and sulfate. This is probably because of the very limited oxidation of pyrite under saturated conditions. Calcareous minerals are rather soluble in groundwater, whereas pyrite is not. The acid in acid mine drainage is not produced by a simple dissolution process, but by an oxidation process. Pyrite in unmined areas remains largely in an unoxidized state. Premining alkalinity in deeper drill holes provides a second confirmatory tool, along with acid-base accounting NP, to determine the relative presence or absence of calcareous rock and its distribution within the proposed mine area.

Work in other parts of the Appalachian Plateau suggests that the observations regarding groundwater chemistry and hydrology in Pennsylvania are probably

applicable to other portions of the Appalachian Plateau.

Implications and Conclusions

All of the Pennsylvania sites studied were isolated hill tops within groundwater recharge areas. In all cases the coal outcropped on the sides of the hill. The dominant flow systems for all mines are relatively shallow, with the deepest monitoring wells (completed to the coal seam) on the order of 120 ft (35 m) deep. Where conditions are similar to those given in the examples above, groundwater alkalinity reflects the presence or absence, and relative abundance of calcareous rock.

Water quality is directly related to the flow path, the dissolution of minerals contacted by the groundwater, and the contact time of the water with the rock. Cropline springs and shallow wells (6 to 9 m deep) that have low or no alkalinity are indicative of shallow leached/weathered overburden. No significant calcareous strata (measured as NP) are likely to occur within this zone. Where calcareous rocks are present, such as some deeper cover situations, the calcareous minerals will dissolve in the water and can be measured as alkalinity. Low alkalinity in well or spring water indicates the absence of calcareous strata within the groundwater flow path for that well or spring. It might be expected that sulfate would reflect the amount of pyrite that is present, but there is no relationship between the amount of pyrite (in terms of MPA) and sulfate concentrations, thus indicating that pyrite oxidation prior to mining is negligible.

These findings have several important implications. These are:

1. Coal cropline springs typically reflect very shallow flow through the regolith and do not necessarily reflect water quality under deep groundwater conditions.
2. Wells are needed to ascertain water quality in the deeper unweathered-rock zone.
3. There is a relationship between overburden neutralization potential and groundwater alkalinity. If the site is hyrologically isolated such that the only recharge to the site is precipitation, and if alkalinity in wells is high (> 50 mg/L), calcareous minerals are within the flow system and probably near the water sampling point. Where alkalinity is low (< 15 mg/L) the rocks within the recharge area lack appreciable calcareous minerals.
4. Groundwater alkalinity can be used to help determine whether overburden sampling for NP has been representative. If overburden analysis does not indicate significant calcareous rocks to be present, but water wells into the same units are alkaline, the overburden sampling may not be representative of site conditions and additional drilling would be warranted. The combination of groundwater alkalinity and overburden NP can be used together to better define the extent of calcareous overburden.
5. Overburden sampling and water sampling must represent both shallow and deep overburden cover to adequately represent the entire mine site hydrology and overburden chemistry. Holes drilled at greater than the maximum cover to be mined may overestimate NP in the overburden that will be disturbed by mining.
6. There is no relationship between MPA in the overburden and sulfate in the groundwater, nor for that matter, between MPA and any other measured parameter. Sulfate in groundwater from unmined watersheds is typically less than 40 mg/L, regardless of location within the flow system.
7. The above conclusions are probably applicable to a large portion of the Appalachian Plateau. However, the applicability to areas with different climate, physiography and/or geology is unknown.

Acknowledgments

Much of the content of this chapter appeared in a paper by Brady et al. (1996), although an early draft of this chapter predated the paper. This chapter benefited greatly from the insights and advise of the paper's co-authors Arthur W. Rose and Jay Hawkins, and Michael DiMatteo's help with the maps. The chapter has further benefited from reviews by A.W. Rose and Thomas McElroy.

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Chapter 11

INTERPRETATION OF ACID-BASE ACCOUNTING

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Introduction

This chapter presents the application and interpretation of Acid-Base Accounting (ABA) to prediction of mine drainage quality. ABA is one mechanism for assessing postmining water quality. Its utility is amplified when used in conjunction with other premining information including baseline water quality, examination of adjacent and previous mining, and evaluation of geologic and hydrologic conditions. This chapter presumes collection, preparation, and analysis of samples following the approach suggested in Chapters 5 and 6 (Overburden Sample Collection and Preparation, and Laboratory Methods for Acid-Base Accounting). The concepts presented here are drawn largely from research and experience with ABA in Pennsylvania, supplemented, where appropriate, with information from other sources.

Development and Application of Acid-Base Accounting

Acid-Base Accounting was developed at West Virginia University by Richard M. Smith and coworkers (Skousen et al., 1990). The approach grew from early attempts at classifying mine spoils for revegetation potential, based principally on acidity or alkalinity, and rock type. From these broad classifications, the need for lime and suitability for plant species could be assessed.

In 1971, Richard Smith and associates reported on the acid producing potential of rocks associated with the Freeport and Kittanning seams in Preston County, West Virginia (West Virginia University, 1971) and began to formally develop a system of balancing the acid and alkaline producing potential of rocks. Acid-base characterization work was gradually broadened to include rocks throughout the Appalachian and Interior coal basins, including Pennsylvania. The importance of acid neutralizing minerals was recognized and quantified, and the term "neutralization potential" (NP) was introduced. This work was published in a series of reports (e.g. Smith et al., 1974; 1976) and culminated in a manual of recommended field and laboratory procedures (Sobek et al.,1978). ABA in its original and modified forms has been widely adapted in both the coal and mineral mining industries in the United States, Canada, Australia and southeast Asia (Miller, 1991; British Columbia Acid Mine Drainage Task Force, 1989).

Although the potential utility as a water quality predictor was quickly recognized, the early developmental work on ABA was directed mainly toward assessing the agronomic potential of overburden and minespoil. At that time "topsoiling" (i.e. saving and reapplying topsoil) was not widely practiced and ABA was useful for identifying overburden as root zone material. The first attempts to define levels of significance for ABA data were "potentially toxic" materials having a net ABA of less than -5 ppt $CaCO_3$ (tons $CaCO_3$ equivalent/1000 tons of material), or "acid toxic" if paste pH was less than 4.0 (Smith et al., 1974, 1976; Surface Mine Drainage Task Force, 1979). These values were based on an assessment of lime requirements of native soils in the Appalachian region and plant growth needs, and not water quality conditions per se.

ABA was adapted in Pennsylvania for mine drainage prediction, beginning in the late 1970's. It soon became apparent, however, that application of a -5 ppt $CaCO_3$ significance level did not always forecast acid drainage conditions, and was not an appropriate guide to water quality prediction. The Pennsylvania Department of Environmental Protection (PaDEP) began to evaluate other analytical methods, such as weathering tests, and modifications to ABA to improve mine drainage prediction capability.

A first approximation was the development of a two by two matrix for qualitative interpretation of overburden analyses (Figure 11.1, Brady and Hornberger, 1990). The four fields were broadly classed into high and low sulfur and neutralization potential content. The boundaries between the four fields were not numerically defined, and the matrix served as a conceptual approach rather than explicit criteria.

	Low Sulfur	High Sulfur
Low NP	Evaluate Additional Data	Probable Denial
High NP	Probable Issuance	Possible Issuance or Denial

(After Brady and Hornberger, 1990)

Figure 11.1 Conceptual Decision Matrix for Acid Drainage Potential Used in the Early 1980's.

As the PaDEP and industry continued to gain experience with ABA interpretation, it became possible to focus on rock strata that were likely to be significant generators of alkalinity or acidity. These significant strata could then be evaluated in a broader context of the overall mining and reclamation plan and hydrologic and geologic conditions. Significant strata are defined by "threshold" values (Brady and Hornberger,1990) for sulfur content and neutralization potential as:

- Total sulfur content greater than 0.5 percent, and
- NP greater than 30 ppt $CaCO_3$ with a "fizz".

The numbers were intended for general guidance, while recognizing that rock strata with NP less than 30 or sulfur content less than 0.5 percent do influence mine drainage quality.

The PaDEP also evaluated means for representing the mass, volume, and distribution of ABA parameters within a mine site to further refine predictive capabilities. A computer spreadsheet was developed (Smith and Brady, 1990) that mass weights ABA data by strata using the Thiessen polygon method. Summary values of ABA data are calculated that adjust for the horizontal and vertical extent of each analyzed stratum. The PaDEP now also has a mainframe overburden database capable of performing and reporting the summary calculations of ABA data in various ways (Bureau of Information Services, 1993).

Principles of Acid-Base Accounting Measurements

ABA, as originally developed, and used in Pennsylvania, consists of measuring the acid generating and acid neutralizing potentials of a rock sample. These measurements of Maximum Potential Acidity (MPA) and Neutralization Potential (NP) are subtracted to obtain a Net Neutralization Potential (NNP), or net Acid-Base balance for the rock as follows:

Net Neutralization Potential (NNP) =
NP - MPA (11.1)

The results are customarily reported in tons per thousand tons of overburden or parts per thousand. The units designation reflects the agronomic origins of ABA. An acre furrow slice of agricultural soil weighs about 1000 tons, and liming requirements are usually expressed in tons per acre (tonnes/hectare). The units of measure for ABA are therefore comparable to lime requirement designations for agricultural lands.

The components of ABA measurements are sometimes referred to by other terms, as they have been adapted for use in metal mining and other applications (Miller and Murray, 1988). The term "Acid Production Potential" (APP) is equivalent to MPA, "Acid Neutralizing Capacity" (ANC) is equivalent to NP; and "Net Acid Producing Potential" or NAPP is the same as NNP.

The measurements and calculations of NP, MPA, and NNP are based on the following assumed stoichiometry (Cravotta et al., 1990):

$$FeS_2 + 2CaCO_3 + 3.75O_2 + 1.5H_2O \rightarrow 2SO_4^{2-} + Fe(OH)_3 + 2Ca^{2+} + 2CO_2 \quad (11.2)$$

For each mole of pyrite that is oxidized, two moles of calcite are required for acid neutralization. On a mass ratio basis, for each gram of sulfur present, 3.125 grams of calcite are required for acid neutralization. When expressed in parts per thousand of overburden, for each 10 ppt of sulfur (equal to 1 percent sulfur content) present, 31.25 ppt of calcite is required for acid neutralization.

Cravotta et al. (1990) noted that the stoichiometry in Equation 11.2 is based on the exsolving of carbon dioxide gas out of the spoil system. They suggested that in a closed spoil system, carbon dioxide is not exsolved, and additional acidity from carbonic acid is generated. Cravotta et al. (1990) proposed that up to four moles of calcite might be needed for acid neutralization as follows:

$$FeS_2 + 4CaCO_3 + 3.75O_2 + 3.5H_2O \rightarrow 2SO_4^{2-} + Fe(OH)_3 + 4Ca^{2+} + 4HCO_3^- \quad (11.3)$$

The stoichiometry of Equation 11.3 shows that twice as much calcite would be required for acid neutralization. On a mass basis, for each 10 ppt of sulfur present, 62.5 tons of calcite is needed for acid neutralization in one thousand tons of overburden.

The choice of which stoichiometry most closely describes a minespoil system directly affects the ABA calculation, alkaline addition rates, and prediction of expected postmining water quality. Brady and Cravotta (1992) in analyzing ABA and water quality data from 74 mine sites, showed that correct prediction of postmining net alkalinity was improved from 52 to 57 using a stoichiometric equivalence of 62.5. They also found that the "errors" in prediction become more balanced using a 62.5 factor, with equal proportions of sites erroneously predicted to yield acid water and sites predicted to yield alkaline water. However, a later study initiated by the PaDEP (Brady et al., 1994) showed that the 31.25 equivalence factor was most accurate, correctly predicting postmining net alkalinity on 31 of 38 mines (82%), while the 62.5 factor correctly predicted 22 of 38 (58%). The diverse results from these two studies underscore the complex geochemical processes at work and unique character of each minesite. Data reduction methods may also influence site rankings.

The PaDEP's mainframe ABA database processes overburden data using both the 31.25 and 62.5 factors. The experience base of ABA interpretation has been built largely on using the 31.25 factor, and this convention is followed in most of the subject literature.

Neutralization Potential (NP)

Neutralization potential is presumed to measure carbonate minerals, exchangeable bases, and weatherable silicate minerals (Sobek et al., 1978), and provide an index of available acid neutralizers in the rock. The procedure does not discriminate among forms of neutralizers and represents a theoretical maximum value for NP.

Carbonate minerals are the most important source of NP, and calcite is the most important carbonate found in Pennsylvania overburden rocks. Dolomite, a calcium-magnesium carbonate mineral is sometimes present and dissolves more slowly, that is, neutralizes acid less quickly (Stumm, 1992). Iron carbonate, siderite ($FeCO_3$), is a common accessory mineral in Pennsylvanian rocks and may contribute to the laboratory NP measurement (Wiram, 1992; Morrison et al., 1990; Evans and Skousen, 1995; Skousen et al., 1997). However, it does not provide net acid neutralization (Williams et al., 1982) as illustrated below:

$$FeCO_3 + 2H^+ \rightarrow Fe^{2+} + CO_2 + H_2O \quad (11.4)$$

$$Fe^{2+} + 0.25O_2 + H_2O + H^+ \rightarrow Fe^{3+} + 1.5H_2O \quad (11.5)$$

$$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3 + 3H^+ \quad (11.6)$$

Summary Reaction:

$$FeCO_3 + 0.25O_2 + 1.5H_2O \rightarrow Fe(OH)_3 + CO_2 \quad (11.7)$$

The initial dissolution of siderite and ferrous iron oxidation consumes acid and may provide temporary neutralization. However, iron hydrolysis ultimately generates acidity equal to that initially consumed, resulting in no net neutralization.

Interpretation of NP data and the possible carbonate minerals present is facilitated by examination of "fizz" or reaction with room temperature hydrochloric acid. Samples with NP less than 20 ppt $CaCO_3$ generally will not fizz or effervesce (Sobek et al., 1978). Where present in sufficient concentrations, calcite will fizz readily, dolomite fizzes slowly and siderite will not react at ambient temperature. Thus the PaDEP's "rule of thumb" for NP greater than 30 ppt $CaCO_3$ with fizz serves as a qualitative check on the carbonate mineralogy and the rock's ability to neutralize acid.

Besides carbonates and bases, the NP procedure may extract some silicate minerals which weather only slowly under field conditions. The alteration of silicate minerals can consume large amounts of acidity over periods of geologic weathering (Appelo and Postma, 1993) but are a minor source of short term acid neutralization. Inclusion of acid extractable silicates in NP can overestimate the readily available neutralizing capability.

Lappako (1994), working with metal mine wastes, found that NP was overestimated in samples containing calcium feldspar and other minerals.

Maximum Potential Acidity (MPA)

Maximum potential acidity is based on a measure of sulfur content of the rock. The presumption is that this accurately represents the amount of acid generating sulfur minerals. Sulfur in overburden occurs in sulfide, sulfate, or organically bound forms (see Chapter 10). Metal sulfides, mainly pyrite, are the principal source of acid generation and the dominant sulfur form in Appalachian overburden (Smith, et al., 1976). For overburden analysis performed in Pennsylvania, the PaDEP has found MPA from total sulfur to be a reliable index of acid generating potential. Acid-base accounting stoichiometry assumes the sulfur is all present as pyrite, and complete oxidation and acid generation occurs. Thus the designation of maximum potential acidity.

Sulfate sulfur exists in many minerals such as gypsum (calcium sulfate), jarosite (potassium-iron sulfate), and alunite (potassium-aluminum sulfate). Sulfate minerals are usually present in significant quantities only in weathered spoil or refuse; and otherwise absent from fresh overburden in Pennsylvania. Alkaline earth sulfate salts like gypsum are nonacid formers. Metal sulfate salts, however, are intermediate products of pyrite oxidation, and represent "stored acidity". These minerals can undergo dissolution and hydrolysis with acid generation. Sulfate sulfur cannot be ruled out as a potential acid source unless the mineralogy is known, and the common lab procedures for sulfur fractionation do not identify the specific minerals present.

Sulfate minerals such as gypsum are common in the arid and semi-arid regions of the western United States and total sulfur may not be a reliable index of MPA. Adjustments to ABA analysis, such as sulfur fractionation, for western mine lands are discussed in Williams and Schuman (1987).

Organically bound sulfur is generally considered to be to nonacid forming and is found in coals, carbon rich shales, partings, "bone coal", etc.

Sulfur fractionation may be useful where the material analyzed is refuse or weathered spoil and significant partitioning of sulfur among the three fractions is suspected.

Net Neutralization Potential (NNP) Calculation

Computation methods for NNP imply that acid generation from MPA and acid neutralization from NP take place concurrently and at equal rates. In fact, acid generation can proceed more rapidly (see Chapter 1, Geochemistry of Coal Mine Drainage), and is catalyzed by *Thiobacillus ferrooxidans* bacteria. The solubilities of acid products are such that total acidity may range from hundreds to thousands of mg/L. Carbonate mineral dissolution is a function of pH and partial pressure of carbon dioxide (Plummer et al., 1978) and does not occur as rapidly. Alkalinity in mine waters is seldom greater than 400 mg/L due to the limited solubility of calcite and other carbonate minerals.

The traditional computation method for NNP utilizes MPA calculated from total sulfur times a 31.25 equivalence factor. Numerous modifications to the NNP calculation have been developed based on specific needs. Joseph et al. (1994) give a summary of various ways of calculating NNP for both hydrologic and agronomic interpretations. Some examples and applications are as follows:

$$NNP = NP - MPA, \quad (11.8)$$

where MPA is percent total sulfur x 31.25.

The traditional method assumes all sulfur is in a potentially acid generating form, and is usually appropriate for fresh unweathered overburden in Pennsylvania.

$$NNP = NP - PA, \quad (11.9)$$

where PA is percent pyritic sulfur x 31.25.

This method assumes sulfide sulfur is the only acid generating source; sulfate and organic sulfur are assumed to be nonacid generating. This is applicable where alkaline earth sulfate salts are present, but not applicable for metal sulfate salts.

$$NNP = NP - MPA, \quad (11.10)$$

where MPA is percent total sulfur x 62.5

This assumes a closed system with no carbon dioxide gas exsolved where both sulfuric and carbonic acid must be neutralized.

$$NNP = NP - (PA + EA), \quad (11.11)$$

where PA is percent pyritic sulfur x 31.25, and EA is exchangeable acidity.

This applies to soils and agronomic interpretations.

$$NNP = NP - (PA + SMP), \quad (11.12)$$

where PA is percent pyritic sulfur x 31.25, and SMP is the lime recommendation from buffer pH.

This applies to soils and agronomic interpretations.

Calculations based on the traditional method shown in Equation 11.8 are the most common method of computation in Pennsylvania and other Appalachian states.

Paste pH

Paste pH was originally included by Smith and coworkers as one of the ABA parameters. It is seldom applied today in Pennsylvania, but continues in use in some other states. Paste pH shows the current acidity status of the sample but may provide little indication about the future behavior of the rock.

Metals

Postmining drainage concentration of metals and dissolved constituents such as sulfate are not directly predictable from ABA analysis. The ABA procedure

quantifies mineral groups and not individual elements or chemical species. The behavior of individual metals or other dissolved constituents is best evaluated from consideration of pH, redox status, and solubility considerations.

Analyzing and Interpreting Acid-Base Accounting

Acid-base accounting is one of a group of interpretive tools for predicting mining impacts to hydrologic systems. The accumulated experience, developed from over 15 years of using ABA in Pennsylvania, shows that the strongest interpretations come from collective evaluation of several factors. These include ABA data, historical performance, premining water quality, stratigraphy and lithology, ground water flow systems, weathering effects, and the proposed mining and reclamation plan. A prediction of mine drainage quality results from an integrated evaluation of all of these factors. In this chapter, however, the discussion is limited to ABA data.

Almost from the inception of acid-base accounting, there have been attempts to define numerical criteria or levels of significance for classifying ABA results and expected rock behavior. These numeric criteria have taken the form of (1) boundaries on NNP values; (2) ratios of NP to MPA; and (3) boundaries on values for NP or MPA. Some of these criteria, and their geologic and geographic applications, are presented in Table 11.1.

Values in the table refer to characteristics of individual rock samples. Variation exists in the reported values, which are drawn from diverse geologic settings and climates. Some general conclusions are summarized as follows:

- A deficit of carbonate material or NP increases the likelihood of acid drainage,
- Conversely, excess carbonate lessens the potential for acid drainage.
- A range of ABA values exists where drainage quality is variable.
- A universal ABA criteria for separating acid and alkaline producing rocks does not exist.

The lack of universal criteria is not surprising since mine drainage quality is a product of the interaction of many geologic, hydrologic, climatic, and mining factors. diPretoro and Rauch (1988) stated "Because of the complexity of coal mining and reclamation operations, professional judgment (taking into account lithology and history of drainage quality in a given area, as well as acid-base account parameters) will always be required to arrive at a final determination." Miller et al., (1991) noted that "... the application of a single absolute cut-off criterion can be misleading and result in overdesign of the waste management requirements." For metal mines, it has been suggested that ABA criteria are site specific and mineral dependent. (Miller and Murray, 1988; Morin and Hutt, 1994).

Application of ABA has been likewise proposed either as (1) the principal overburden analysis tool (Sobek et al., 1978) or (2) as an initial screening tool. Where ABA results are unclear, simulated weathering tests, mineralogic characterization, or other analyses have been recommended (Carruccio and Geidel, 1980; Miller et al., 1994; British Columbia Acid Mine Drainage Task Force, 1989).

Dual interpretive criteria have evolved for applications to water quality predictions, and soils and revegetation concerns. Efforts in Pennsylvania and other eastern coal states have focused heavily on water quality predictions with ABA as the primary overburden analysis tool.

Acid-Base Accounting and Coal Mine Drainage Studies in Appalachia

ABA and mine drainage quality relations have been evaluated in Pennsylvania and northern Appalachia in three studies, including projects initiated by the PaDEP, West Virginia University, and the U.S. Bureau of Mines. These studies have shown that carbonate content of the overburden or NP is a very important factor controlling mine drainage quality. In each study, net alkalinity (alkalinity minus acidity) was used as the primary index of postmining drainage quality. The parameters acidity, alkalinity, and net alkalinity are measures of the complete acidity or alkalinity generating capacity of a water. They are also the aqueous analogues of the ABA rock parameters of MPA, NP, and NNP.

Pennsylvania Study

The PaDEP conducted a study that included about 40 surface mines from Pennsylvania's bituminous coal field (Brady et al., 1994, and Perry and Brady, 1995). Each mine had two or more ABA drill holes and multiple postmining water quality samples from seeps, springs, or monitoring wells. Raw ABA data were processed into a summary value for the entire mine using mass weighting procedures described by Smith

Table 11.1 Summary of Suggested Criteria for Interpreting Acid-Base Accounting [1]

CRITERIA	APPLICATION	REFERENCE
Rocks with NNP less than -5 ppt $CaCO_3$ are considered potentially toxic.	Coal overburden rocks in northern Appalachian basin for root zone media in reclamation; mine drainage quality.	Smith et al., 1974, 1976; Surface Mine Drainage Task Force, 1979; Skousen et al., 1987
Rocks with paste pH less than 4.0 are considered acid toxic.	Coal overburden rocks in northern Appalachian basin for root zone media, mine drainage quality. Base and precious metal mine waste rock in Australia and southeast Asia.	Smith et al., 1974, 1976; Surface Mine Drainage Task Force, 1979 Miller and Murray, 1988
Rocks with greater than 0.5% sulfur may generate significant acidity.	Coal overburden rocks in northern Appalachian basin, mine drainage quality. Base and precious metal mine waste rock in Australia and southeast Asia.	Brady and Hornberger, 1990 Miller and Murray, 1988
Rocks with NP greater than 30 ppt $CaCO_3$ and "fizz" are significant sources of alkalinity.	Coal overburden rocks in northern Appalachian basin, mine drainage quality.	Brady and Hornberger, 1990
Rocks with NNP greater than 20 ppt $CaCO_3$ produce alkaline drainage.	Coal overburden rocks in northern Appalachian basin. Base and precious metal mine waste rock and tailings in Canada.	Skousen et al., 1987; British Columbia Acid Mine Drainage Task Force, 1989; Ferguson and Morin, 1991
Rocks with NNP less than -20 ppt $CaCO_3$ produce acid drainage.	Base and precious metal mine waste rock and tailings in Canada.	British Columbia Acid Mine Drainage Task Force, 1989; Ferguson and Morin, 1991
Rocks with NNP greater than 0 ppt $CaCO_3$ do not produce acid. Tailings with NNP less than 0 ppt $CaCO_3$ produce acid drainage.	Base and precious metal mine waste rock and tailings in Canada.	Patterson and Ferguson, 1994; Ferguson and Morin, 1991
NP/MPA ratio less than 1 likely results in acid drainage.	Base and precious metal mine waste rock and tailings in Canada.	Patterson and Ferguson, 1994; Ferguson and Morin, 1991
NP/MPA ratio is classified as less than 1, between 1 and 2, and greater than 2.	Base and precious metal mine waste rock and tailings in Canada.	Ferguson and Robertson, 1994
Theoretical NP/MPA ratio of 2 is needed for complete acid neutralization.	Coal overburden rocks in northern Appalachian basin, mine drainage quality.	Cravotta et al., 1990
Use actual NP and MPA values as well as ratios to account for buffering capacity of the system.	Base metal mine waste rock, United States.	Filipek et al., 1991

(1) Criteria in this table were developed for classification of individual rock samples

and Brady (1990). Summary ABA data were compared to median water quality values. Summary NP and NNP values were computed with and without the "threshold" criteria of 0.5 percent sulfur and NP of 30 ppt CaCO3 with fizz. Eleven different coal beds are represented from the Allegheny, Conemaugh, Monongahela, and Dunkard groups as shown in Table 11.2. Sites included single and multiple seam operations with mining methods ranging from small block cut operations to area mining by dragline.

Principal findings of the study are:

- Carbonate content, represented by NP and NNP, most clearly predicted post mining water quality conditions. Carbonate contents as low as two to three percent (NP of 20 to 30 ppt $CaCO_3$) effectively controlled net alkalinity of mine drainage.
- No significant relationships were found between MPA and postmining water quality except where carbonates were absent.
- The use of threshold criteria improved predictive accuracy, especially for acid sites.
- Pyrite oxidation and acid generation is inhibited by the presence of carbonate minerals.

Table 11.2 Coal beds represented in Pennsylvania acid-base accounting study.

Group	Coal Bed	Number of Mines
Dunkard	Waynesburg	6
Monongahela	Pittsburgh	1
Conemaugh	Brush Creek	1
Allegheny	Upper Freeport	4
	Lower Freeport	5
	Upper Kittanning	11
	Luthersburg	1
	Middle Kittanning	12
	Lower Kittanning	8
	Clarion	6
	Brookville	3

Mines with NP greater than 21 ppt $CaCO_3$ (mass weighted basis) all produced net alkaline water. Eight of eleven mines with NP less than 10 ppt $CaCO_3$ had net acid water. Five of these mines had net alkalinity of less than -200 mg/L. Mines with mass weighted NP between 10 and 21 ppt $CaCO_3$ included six acid and ten alkaline sites with most waters between -125 and +150 mg/L net alkalinity. A scatterplot of these data is shown in Figure 11.2.

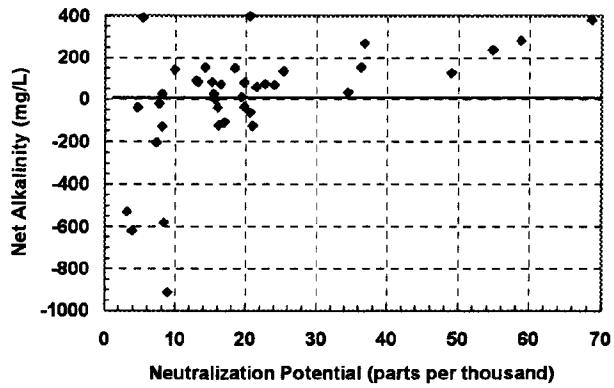

Figure 11.2 Pennsylvania ABA-Mine Drainage Study Neutralization Potential vs. Net Alkalinity

All mines with mass weighted NNP greater than about 10 ppt $CaCO_3$ produced alkaline water. Seven of nine sites with NNP less than 0 ppt $CaCO_3$ produced acid water. Mines with NNP between 0 and 10 ppt $CaCO_3$ included six acid and 13 alkaline sites with most waters between -130 and +150 mg/L net alkalinity. Some sites with low NNP but alkaline water were anomalous and could result from nonrepresentative overburden sampling or an influx of alkaline water from off site. A scatterplot of NNP and net alkalinity are shown in Figure 11-3.

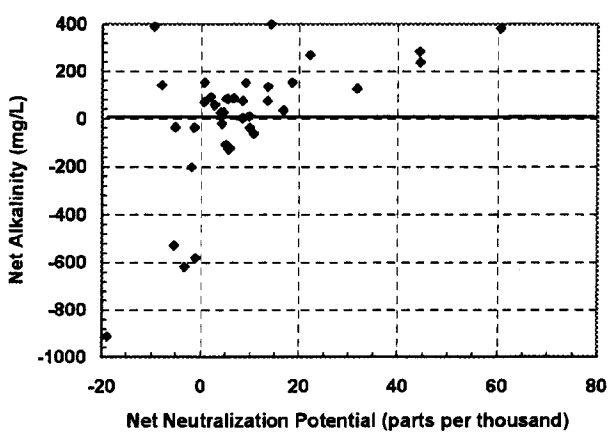

Figure 11.3 Pennsylvania ABA-Mine Drainage Study Net Neutralization Potential vs. Net Alkalinity

Net alkalinity was also compared to NNP and NP computed with threshold criteria applied. Results for NP and NNP with and without thresholds are summarized in Table 11.3.

Table 11.3 [1] Summary of water quality prediction from three studies of mine drainage and ABA in Northern Appalachia.

Overburden Quality	Water Quality			Study Source
	Net Acid	Variable	Net Alkaline	
Neutralization Potential (NP)	< 10 ppt	10 to 21 ppt	>21 ppt	Pennsylvania (Brady et al., 1994; Perry and Brady, 1995)
Neutralization Potential (NP) with thresholds	< 1 ppt	1 to 10 ppt	>10 ppt	Pennsylvania (Brady et al., 1994; Perry and Brady, 1995)
Neutralization Potential (NP)	< 20 ppt	20 to 40 ppt	>40 ppt	West Virginia (diPretoro and Rauch, 1988)
Net Neutralization Potential (NNP)	< 0 ppt	0 to 12 ppt	>12 ppt	Pennsylvania (Brady et al.,1994; Perry and Brady, 1995)
Net Neutralization Potential (NNP) with thresholds	< -5 ppt	-5 to +5 ppt	>5 ppt	Pennsylvania (Brady et al., 1994; Perry and Brady, 1995)
Net Neutralization Potential (NNP)	< 10 ppt	10 to 30 ppt	>30 ppt	West Virginia (diPretoro and Rauch, 1988)
Net Neutralization Potential (NNP)	< 10 ppt	10 to 20 ppt	?	Bureau of Mines (Erickson and Hedin, 1988)

[1] Overburden criteria in this table are developed from volume weighted summaries of overburden data.

Figure 11.4a is a cumulative frequency plot of mass weighted NP for mines with net alkaline water. About 90 percent of these mines had NP greater than 10 ppt $CaCO_3$. Thus, the likelihood of obtaining alkaline drainage at low NP values (less than 10 ppt $CaCO_3$) is rather small. Figure 11.4b is a cumulative frequency plot of NNP for mines with alkaline water. All of the sites plotted had positive NNP (excess carbonate present) to produce alkaline drainage.

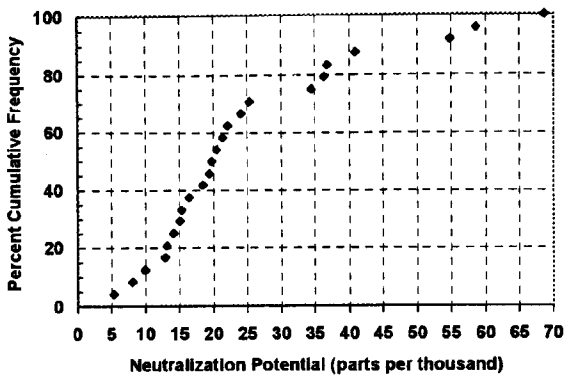

Figure 11.4a Plot of Cumulative Frequency of Alkaline Waters vs. Neutralization Potential

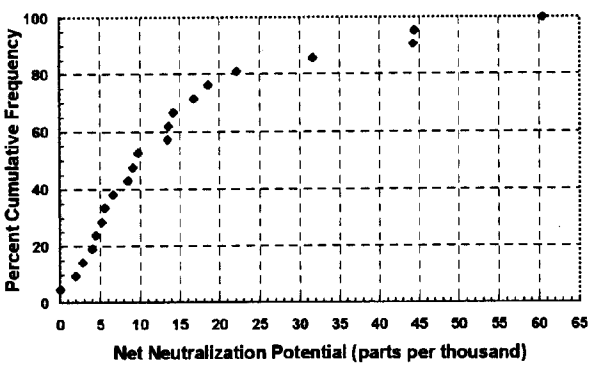

Figure 11.4b Plot of Cumulative Frequency of Alkaline Waters vs. Net Neutralization Potential

Figure 11.5 is a scatterplot of MPA versus acidity in postmining waters. There is no apparent relationship between the two, and MPA by itself is not a good predictor of mine drainage quality. Obviously, pyrite must be present for acid generation to occur, but the abundance or lack of carbonate minerals controls the overall evolution of acid-base properties of mine drainage. Smith et al. (1976), examining ABA data in the southern Appalachians, concluded that some rocks are so low in sulfur content that they are incapable of generating acid conditions regardless of their carbonate content.

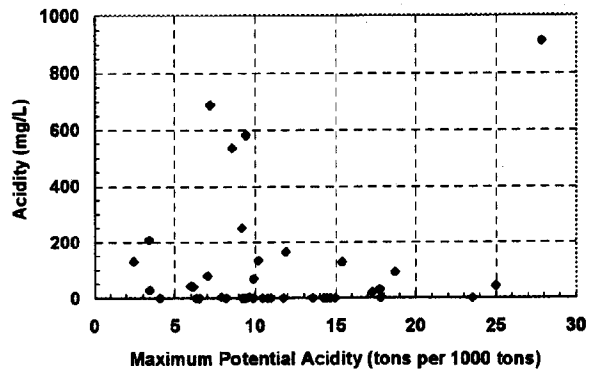

Figure 11.5 Pennsylvania ABA-Mine Drainage Study Acidity vs. Maximum Potential Acidity

Mine drainage sulfate concentrations, normalized with respect to percentage of sulfur in the overburden, and NP values are plotted in Figure 11.6. In general, as NP increases, the production of sulfate declines. These trends were interpreted as showing that carbonates inhibit acid generation. Carbonates, with the exception of siderite, have at least three different inhibiting effects on acid generation. First, alkaline conditions created by carbonate dissolution are not conducive to bacterial catalysis of ferrous iron oxidation. Singer and Stumm (1970) showed that the activity of *Thiobacillus ferrooxidans* could increase the rate of ferrous to ferric iron conversion by several orders of magnitude. These bacteria are most active in the pH range of about 2 to 4. Ferrous to ferric iron conversion is the "rate determining step" in the overall sequence of acid generation from pyrite (Singer and Stumm, 1970). Thus, inhibiting bacterial activity slows pyrite oxidation.

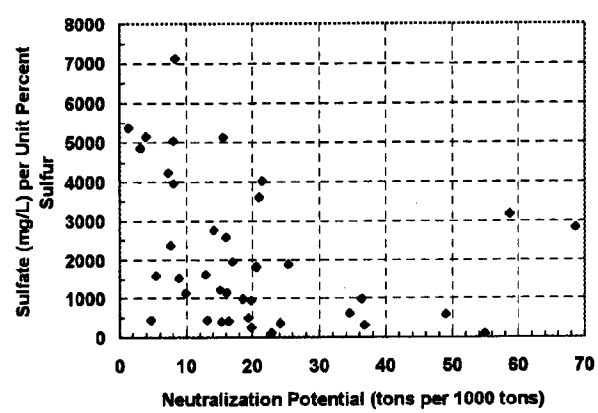

Figure 11.6 Pennsylvania ABA-Mine Drainage Study Sulfate Production (Normalized) vs. Neutralization Potential

Alkaline conditions greatly limit the activity of dissolved ferric iron. Removal of dissolved ferric iron by alkaline conditions is important since it interrupts the self propagating acid cycle. Dissolved ferric iron is capable of rapidly oxidizing pyrite as follows:

$$FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO^{2-}_4 + 16H^+ \quad (11.13)$$

Finally, carbonates are acid reactive, with their dissolution rate a function of H^+ activity (pH) and the partial pressure of CO_2 (Plummer et al., 1978). As acidity increases, the rate of carbonate dissolution increases. Conversely, under alkaline conditions, carbonate dissolution slows until equilibrium is reached.

The inhibitory effects of carbonate minerals on acid generation have been observed in laboratory weathering studies (Williams et al., 1982; Carrrucio and Geidel, 1980) which showed that rocks containing several percent pyrite produced less acidity and sulfate when carbonate was present at a few percent concentration. Lorenz and Tarpley (1963) noted that in coal samples containing calcite, "calcite increased the pH of the reaction from 3.5 needed for optimum growth of *Ferrobacillus ferroxidans* to a higher value that inhibited the catalytic effect of the bacterium".

West Virginia Study

A study by diPretoro and Rouch (1988) of ABA and mine drainage quality in northern West Virginia included many of the same coals and stratigraphic sequences mined in Pennsylvania such as the Waynesburg and upper Freeport intervals. Their study also used mass weighting of ABA data and shows results similar to the Pennsylvania study. The findings of diPretoro and Rauch are summarized as follows:

- Excess carbonate was needed to ensure alkaline drainage. Mines with NP > 40 ppt $CaCO_3$ or NNP > 30 ppt $CaCO_3$ produced net alkaline water.
- Mines with NP < 20 ppt $CaCO_3$ or NNP < 10 ppt $CaCO_3$ produced acid water.
- For NNP between 10 and 30 ppt $CaCO_3$, six sites were alkaline and four were acid.
- Eleven of 14 mines with NP/MPA ratios > 2.4 had net alkaline water; 15 mines with ratios < 2.4 had net acid water.

MPA showed no apparent relationship to net alkalinity. Also, diPretoro and Rauch noted lithologic effects, in that mines with a large proportion of sandstone overburden could produce acid drainage even at low sulfur contents.

Bureau of Mines Study

Erickson and Hedin (1988) examined ABA and water quality relations on 32 mines. About half the sites were in Pennsylvania; the remainder were in other northern Appalachian states and the Illinois basin. Their study also used volume weighted ABA data. Findings are summarized as follows:

- The -5 ppt $CaCO_3$ criterion for NNP was not useful for predicting the acid or alkaline character of mine drainage.
- Fifteen of 20 mines with NNP < 10 ppt $CaCO_3$ produced net acid water, and nine of 11 sites with NNP < 0 ppt $CaCO_3$ had acid water.
- For NNP between 0 and 20 ppt $CaCO_3$, eight mines produced acid water and seven mines had alkaline drainage.
- Calculation of MPA based on pyritic sulfur did not improve predictive capability.

The sample group did not have any sites with NNP between 20 and 80 ppt $CaCO_3$. The authors also cautioned against using ABA data alone, and suggested analyzing other information such as past water quality data.

Data reported elsewhere (Engineer's International, 1986) from the same mines in Erickson and Hedin's study showed that pH and alkalinity were generally related to NP and NNP, and specific conductance and NP were also correlated.

NP and NNP results from the three Appalachian studies are compared in Table 11.3. Variation in results among the studies may stem from differences in how ABA data were processed and summarized. The Pennsylvania study used slightly different geometric approximations. Differences may also reflect regional or stratigraphic variation in rock properties.

Other Mine Drainage Studies

Other coal overburden and metal tailings studies have examined the utility and predictive capabilities of ABA against weathering tests. Sturey et al. (1982), in a comparison of ABA and column weathering studies, concluded that both methods were adequate to show acid and nonacid trends and that ABA provided more information on individual strata. Bradham and Carrucio (1991) analyzed 10 metal mine tailings samples and compared them to field weathering test pads. ABA predictions for acid or alkaline quality agreed with field performance for eight samples, while laboratory

weathering tests agreed with field performance of all 10 samples. Most samples were acid producing.

Ferguson and Morin (1991) found that Canadian metal tailings with NNP < 0 ppt $CaCO_3$ were generally acid producing and concluded that the NP to MPA ratio was useful as a qualitative predictor. They noted that waste rock drainage quality was more difficult to predict due to heterogeneous properties of the spoil. Ferguson and Robertson (1994) reported that no rock with an NP to MPA ratio greater than 1 had been conclusively identified as producing acid in the field. However, for screening ABA data, they propose a ratio of greater than 2 as "nonacid generating", and ratios of 1 to 2 as "possibly." Patterson and Ferguson (1994) found that an NP to MPA ratio of 1 separated acid from nonacid producing metal mines in Canada and Sweden.

Plumlee et al. (1993), sampling metal mine drainages in Colorado, concluded that drainage quality was controlled by ore deposit geology, climate, and mining method. Pyrite content and acid buffering capacity were considered to be the most important geological controls on pH and metal content of the mine waters.

An Example of Acid-Base Accounting Data Interpretation

This section presents an abbreviated example of review and interpretation of an ABA data set from Pennsylvania, and the resultant postmining water quality.

Weathered Zone

ABA interpretation begins with review of the overburden analysis report, including drill logs and lithologic descriptions. Within each ABA drill hole, a zone of geologic weathering occurs where carbonates (NP) and sulfides (MPA) have been removed. Highly weathered rocks are not capable of generating significant alkalinity, and the lack of sulfur precludes the formation of acid drainage. The weathered zone can be considered chemically inert and contributes little to postmining drainage quality. Weathered materials are characterized by shades of brown, yellow, or red (Munsell color chromas greater than 2), and the rocks are often weakly cemented or partly decomposed. Smith et al. (1974, 1976) suggested that the weathered zone in Appalachia is about 20 ft (6 m) deep. A study in Saltlick Township Fayette County, Pennsylvania found sulfide sulfur weathered to depths of 16 to 20 ft (5 to 6 m), (Figure 8.59, Chapter 8) while carbonate leaching in Wharton Twp., Fayette County was also about 20 ft (6 m) (Brady et al., 1988).

An example drill log and ABA data from southwestern Pennsylvania (Figure 11.7) illustrates the effects of weathering on sulfur and carbonate content. Weathering in this locale has proceeded to a depth of about 18 ft (5.5 m). Weathering is indicated by the soil zone, brown clay (probably weathered shale) and light brown shale. Below 18 ft (5.5 m), the rocks are described in shades of light and dark gray, rather than brown. Total sulfur values in the upper 18 ft (5.5 m) are very low (less than 0.2 percent). NP values are also quite low (less than 5 ppt $CaCO_3$). The upper 18 ft (5.5 m) of overburden lacks the ability to generate either significant acidity or alkalinity. At depths below 18 ft (5.5 m), both sulfur content and neutralization potential values increase. These rocks will determine the post mining water quality.

Identification of Significant Strata

Significant acid and alkaline producing rock strata can be identified from the PaDEP's "rule of thumb" of greater than 0.5 percent sulfur and NP greater than 30 ppt $CaCO_3$ with fizz. For the drill log in Figure 11.7, potentially acid strata (greater than 0.5 % sulfur) are present from 23 to 47 ft (7 to 14 m) and immediately above and below the coal. Significant alkaline strata (NP greater than 30 ppt $CaCO_3$) are present from 32 to 40 ft (10 to 12 m) and below the coal. Some rocks met the criteria for both acid and alkaline strata; for example the shale sequence from 32 to 40 ft (10 to 12 m). These rocks contain excess carbonate (positive NNP) with NP to MPA ratios of about 2 to 4 and are expected to generate net alkalinity. The strata immediately above and below the coal have MPA in excess of NP (negative NNP) and are potential sources of acidity.

Correlation to Other Drill holes

Lithologic logs of drill holes analyzed for ABA can be compared and correlated to other drill hole logs whether or not they have geochemical analyses. ABA is usually run on only a fraction of the exploratory borings drilled on a minesite. Lithologic comparisons are useful to determine the type and degree of variation in stratigraphy, depth of weathering, or structural considerations that may signal changes in overburden geochemistry. Lithologic comparisons are also useful to correlate significant acid or alkaline strata among drill holes. If these significant strata can be correlated across a mine site and are identifiable in the field,

Depth	Thick -ness	Scale	Graphic Log	Lithologic Description and Water Conditions	Log Interval	% Total Sulfur	Fizz Rating	Neutralization Potential
2	2			SOIL	1 - 2	0.02	0	0.71
					3 - 5	0.02	0	2.29
9	7			LT. BROWN CLAY	6 - 9	0.02	0	2.29
		10			10 - 12	0.04	0	2.14
					13 - 15	0.10	0	1.72
18	9			LT. BROWN SHALE	16 - 18	0.15	0	4.43
		20						
22	4			LT GRAY SHALE	19 - 22	0.40	0	13.59
					23 - 25	0.57	0	23.60
					26 - 28	0.56	0	16.30
		30			29 - 31	0.58	1	22.31
					32 - 34	0.85	3	129.77
					35 - 37	1.05	3	148.14
		40			38 - 40	0.76	2	44.05
43	21			LT. GRAY CALC. SHALE	41 - 43	0.77	1	29.46
44	1			LT. GRAY SHALE	44	1.09	1	25.74
					45 - 47	0.62	1	25.03
					48 - 50	0.20	1	26.32
		50						
54	10			LT. GRAY CALC. SHALE	51 - 54	0.47	1	27.46
55	1			GRAY SHALE W/ COAL	55	1.66	0	13.010
57	2			COAL - BRUSH CREEK	56 - 57	NO SAMP	LE	
59	2			GRAY SHALE	58 - 59	0.91	1	46.63
		60						
63	4			LT. GRAY SHALE	60 - 63	0.15	3	202.57

Figure 11.7 Example Log Showing Distribution of Sulfur and Neutralization Potential, Drillhole 17

analysis of overburden quality and mine planning can be more rigorous. If the materials cannot be clearly correlated or the materials cannot be distinguished in the field, overburden interpretation and material handling are more speculative.

Data Reduction and Interpretation

Volume weighting has been used to improve the representation of the vertical and horizontal extent of strata in a mine site. This is necessitated by the hilly topography and more or less flat lying strata of Pennsylvania's coal fields which make the upper strata less extensive than the deeper rocks. The department uses the algorithms described by Smith and Brady (1990) which incorporate area, volume and density of rock, and fraction of unit spoiled to calculate mass weighted ABA data for individual samples, entire drill holes, or multiple drill holes within a mine. These data can be further refined by calculations with and without "threshold" values for sulfur and NP, stoichiometric equivalence factors of 31.25 or 62.5, inclusion of alkaline addition rates, and these can be reported in various formats.

An "area of influence" is defined for each ABA drill hole by delineating the limits of mining and dividing the area into polygons. Figure 11.8 shows a mine with five ABA drill holes, and the polygons (area of influence) drawn for each drill hole. The areas are planimetered or digitized and the weights of NP and MPA calculated. More elaborate calculations can be made with volumetric and contouring software. However, the Thiessen polygon process described by Smith and Brady (1990) is simple enough to perform on a computer spreadsheet and can be easily modified to site specific situations.

Figure 11.9 shows an example printout of the raw and calculated ABA parameters for drill hole 17. The printout provides information by sample on depth, thickness, rock type, percent sulfur, NP, unit weight of the rock, area represented, fraction of unit spoiled (portion of overburden returned to the backfill), mass of NP, mass of MPA, mass of Net NP, and mass of overburden represented. In this example, area values increase with depth, reflecting the greater areal extent of the deeper rocks, and the overburden is modeled as a truncated cone. NP and MPA values for these deeper strata are given greater weighting in the summary calculations. Smith and Brady (1990) discuss appropriate means of modeling various overburden geometries in more detail.

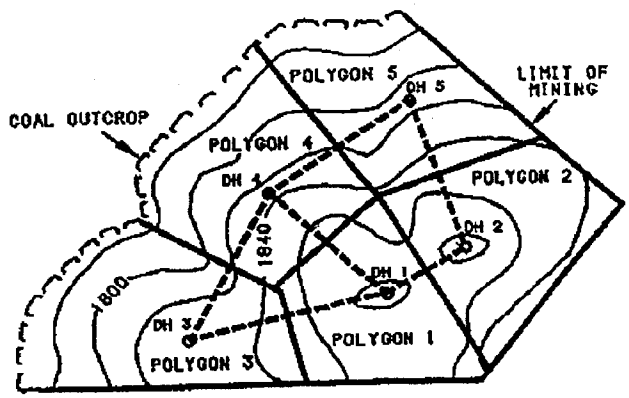

Figure 11.8 Example Mine Plan Showing Theissen Polygon Construction for Determining Areas of Influence from Smith and Brady, 1990.

Figure 11.10 provides acreage weighted ABA summary numbers for the entire drill hole calculated with and without "threshold" criteria using stoichiometric equivalence factors of 31.25 and 62.5. For drill hole 17, the overburden has an overall NP of about 35 ppt $CaCO_3$, overall NNP of 17.8 ppt $CaCO_3$ and NP to MPA ratio of 2 when calculated without thresholds and equivalence factor of 31.25 (upper left box in Figure 11.10). These results show overburden that would be expected to produce alkaline drainage.

Summary data computed with "threshold" values include only NP and percent sulfur values that exceed 30 ppt $CaCO_3$ and 0.5 percent respectively. Samples that do not meet these criteria are assigned a value of zero, and in essence are treated as chemically inert. For drill hole 17, the overburden has an overall NP of about 21.6 ppt $CaCO_3$ and overall NNP of 7.1 ppt $CaCO_3$ when summarized in this manner (lower left box in Figure 11.10). These results also show overburden that would be expected to produce alkaline drainage.

ABA data from multiple drill holes can be combined to produce summary data for the entire mined area. These summary outputs reduce a large amount of raw data to a manageable output sufficient to analyze and interpret a mine site. Drill hole 17 was combined with two other ABA holes of similar geochemistry. Summary ABA results for the combined three drill holes are shown in Table 11.5.

Overburden Analysis Data System
Acid Base Accounting
Drill Hole Data

Id: _____ Permit: _____ or Project Code:_____
Operator: _____ Mine Name: _____
County: _____ Municipality: _____
Quad Map: _____ Stream Code: _____
Drill Hole Id: 17 Latitude:_____ Longitude: _____
UTH Zone: _____ Northing: _____ Easting: _____ Date Drilled 04-SEP-90
Driller: _____
Drilling Method: 1 AIR ROTARY
Interpreter: _____
Laboratory: _____
Added Alkaline: Threshold Values: Sulfur: 0.500 NP: 30.00 Fizz:

Intervals @ 31.25

Bottom Depth	Thick-ness	Rock Type	Coal Seam	Percent Sulfur	Fizz Rat-ing	NP	Ton-nage	Acres	Fraction Spoiled	Tons MPA	Tons MP	Net Tons NP	Tons Over-burden
2.00	2.00	SOIL		0.200	0	0.71	2000	1.00	1.00	2.50	2.84	0.34	4000.00
5.00	3.00	CLAY		0.020	0	2.29	3450	1.14	1.00	7.34	26.91	19.56	11749.88
9.00	4.00	CLAY		0.020	0	2.29	3450	1.27	1.00	10.96	40.15	29.19	17533.02
12.00	3.00	SHLE		0.040	0	2.14	3700	1.41	1.00	19.50	33.39	13.89	15603.97
15.00	3.00	SHLE		0.100	0	1.72	3700	1.52	1.00	52.78	29.05	-23.73	16890.81
18.00	3.00	SHLE		0.150	0	4.43	3700	1.64	1.00	85.21	80.53	-4.68	18177.66
22.00	4.00	SHLE		0.400	0	13.59	3700	1.75	1.00	324.41	352.70	28.29	25952.68
25.00	3.00	SHLE		0.570	0	23.60	3700	1.91	1.00	377.27	499.86	122.58	21180.31
28.00	3.00	SHLE		0.560	0	16.30	3700	2.02	1.00	393.18	366.21	-26.96	22467.15
31.00	3.00	SHLE		0.580	1	22.31	3700	2.14	1.00	430.54	529.95	99.41	23754.00
34.00	3.00	SHLE		0.850	3	129.77	3700	2.26	1.00	665.15	3249.55	2584.40	25040.85
37.00	3.00	SHLE		1.050	3	148.14	3700	2.37	1.00	863.88	3900.18	3036.31	26327.69
40.00	3.00	SHLE		0.760	2	44.05	3700	2.49	1.00	655.85	1216.42	560.58	27614.54
43.00	3.00	SHLE		0.770	1	29.46	3700	2.60	1.00	695.44	851.43	156.00	28901.39
44.00	1.00	SHLE		1.090	1	25.74	3700	2.68	1.00	337.89	255.33	-82.56	9919.76
47.00	3.00	SHLE		0.620	1	25.03	3700	2.76	1.00	593.21	766.35	173.14	30617.19
50.00	3.00	SHLE		0.200	1	26.32	3700	2.87	1.00	199.40	839.71	640.31	31904.03
54.00	4.00	SHLE		0.470	1	27.46	3700	3.01	1.00	654.19	1223.08	568.89	44540.47
55.00	1.00	SHLE		1.660	0	13.01	3700	3.11	1.00	596.18	149.52	-446.66	11492.58
57.00	2.00	COAL		2.500	0	0.00	1800	3.16	.10	88.99	0.00	-88.99	1139.06
59.00	2.00	SHLE		0.910	1	46.63	3700	3.28	1.00	690.24	1131.80	441.57	24272.00

LEGEND: (<=Less Than) (>=Greater Than) (+ = Plus) (-= Minus) (*=Degree of Error)

Coal Seam Names:

Figure 11.9 Example of Calculated Acid Base Accounting Data, Drillhole 17

Overburden Analysis Data System
Acid Base Accounting Summary Numbers
Acreage Weighted Calculations

	Acres (Bottom) 3.28				Tons Overburden 439,079.05		
	Without Thresholds @ 31.25				Without Thresholds @ 62.50		
MPA Total Tons)	7,744.10	(Tons/1000 Tons)	17.64	MPA (Total Tons)	15,488.20	(Tons/1000 Tons)	35.27
NP (Total Tons)	15,544.98	(Tons/1000 Tons)	35.40	NP (Total Tons)	15,544.98	(Tons/1000 Tons)	35.40
Net Tons NP	7,800.88	(Tons/1000 Tons)	17.77	Net Tons NP	56.78	(Tons/1000 Tons)	0.13
NP/MPA Ratio	2.01	Tons/Acre Required	2,378.32	NP/MPA Ratio	1.00	Tons/Acre Required	17.31
		EXCESS				EXCESS	
	With Thresholds @ 31.25			With Thresholds @ 62.50			
MPA (Total Tons)	6,387.80	(Tons/1000 Tons)	14.55	MPA (Total Tons)	12,775.60	(Tons/1000 Tons)	29.10
NP (Total Tons)	9,497.96	(Tons/1000 Tons)	21.63	NP (Total Tons	9,497.96	(Tons/1000 Tons)	21.63
Net Tons NP	3,110.16	(Tons/1000 Tons)	7.08	Net Tons NP	-3,277.65	(Tons/1000 Tons)	-7.46
NP/MPA Ratio	1.49	Tons/Acre Required	948.22	NP/MPA Ratio	0.74	Tons Acre Required	999.28
		EXCESS				DEFICIENCY	

Figure 11.10 Example of Summary Acid Base Accounting Date, Drillhole 17

Table 11.5 Example weighted summary overburden data for three drill holes.

	Neutralization Potential (NP)	Net Neutralization Potential (NNP)
No Threshold Criteria Applied	36.7 ppt	22.8 ppt
With Threshold Criteria Applied	23.2 ppt	11.94 ppt

These results are also indicative of rocks expected to produce net alkaline drainage.

Mine Drainage Quality

Postmining drainage quality on the example mine is net alkaline (Table 11.6) as predicted from examination of ABA data. Baseline water quality from a spring is presented for comparison.

Data for both the spring and mine drainage are median values. The mine drainage has much higher alkalinity than the spring, as would be expected from the accelerated weathering of calcareous rocks in the minespoil. Both the mine drainage and the spring contain very low levels of metals. Sulfate concentrations in the mine drainage indicate that some sulfide oxidation has occurred within the minespoil. However, the production of alkalinity is sufficient to neutralize and/or inhibit in-situ acid generation.

Table 11.6 Postmining Water Quality Resulting From Mining of Overburden in Drill hole 17

Water Quality Parameter	Unmined Spring Quality	Mine Drainage Quality
pH	6.4	6.8
Alkalinity (mg/L)	39	268
Acidity (mg/L)	8	0
Tot. Iron (mg/L)	0.09	0.15
Tot. Manganese (mg/L)	0.2	0.65
Sulfate (mg/L)	8.3	139

Conclusions

Acid-Base Accounting has been applied to the prediction of overburden and water quality properties on mined land for about 25 years. An extensive institutional knowledge base and "rules of thumb" have developed on the interpretation of ABA data, and have been supplemented with a few formal studies. Carbonate or NP content exerts major control over the postmining water quality. NP contents of as little as 20 to 30 ppt $CaCO_3$ equivalent are effective in producing alkaline drianage. ABA is a valuable assessment and prediction tool. Its application is most effective as part of a group of interpretive techniques for analyzing the

interaction of geologic and hydrologic conditions, and mining and reclamation practices.

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Chapter 12

RECLAMATION AND REVEGETATION

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Introduction

Mine reclamation practices can influence postmining water quality and the extent to which acid mine drainage is generated. Research suggests mine site rock geochemistry and lithology have more influence on postmining drainage chemistry than does reclamation (diPretoro and Rauch, 1987). Nevertheless, a discussion of reclamation and its relationship to acid mine drainage is warranted. The practices of alkaline addition and special handling of rock overburden during mining and reclamation are discussed in Chapters 13 and 14, respectively. This chapter discusses reclamation and revegetation and the relationship to acid mine drainage. The information presented is based primarily on research and experience with reclamation and revegetation of coal mined lands in Pennsylvania.

Revegetation of Coal Mined Land

Establishing vegetation on coal mined land is required in accordance with state and federal coal mining laws and regulations. Revegetation is an important step in the overall reclamation process. Vegetation aids in stabilizing the soil surface from erosion and controlling siltation. From the standpoint of preventing acid mine drainage, vegetation is beneficial for reducing the amount of water and atmospheric oxygen entering the mine soil/spoil environment.

The Federal Surface Mining Control and Reclamation Act of 1977 (Section 515(b)(20)) requires regions of the country where annual average precipitation is 26 inches (66 centimeters) or less to maintain a minimum period of liability for revegetation success of 10 years on coal mined lands. For regions where annual average precipitation is greater than 26 inches (66 centimeters), the minimum period of liability for revegetation success under the Act is 5 years. The longer liability period for assuring revegetation success reflects the more difficult conditions in arid and semi-arid climates for revegetating mined lands. Problems of revegetating coal mined areas in the arid and semi-arid regions of western United States differ drastically from those in the humid regions of eastern United States (Grimm and Hill, 1974). Pennsylvania's annual precipitation generally ranges between 34 and 52 inches (86 and 132 centimeters) (Dailey, 1971). The arid and semi-arid regions of the country experience extremely adverse conditions for vegetation establishment on mined land in comparison to Pennsylvania with its humid climate. However, even with Pennsylvania's humid climate, vegetation on mined land may not be successful if plant rooting is limited or restricted by acid and toxic materials.

Relationship of Vegetation to Mine Hydrology

Vegetation is a factor in the hydrologic cycle and affects both surface and groundwater. The extent to which the soil/spoil surface is exposed or unvegetated affects evapotranspiration. The rate of evapotranspiration increases as the vegetative cover increases. Evapotranspiration losses may range from 15 inches (38.1 centimeters) per year for barren rocky areas to 35 inches (89 centimeters) per year for heavily forested areas (Wisler and Brater, 1963). The type of vegetation, stage of vegetative growth and density of vegetation affects the amount of water loss through evapotranspiration. Transpiration is limited by the growing season and by available soil moisture.

The grading and vegetation of the surface can have a substantial impact on the quantity of mine drainage generated. For example, average annual precipitation in the West Branch of the Susquehanna River watershed is approximately 40 inches (102 cm). Of this 40 inches (102 cm), an average of 17 inches (43.18 cm) is lost annually through evapotranspiration and 8 inches (20 cm) is lost through overland runoff (Taylor et al., 1983). This leaves an average of 15 inches (38 cm) per year to infiltrate into the groundwater flow system, eventually to discharge directly as baseflow to streams or via springs and seepage zones.

The practical reality of this is that in Pennsylvania and other humid areas where precipitation exceeds evapotranspiration, virtually all mine sites will receive groundwater recharge and generate drainage - acidic or alkaline. That there may be no obvious springs or

seeps does not imply that there is no drainage from the site. To illustrate what 15 inches (38 cm) of infiltration per year means in terms of the quantity of mine drainage which can be generated, each acre of spoil surface would produce an average flow rate of 0.75 gallons per minute (gpm) (2.84 L/min). A 100-acre surface mine, then, would yield 75 gpm (284 L/min) of groundwater flow.

Where vegetation is poor, precipitation can rapidly enter mine spoil leaving less opportunity for evapotranspiration and uptake by plants. Further, the sparse vegetation consumes less water, allowing more to infiltrate below the rooting zone. A site with little or poor vegetation would generate much less evapotranspiration and therefore, much higher infiltration into the groundwater system - - ultimately increasing the volume of mine drainage generated by the site.

Hawkins (1995, and Chapter 17, this report) noted that many Pennsylvania remining operations showed reduced pollution loading rates, not so much from changes in mine drainage chemistry but rather due to decreased groundwater recharge. This reduction was due to two factors: the regrading of abandoned mine lands and improved vegetation. Regrading can be particularly important where there is no positive surface drainage. Surface runoff is directed to abandoned pits and surface depressions, ultimately to infiltrate into the subsurface and increase the availability of groundwater in the spoil. Again, using the average runoff rates reported by Taylor, an unreclaimed, internally-drained site may divert approximately 8 inches (20 cm) of precipitation per year (0.4 gpm/acre) (3.74 L per min/ha) into the subsurface. Clearly, proper regrading and revegetation is one effective but frequently overlooked means of minimizing AMD production.

Vegetation and associated microbiological activity also influence the composition of the mine soil/spoil environment. A well vegetated and biologically active mine soil/spoil increases carbon dioxide levels in the mine soil/spoil and reduces oxygen flux into the mine soil/spoil. The oxygen content of mine soil/spoil is frequently inversely related to the carbon dioxide content (i.e. oxygen levels decline as carbon dioxide increases). Oxygen concentrations have been shown to be rate limiting in the oxidation of pyrite in laboratory studies (Erickson, Kleinmann, and Campion, 1982). Oxygen consumption by plants, soil biota and organic material decay provide potential means of limiting oxygen availability for pyrite oxidation and production of acid mine drainage. In addition, high concentrations of carbon dioxide increase the solubility of carbonate minerals. In theory, more alkalinity is generated in groundwater having high carbon dioxide content, all other factors being constant. Gas composition in mine soil/spoil has been reported by a few investigators (Erickson, 1985; Guo, Parizek, and Rose, 1994; and Jaynes, Rogowski, Pionke, and Jacoby, 1983).

Plant Species as Indicators of Mine Spoil / Overburden Chemistry

Plant species may be used as indicators of mine spoil/overburden chemistry. On disturbed mine land with exposed acidic spoil/overburden, the plant species which volunteer and become established are species which are capable of surviving under acidic conditions.

Observations and field studies by McKee and associates (1982) on several Pennsylvania bituminous strip mine sites found that sites with little or no vegetative cover had mine spoil pH values below 4.5 and were relatively high in soluble aluminum, whereas mine sites with relatively adequate vegetative cover had mine spoil pH values of 4.5 or above and very minimal, if any, soluble aluminum. Greenhouse studies by McKee and associates identified the effects of both low pH and aluminum on plants which they found volunteering or naturally invading Pennsylvania bituminous mine spoils. These studies found volunteer plant species such as poverty grass (*Danthonia* spp.), deertongue grass (*Panicum clandestinum*), dewberry (*Rubus flagellaris*) and fleeceflower (*Polygonum cuspidatum*) survived at mine spoil 3.3 pH and 17 ppm water soluble aluminum while goldenrod (*Solidago* spp.), and wild carrot (*Daucus carota*) did not survive at mine spoil 4.2 pH and 0.5 ppm water soluble aluminum (McKee, Raelson, Berti, and Peiffer, 1982).

Abandoned mine land may remain sparsely vegetated for several years. A study of 20 abandoned mine spoil banks (ranging from 2 to 35 years in age) in central Pennsylvania found extremely acidic spoils with a pH of 3.5 or less with no vegetation and some areas remaining barren or unvegetated after 20 years or more. The study also evaluated the rate of development of vegetative cover on the spoil banks and found spoil banks nearly barren of naturally invading vegetation until about 4 years old. Spoil banks 10 years of age or less did not exceed 50 percent vegetative cover with one bank 29 years of age having only 15 percent vegetative cover (Bramble and Ashley, 1955).

Where vegetation is sparse or nonexistent, the surface of the mine spoil may provide further indications

of the mine spoil chemistry. Extremely acid conditions can dissolve many minerals resulting in saline mine spoil conditions. "Greasy/wettish spots" on the mine spoil surface caused by the hygroscopic nature of free acid produced by pyrite oxidation are field indicators of acid saline conditions (Singh, Grube, Smith, and Keefer, 1982). White or yellowish coating or crusting on the mine spoil surface result from evaporated salts when evapotranspiration exceeds rainfall and salts migrate to the surface of the mine spoil. High salt concentrations in the mine spoil inhibit plant growth. The saline conditions increase the osmotic pressure that plants must overcome to extract moisture and render water unavailable to the plants. In addition, essential nutrients may be unavailable to plants under saline spoil conditions. Struthers and Vimmerstedt (1965) concluded that revegetation of mine spoil was generally more successful in the spring months as plant establishment and growth are improved by precipitation infiltrating the mine spoil and leaching the salts from the surface layer.

Plant Tolerance / Adaptability to Acid and Toxic Conditions

Species of plants vary widely in tolerance to acid and toxic conditions. Plant physiologists have found that only below pH of 3.0 are plants harmed directly by acidity alone (Arnon and Johnson, 1942). Indirect effects of acidity are the cause of limited plant growth under acid conditions above 3.0 pH. Indirect effects of acidity on plants result from increased solubility and availability of metals such as aluminum and manganese to plants under acid conditions. Aluminum and manganese are known to cause plant toxicity problems on acidic mine spoils.

Aluminum is a major growth limiting factor for plants in many acid soils below 5.0 pH and can be limiting at pH values as high as 5.5 (Foy, Chaney, and White, 1978). Concentrations of soluble aluminum that could be toxic to plants are found in mine spoils that have a pH of 5.5 or below (Berg and Vogel, 1973). Aluminum inhibits root growth and interferes with the uptake of phosphorus, an essential plant nutrient (Foy, Chaney, and White, 1978).

Manganese toxicity in plants is a problem in mine spoils below pH 5.5 where parent materials are high in total manganese (Foy, Chaney, and White, 1978). Decreasing soil pH as well as reducing soil aeration by compaction increases solubility and availability of manganese to plants (National Academy of Science, 1973).

The tolerance of plant species to acidic and toxic mine soil/spoil conditions varies between species and within species. Grasses such as deertongue grass (*Panicum clandestinum*) and switchgrass (*Panicum virgatum*) tolerate more acidic conditions than tall fescue (*Festuca arundinacea*) and perennial ryegrass (*Lolium perenne*) (Mckee and Harper, 1985). Kenland and Pennscott varieties of red clover (*Trifolium pratense*) are more adapted to acid mine spoil conditions than Chesapeake and Mammoth varieties of red clover (Bennett, Armiger, and Jones, 1976). Berg and Vogel (1973) reported sericea lespedeza (*Lespedeza cuneata*) usually had manganese toxicity symptons on mine spoils with 5.0 or lower pH while kobe lespedeza (*Lespedeza striata*), birdsfoot trefoil (*Lotus corniculatus*) and black locust (*Robinia pseudoacacia*) seldom developed manganese toxicity symptons on mine spoils above 4.4 pH. McCormick and Steiner (1978) reported hybrid poplar (*Populus maximowiczii* x *trichocarpa* clone NE-388) was very sensitive to low concentrations of aluminum while species of oak (*Quercus* spp.), pine (*Pinus* spp.) and birch (*Betula* spp.) were tolerant of much higher concentrations of aluminum. Tall fescue (*Festuca arundinancea*) is moderately tolerant of saline soils while red clover (*Trifolium pratense*) is relatively sensitive to salt conditions (USDA 1954).

Some Other Factors Affecting Establishment of Vegetation

Many factors in addition to chemical properties of mine spoil or overburden affect plant species establishment. Physical properties of the spoil or overburden, degree and aspect or direction of slope, and biological conditions are additional factors which may also affect plant species establishment. As an example, Hedin's (1988) studies of volunteer vegetation on 20 abandoned bituminous surface mines in northwestern Pennsylvania (varying in age from 12 to 41 years since abandonment) found sparsely vegetated spoils with few trees and the ground cover dominated by lichens (primarily *Cladonia*) and mosses (primarily *Polytrichum*). Chemicals produced by the lichens plant *Cladonia* have been shown to reduce tree seed germination and also to inhibit growth of mycorrhizae fungi that are important symbionts or companions of successful colonization and establishment of woody plants on acid spoils (Hedin 1988).

Topsoiling of Coal Mined Land

Removal of topsoil prior to mining and replacement of the topsoil as the final cover following coal mining is a requirement of state and federal coal mining laws and regulations. The removal and replacement of topsoil is one of the most beneficial methods for assuring establishment of vegetation (Grim and Hill, 1974). In addition to the benefits of topsoiling for improving vegetation success and restoring premining soil productivity, topsoil also serves to retain water or limit the movement of water; decreases the influx of atmospheric oxygen into the underlying mine spoil; and increases neutralization capacity. These effects of topsoiling on water movement, oxygen influx and developing alkalinity are beneficial for limiting the generation of acid mine drainage.

Topsoiling, Reclamation and Mine Hydrology

Topsoil affects the infiltration rate of water. Generally a final cover of topsoil on a mine backfill will have a significantly less infiltration rate of water than a final cover consisting of mine spoil. Rogowski's (1977) research on mine spoil from lower and middle Kittanning coal seams in central Pennsylvania found the infiltration rate of water into mine spoil to be much higher (i.e. greater than 189 cm/hr) than into mine spoil with a final cover of topsoil (i.e. less than 30 cm/hr).

Compaction of topsoil or other final cover material on a mine backfill could occur during reclamation activities resulting in slower rates of water infiltration. However, compaction of the final cover to reduce infiltration rates should be avoided because of the adverse affects on establishing and maintaining vegetation. Compacted soils impede plant root growth. Soil bulk density is commonly used as an index of compaction. In general, bulk densities suitable for plant growth range from 1.3 to 1.8 g/cm^3 (Rogowski and Weinrich, 1983; Pearson, 1965; and Bowen, 1981).

A final cover of topsoil on a mine backfill contributes towards reducing the influx of atmospheric oxygen and decreasing the oxygen concentrations within the underlying mine spoil. Rogwoski's (1977) research indicated oxygen concentrations within the mine spoil profile decreased when the mine spoil was covered with topsoil. The effects of topsoil on oxygen concentrations within underlying mine spoil becomes more significant considering that mine spoil is typically comprised of coarse rock fragments resulting in substantial pore or void space which provides pathways for oxygen transport. Pennsylvania mine spoils have been found to have from 40 to 60 percent coarse rock fragments (i.e. greater than 2 mm in diameter) in the upper portion of the mine spoil profile (Ciolkosz, Cunningham, Petersen, and Crone, 1979). A discussion of the role of oxygen in pyrite oxidation and generation of acid mine drainage is found in Chapter One.

Caruccio (1968) found in his work in evaluation factors affecting acid mine drainage that a soil cover plays an important role in preventing acid mine drainage. He concluded that the most critical factor determining the presence or absence of acid mine drainage is calcium carbonate. Caruccio also found soil cover to be extremely important in developing alkalinity as high carbon dioxide levels found in soil air contribute towards increasing neutralization capacity.

Conclusions

Replacing topsoil and establishing vegetation following mining are very important reclamation practices in the surface mining of coal. Abandoned coal mined lands may remain sparsely vegetated for several years when dependent upon naturally invading vegetation, especially where the top material is acidic or has high concentrations of aluminum or manganese. In addition to the benefits of topsoil for restoring premining soil productivity and of a good vegetative cover for controlling erosion and siltation, topsoil and vegetation aids in reducing water movement to the underlying mine spoil, decreasing oxygen concentrations, and increasing the capacity for carbonate dissolution. These effects on water movement, oxygen concentrations and neutralization capacity aid in reducing or preventing acid mine drainage.

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Chapter 13
ALKALINE ADDITION

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Introduction

It is widely recognized that mine sites with an abundance of naturally occurring limestone or alkaline strata produce alkaline water, even in the presence of high-sulfur strata. But many sites contain little or no alkaline materials and, as a consequence, often produce acidic drainage even when sulfur contents are relatively low. One approach to alkaline-deficient sites would be to import alkaline material and amend the spoil in order to obtain alkaline drainage.

This approach, although perfectly logical and reasonable, is deceptively simple. How much material needs to be added and how should it be applied to the backfill? When is additional alkaline material needed? What are the prospects of obtaining alkaline drainage for a given application rate and how much risk of acidic drainage can be tolerated? Ultimately, whether or not alkaline addition is a feasible alternative is driven by the economics of the operation. Therefore, it is important that an alkaline addition project be carefully evaluated and conceived before it is put into place. This chapter reviews the theoretical aspects of alkaline addition and empirical studies of alkaline-addition research, and summarizes the current state of the art in the use of alkaline addition to prevent acid mine drainage (AMD).

Theory of Alkaline Addition

AMD is formed when pyrite and other iron disulfide minerals present in coal and overburden are exposed to oxygen and water by mining. The oxidation of pyrite releases dissolved iron, hydrogen ions (acidity), and sulfates (Equation 13.1). Although this process occurs very slowly in undisturbed conditions, it can be greatly accelerated by both surface and underground mining.

$$2\ FeS_2 + 7\ O_2 + 2\ H_2O \rightarrow 2\ Fe^{2+} + 4\ SO_4^{2-} + 4\ H^+ \qquad (13.1)$$

The pyrite oxidation process is further accelerated by the iron-oxidizing bacterium *Thiobacillus ferrooxidans*, which thrives in a low-pH environment and oxidizes ferrous iron to ferric iron (Kleinmann et al., 1980) (Equation 13.2). Under low pH conditions, ferric iron remains in solution and can directly oxidize pyrite (Equation 13.3). Thus, once AMD formation gets started, decreasing the pH of the mine environment, the AMD reaction is further accelerated by bacteria and the production of ferric iron, resulting in severe acid mine drainage.

$$4\ Fe^{2+} + O_2 + 4\ H^+ \rightarrow 4\ Fe^{3+} + 2\ H_2O \qquad (13.2)$$

$$FeS_2 + 14\ Fe^{3+} + 8\ H_2O \rightarrow 15\ Fe^{2+} + 2\ SO_4^{2-} + 16\ H^+ \qquad (13.3)$$

Acidity produced by acid mine drainage can be neutralized in the presence of sufficient carbonate minerals. This reaction is shown by Equation 13.4, for which it is assumed that CO_2 will be produced and will exsolve from solution. Using this equation, it takes 31.25 tons of $CaCO_3$ to neutralize 1000 tons of material with 1% sulfur. This is the traditional method used for acid-base accounting calculations. The main shortcoming of this equation is that there is no "alkalinity" (bicarbonate or HCO_3^-) produced. Under normal conditions not all CO_2 escapes to the atmosphere. Some of it dissolves in water and produces acidity. If the reaction product is HCO_3^- (Equation 13.5), twice as much carbonate will be required to neutralize the same amount of material (Cravotta and others, 1990). Both processes occur. Which one is dominant depends on how open or closed the atmospheric system of the mine site is, which is not readily determined.

$$FeS_2 + 2CaCO_3 + 3.75\ O_2 + 1.5\ H_2O \rightarrow Fe(OH)_3 + 2SO_4^{2-} + 2\ Ca^{2+} + 2\ CO_{2(g)} \qquad (13.4)$$

$$FeS_2 + 4CaCO_3 + 3.75\ O_2 + 3.5\ H_2O \rightarrow Fe(OH)_3 + 2SO_4^{2-} + 4Ca^{2+} + 4HCO_3^- \qquad (13.5)$$

Where neutralization is occurring, the pH can remain at a near-neutral value which inhibits bacterial catalysis of iron oxidation and where ferric iron is relatively insoluble. Thus, the quality of drainage produced by a given mine is largely dependent not only on the presence or absence of pyritic sulfur, but also the availability of calcium carbonate or other neutralizing agents in the coal and overburden.

Brady et al. (1994) and diPretoro and Rauch (1988) found a strong empirical relationship between the neutralization potential (NP) of surface coal mine overburden and whether or not the postmining drainage would be alkaline or neutral. Sites with more than 3% naturally occurring carbonates produced alkaline drainage. Sites with less than 1% carbonate generally produced acidic drainage. Perry and Brady (1995) attribute this effect not only to neutralization but also to the limitation of ferrous iron oxidation by bacterial catalysis and direct oxidation of pyrite by ferric iron. Both of these processes are inhibited in the near-neutral pH environment created by the presence of sufficient carbonate.

The role of carbonate is so important in acid mine drainage formation, that NP was found to be a much better predictor of whether a mine would produce alkaline or acidic water than was the maximum potential acidity (MPA), calculated from the overburden sulfur content (Brady and Hornberger, 1990, Brady et al., 1994, Perry and Brady 1995). diPretoro (1986) found net neutralization potential and NP to be useable predictors of drainage quality, while MPA was again shown to be an unreliable predictor. Net neutralization potential (NNP) is defined as NP - MPA. For mines which are naturally deficient in carbonates, and therefore likely producers of acidic drainage, the implication is obvious. If sufficient alkaline material is imported from off-site to make up the deficiency in NP, the site would produce alkaline rather than acidic drainage.

The solubility of calcium carbonate also plays an important role in whether a site can generate sufficient neutralization to prevent acidic drainage. Calcite ($CaCO_3$) solubility is dependent on the partial pressure of CO_2 (Figure 13.1). At atmospheric conditions, the solubility of calcite is limited to approximately 20 mg/L Ca (50 mg/L as $CaCO_3$ or 61 mg/L as HCO_3^- alkalinity) assuming a CO_2 content of only 0.03%. At 20% CO_2 content, which has been measured in some backfill environments (Cravotta, et al, 1994), calcite solubility exceeds 200 mg/L Ca (500 mg/L as $CaCO_3$ or 610 mg/L as HCO_3^- alkalinity). Guo and Cravotta (1996) note that CO_2 partial pressures vary from mine site to mine site depending on the rock type and the configuration of the backfill. Shallow backfills on steep slopes with blocky overburden and thin soil cover, for example, tend to "breathe", thereby reducing CO_2 partial pressures. Deeply buried backfills or sites with restricted airflow or thick soil covers would tend to have higher CO_2 levels, enhancing calcite dissolution. Calcite solubility also has implications for the placement of alkaline materials within the backfill. Near-surface placement of alkaline material, where CO_2 partial pressures approach atmospheric conditions, may not be as desirable as distribution within the backfill.

In theory, almost any acid-prone site could be transformed into an alkaline site if only enough carbonate material were imported. In actual practice, however, it becomes necessary to determine: (1) how much alkaline material needs to be applied to ensure a successful result; and (2) how and where within the backfill should the alkaline material be applied. Additionally, ensuring that a site produces alkaline water does not necessarily guarantee that effluent limitations for metals will be met.

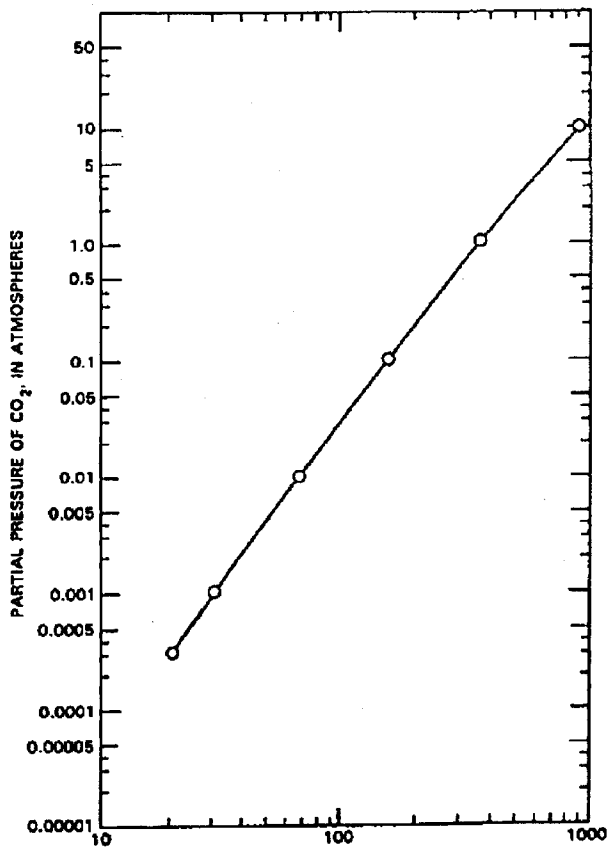

Figure 13.1 Solubility of calcium carbonate (calcite) in water at 25°C as a function of partial pressure of CO_2. From Hem (1985).

Alkaline Addition Studies

The earliest published report regarding the use of imported alkaline material as a method of preventing

the formation of acidic drainage was in the West Virginia Surface Mine Drainage Task Force's guidelines for surface mining in potentially acid-producing areas (1979). It recommended that alkaline material be added to the backfill at the rate of one third of any net deficiency in neutralization potential as determined by acid-base accounting. No specific rationale or empirical evidence was given as to why this rate was selected. Many sites with alkaline application rates based on this recommendation have subsequently failed and are producing acidic drainage.

Waddell and others (1980) used alkaline addition to abate acidic drainage resulting from the construction of Interstate 80 in northcentral Pennsylvania, which disturbed acid-prone overburden. The Waddell study involved a surface application of limestone crusher waste and lime flue dust at the rate of 267 ton/ac (600 t/ha). It improved pH values from 3.9 to 4.4. Sulfate concentrations were also reduced, indicating that the alkaline addition not only neutralized AMD, but slowed its production.

Geidel and Caruccio (1984) examined the selective placement of high-sulfur material in combination with the application of limestone to the pit floor at the rate of 39 tons per acre (87 t/ha). Although the treated site initially produced alkaline drainage, it shortly became acidic. An untreated control site produced acidic drainage throughout the period.

Attempting to abate acidic drainage from a Clarion County, Pennsylvania mine site, Lusardi and Erickson (1985) applied high-calcium crushed limestone at the rate of 120 ton/ac (269 t/ha). Although NNP deficiencies at the site ranged from 25 to 590 ton/ac (56 to 1320 t/ha), they assumed that most acid production occurred near the surface and that it may only be necessary to add enough limestone to balance the NP deficiency in the upper two meters of spoil. The limestone was disked into the upper 1.0 ft (0.3 m) of the spoil surface. One year after the application, no substantial neutralization or inhibition of acid formation was noted.

O'Hagan and Caruccio (1986) used leaching columns to examine the effect of varying rates of limestone application on alkaline and non-alkaline shales. A sulfur-bearing (1.07%) non-calcareous shale produced acidic drainage with no added limestone, mixed neutral / slightly acidic drainage with 1 to 2% admixed limestone, and alkaline drainage with 3% or greater admixed limestone. Later, following longer periods of leaching, the shale with 1 to 2% limestone produced consistently acidic drainage. The alkaline shale produced alkaline drainage regardless of whether or not any limestone was added.

By 1990, there were enough well-documented surface mining operations that had employed alkaline addition to allow an extensive empirical review of the effectiveness of alkaline addition in preventing or ameliorating acid mine drainage. Brady and others (1990) examined 10 Pennsylvania mine sites. Of these 10 sites, 8 employed alkaline addition as a means of preventing postmining AMD. Six of the eight alkaline-addition plans failed to prevent AMD. The sites which were successful in preventing or at least ameliorating AMD had several things in common: (1) alkaline addition rates were among the highest (500 to 648 ton/ac or 1120 to 1450 t/ha) and exceeded permit requirements, (2) pyritic materials were selectively handled, (3) backfilling was timely, and (4) some potentially acid-forming materials were removed from the mine site. The study concluded that most unsuccessful attempts at alkaline addition were too conservative in terms of the application rate, particularly the practice of applying one-third the calculated deficiency. Further, alkaline addition is most effective where incorporated into the backfill, concurrently with mining and reclamation and when done in conjunction with other best management practices.

Although not directly related to alkaline addition, a subsequent study of the use of acid-base accounting (ABA) for predicting surface coal mine drainage quality (Brady et al., 1994) showed a strong empirical relationship between the presence of neutralizing minerals in the overburden (generally carbonates) and the alkalinity of postmining discharges. Critical values of NP and NNP were identified. Mines with NP values greater than about 15 ppt and NNP greater than 10 ppt $CaCO_3$ had net alkaline drainage. Sulfur content alone was not a reliable predictor of postmining water quality except where calcareous strata were absent. The implication for alkaline addition is clear. If it is assumed that imported alkaline material behaves no differently than native alkaline strata, the application of alkaline material at a rate which simulates a naturally alkaline site should assure alkaline postmining water quality.

Skousen and Larew (1995) studied the economics of an alkaline addition project which imported alkaline shale from a nearby mining operation to an operation which was deficient in neutralizers. Significantly, for this discussion, the alkaline addition project successfully prevented AMD. Although the deficiency calcu-

lated from ABA data was equivalent to a one-foot thick layer of the alkaline shale, 3 to 4 ft of shale was actually imported.

Perry and Brady (1995) found that overall NP values in excess of 21 ppt $CaCO_3$ and NNP values greater than 12 ppt $CaCO_3$ would produce net alkaline water. Overall NP and NNP values less than 10 ppt $CaCO_3$ and 0 ppt $CaCO_3$, respectively, produced net acidic water. Variable water quality was found for NP and NNP levels between these limits. The same data were examined using significance thresholds. Sulfur contents less than 0.5% and NP values less than 30 ppt $CaCO_3$ for individual strata were considered to be insignificant producers of acidity or alkalinity, hence, values which do not exceed these thresholds are assigned a value of zero for the NP and NNP calculations. Applying the threshold concept, overall (representing the entire volume of overburden to be mined) NP and NNP values greater than 10 ppt and 5 ppt $CaCO_3$, respectively, produced consistently alkaline water. NP and NNP values less than 1 ppt and -5 ppt $CaCO_3$, respectively, produced consistently acidic drainage. Noting decreased sulfate concentrations with increasing NP, they concluded that the presence of carbonate minerals in amounts as low as 1 to 3 % (10 to 30 ppt of NP) inhibit pyrite oxidation. Moreover, maintenance of alkaline conditions created by carbonate dissolution are not conducive to bacterial catalysis or ferrous iron oxidation and greatly limits the activity of dissolved ferric iron, interrupting the self-propagating acid cycle (Equation 13.3).

Rose et al. (1995) reported the results from an ongoing alkaline addition demonstration project in Clearfield County, Pennsylvania which indicated positive but preliminary results. More recent data from monitoring wells in the backfill show mixed results. Baghouse lime, a waste product from lime production, was applied at rates ranging from 150 to 1,080 ton/ac (336 to 2420 t/ha), adjusted to 100% $CaCO_3$ content, based on ABA calculations using significance thresholds and making up any deficiencies in NP. Areas with the highest alkaline addition rate (and the most acidic overburden) were successful in producing alkaline drainage with low concentrations of dissolved iron and manganese (Figures 13.2a through 13.2d). Backfill wells in areas which received lower alkaline addition rates showed both alkaline and acidic water and relatively high levels of dissolved iron and manganese. Post-reclamation sulfate levels of 300 to 800 mg/L in all of the monitoring wells indicate that AMD is being produced but neutralized.

Based on the experience from the Rose et al. (1995) study site, it is probably unrealistic to precisely adjust alkaline addition rates based on minor overburden quality variations between drill holes. Unless there is a corresponding change in stratigraphy, alkaline addition rates should reflect aggregate (average) overburden quality.

Evans and Rose (1995) also reported the results of alkaline addition to large test cells constructed solely of high-sulfur overburden on the Kauffman site. Cells were constructed of material with 2% pyritic sulfur and mixed with different rates of alkaline material. Although alkaline addition reduced the generation of acidity by as much as 96%, even the highest alkaline addition rate, equivalent to 3.4% $CaCO_3$, was insufficient to prevent AMD formation. Two important considerations were suggested by this study. First, the high-sulfur overburden was exposed to weathering for a considerable time period before construction of the cell and application of alkaline material. The test cells remained exposed without a soil cover for an extended time period thereafter. More rapid application of alkaline material and timely covering may have reduced the likelihood of AMD formation. In other words, once AMD generation starts, it is much more difficult to slow its formation than to keep it controlled in the first place. Second, because complete mixing of alkaline material may be difficult or impossible to achieve, microenvironments within the spoil can still allow acid production and bacterial activity. AMD formation in very high-sulfur mine sites or areas of concentrated high-sulfur refuse, represented by the concentration of highly pyritic material in the cells, may be impossible to ameliorate using alkaline addition rates which have otherwise been successful in mines with more typical sulfur values.

Smith and Dodge (1995) reported on an alkaline addition site in Lycoming County, PA, which was part of the original Brady et al. (1990) study. Alkaline addition rates of 600 ton/ac (1,350 t/ha) and daylighting of an underground mine resulted in dramatic improvements in water quality from the underground mine discharge (Figure 13.3). Pre-mining net acidity values exceeded 100 mg/L. After remining, the discharge was predominately alkaline. Increased sulfate concentrations indicated that the water quality could be attributed to neutralization by imported alkaline material

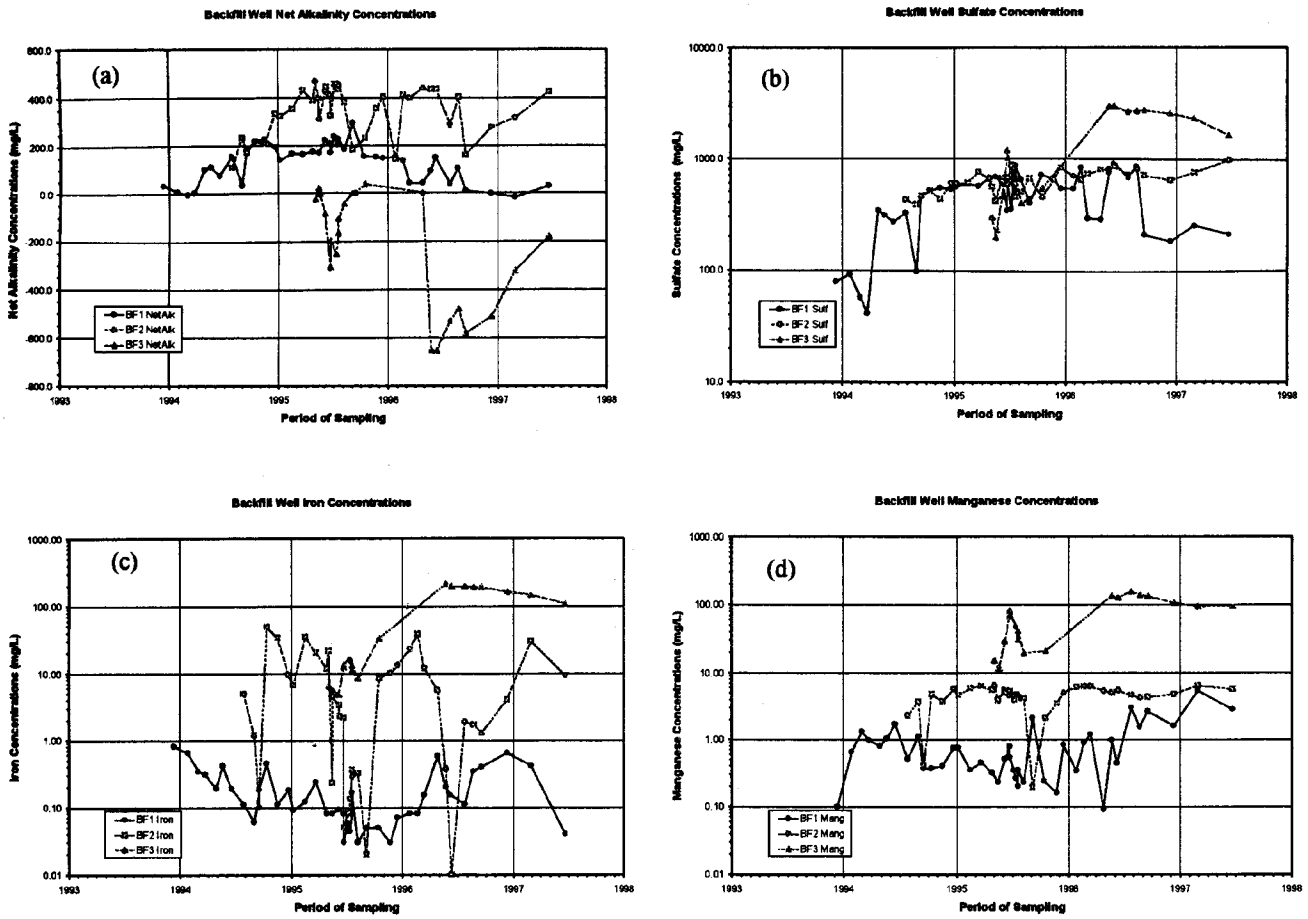

Figure 3.2 Water quality from backfill wells in the Kauffman demonstration surface mine, Clearfield County, PA showing postmining net alkalinity (a), sulfate (b), iron (c), and manganese (d). Well BF1 is located in the area with the highest alkaline addition rate; well BF3 represents the area with the lowest alkaline addition rate; and well BF2 is located near the boundary between the high and low application rate areas.

rather than daylighting. No naturally occurring alkaline material was present. This operation is one of the oldest successful alkaline addition sites. It has exhibited improved water quality since the onset of large-scale alkaline addition in 1986 and produced predominately alkaline water since 1989, suggesting that the impact of alkaline addition will be long-term or permanent.

Most of the published research in alkaline addition has taken place in northern Appalachian states. An exception is the work done by Wiram and Naumann (1996) on an AMD-producing surface mine in Sequatchie County, Tennessee. Alkaline addition was employed as the principal component of a toxic materials handling plan that also included selective overburden placement, and the construction of chimney drains and alkaline recharge basins. Alkaline addition rates were determined for individual stratigraphic intervals having a NNP less than -5, however, a modified NP test was used in order to exclude the apparent NP contribution from siderite ($FeCO_3$). Previous overburden analysis results erroneously predicted alkaline drainage due to the presence of siderite which falsely indicated the presence of significant alkaline strata. The role that siderite plays in mine drainage and acid-base accounting are explained by Skousen and others (1997) and discussed in Chapters 1 and 6 of this report. Limestone application rates for each of these intervals were summed to determine the application rate for the area around each bore hole. Net neutral zones were not factored into the alkaline addition calculations.

The results of the Wiram and Naumann study were favorable. Monitoring wells on the site, which initially produced acidic drainage with excessive iron and manganese, showed marked increases in alkalinity and decreased concentrations of acidity, iron, and manganese.

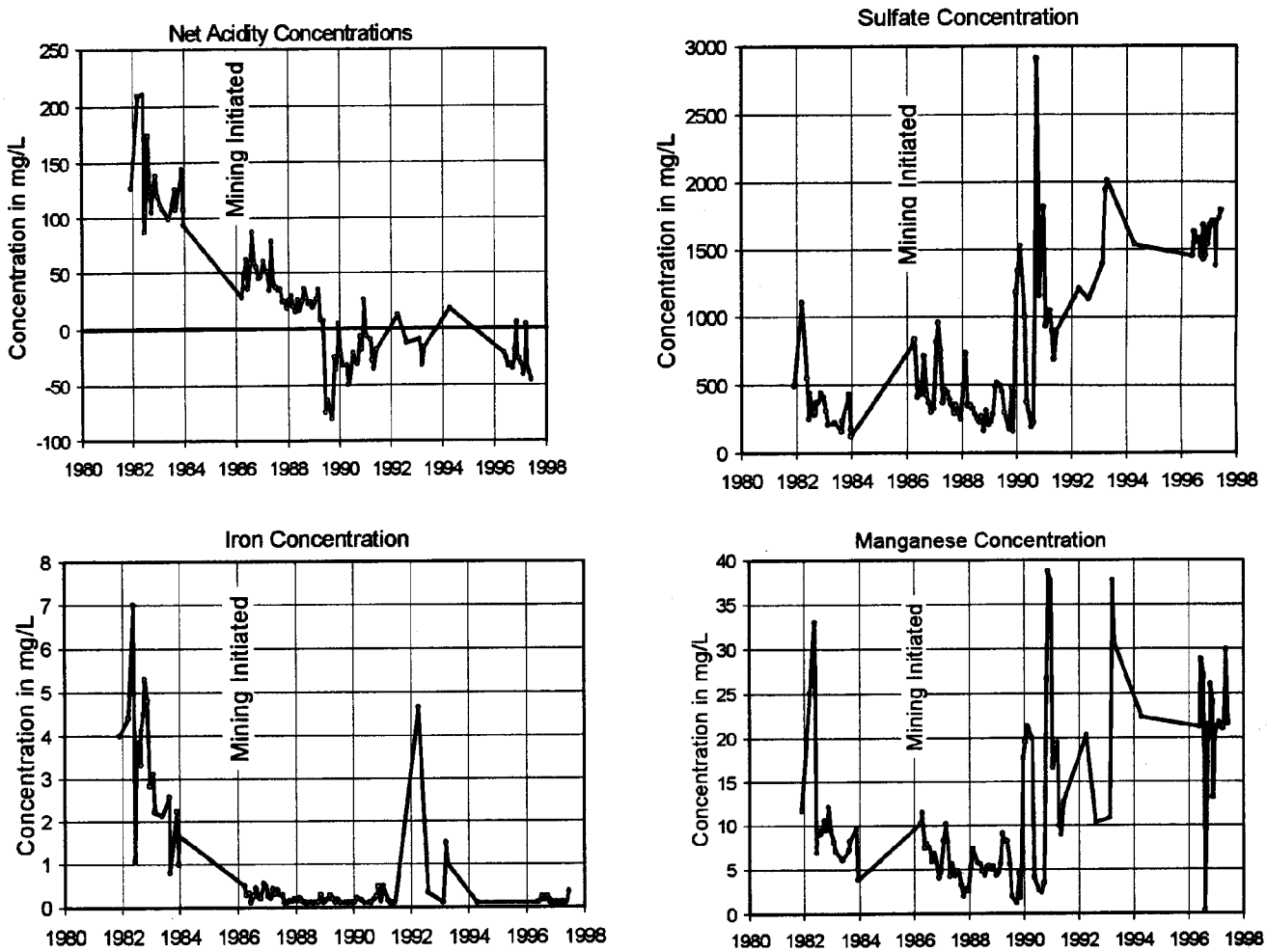

Figure 13.3 Changes in water quality at the Fisher Mining M-1 discharge showing the effects of alkaline addition done in conjunction with daylighting of a deep mine. Updated from Smith and Dodge (1995).

Alkaline Addition Practices

Fifteen years of research into alkaline addition has shown that it can improve water quality and prevent AMD production, but that failures are common, especially where alkaline addition rates are too low. Based on these studies, any alkaline addition project should consider: (1) How much alkaline material and what type of material should be applied? (2) How should the alkaline material be emplaced in the backfill? and (3) Where is it appropriate to use alkaline addition?

Application Rates

Field studies of alkaline addition appear to be converging on a required application rate sufficient to achieve approximately 1.5 to 3% $CaCO_3$ equivalent in order to effectively prevent acidic drainage from typical surface mines with low to moderate pyrite content. This application rate appears deceptively low. One percent $CaCO_3$ equates to approximately 37 tons of $CaCO_3$ (33,600 kg) for each acre-foot of overburden. A 100-acre (40.5 hectare) surface mine with an average overburden thickness of 50 feet (15.2 m) needing 1% additional $CaCO_3$ would require 183,500 tons (166,500 tonnes) of added alkaline material or 1,835 ton/ac (4110 t/ha). So the feasibility of an alkaline addition project usually becomes a matter of economics as well as science. The challenge is to determine the minimum alkaline addition rate which will still be effective in preventing acidic drainage.

Using data from Brady et al. (1994) and Perry and Brady (1995), Tables 13.1a - 13.1d show overall NP and NNP requirements in order to produce alkaline drainage using acid-base accounting data. In all cases, NP and NNP calculations are made using the method

described by Smith and Brady (1990). Total weights of overburden, NP and MPA are determined for each sampled interval based on an approximation of the areal extent of that interval and unit weights for overburden materials. Coal intervals are multiplied by a pit loss factor of 0.1, assuming approximately 10% will be lost in the pit and not removed. A higher or lower pit loss factor can be used if warranted by site-specific conditions. The uppermost 0.5 ft (0.15 m) of strata underlying the bottom coal seam is also included in the calculation. These quantities are summed to determine the total tonnage of overburden, NP, MPA and to represent the overall NP, MPA and NNP in parts per thousand as $CaCO_3$ for the site. Multiple overburden holes are combined by considering an area of influence of each hole using the Theissen polygon method.

Table 13.1a Percentage of Sites Producing Net Alkaline Drainage by Net NP without thresholds

Net NP (ppt $CaCO_3$)	number of sites (n)	% with net alkaline drainage
< -10	1	0.0%
-10 to 0	11	18.2%
0 to 12	17	58.8%
>12	10	100.0%

Table 13.1b Percentage of Sites Producing Net Alkaline Drainage by Total NP without thresholds

Total NP (ppt $CaCO_3$)	number of sites (n)	% with net alkaline drainage
< 5	3	0.0%
5 to 10	9	33.3%
10 to 18	10	50.0%
18 to 22	7	71.4%
>22	10	100.0%

Table 13.1c Percentage of Sites Producing Net Alkaline Drainage by Net NP with thresholds

Net NP (ppt $CaCO_3$)	number of sites (n)	% with net alkaline drainage
< -2	14	28.6%
-2 to 6	14	57.1%
>6	11	100.0%

Table 13.1d Percentage of Sites Producing Net Alkaline Drainage by Total NP with thresholds

Total NP (ppt $CaCO_3$)	number of sites (n)	% with net alkaline drainage
< 2	12	16.7%
2 to 9	12	50.0%
>9	15	100.0%

When all ABA data are considered (i.e., there are no significance thresholds), an overall NNP greater than 12 ppt $CaCO_3$ or a NP greater than 22 ppt $CaCO_3$ is very likely to assure alkaline drainage (Table 13.1). Based on these data, a conservative approach to determining alkaline addition rates would require application of alkaline material at a rate equal to the difference between an overall NNP of 12 ppt $CaCO_3$ or a NP of 22 ppt $CaCO_3$ and the actual premining overall NP or NNP. A site having a NNP of 2 ppt $CaCO_3$, for example, would require the application of an additional 1% $CaCO_3$. An example calculation is shown below:

Tons of overburden: 1,000,000 (907,200 tonnes)

Acres of mining: 20 (8.1 hectares)

Average Net NP: 2 ppt $CaCO_3$

Deficiency: (12 - 2) ppt $CaCO_3$ =
10 ppt $CaCO_3$ = 1%

Tons additional NP required for Net NP of 12:
1% X 1,000,000 tons overburden =
10,000 tons (9,072 tonnes)

Tons per acre required: 10,000 tons / 20 acres =
500 ton/ac (1,120 t/ha)

Adjusted for alkaline material with 80% $CaCO_3$ equivalent: 500 tons/acre / 80% = 625 ton/ac (1,200 t/ha)

Similarly, where significance thresholds are used to analyze ABA data, a "safe" alkaline addition rate would bring the overall NP value above 9 ppt $CaCO_3$ or the NNP above 6 ppt $CaCO_3$. Traditionally, DEP has required most alkaline addition sites to produce an overall NNP of 0 ppt $CaCO_3$ with thresholds. The success rate for sites with this application rate, all other factors being equal, is risky at best with only 59% of the study sites in this class producing alkaline drainage. To a great extent, the selection of the appropriate alkaline addition rate is determined by the risk of failure that can be tolerated, as well as the availability and cost of alkaline additives.

The summary in Table 13,1 is based on a limited number of observations and only separates overburden quality into broad categories. Until more alkaline-addition sites are studied, it may be premature to rigidly apply it to a wide variety of geologic and geographic settings. As more data are compiled, our ability to accurately determine the minimum alkaline addition rate needed to obtain alkaline drainage should improve. Also, based on the limited experience to date with alkaline addition sites, most alkaline addition projects using more than 500 ton/ac (1,120 t/ha) as

$CaCO_3$ have been successful. Except for alkaline addition projects on mines with very low sulfur, projects using less than 500 ton/ac (1,120 t/ha) have consistently failed to produce alkaline drainage. This is based on a very small population of alkaline addition sites and almost no sites having the very worst overburden characteristics. At this point, it would be premature to conclude that alkaline addition of more than 500 ton/ac (1,120 t/ha) will ensure success on all sites or that lower rates guarantee failure.

Materials Handling and Placement

Most successful alkaline addition sites have employed thorough mixing of alkaline material throughout the backfill. This can be done using various methods. One innovative and effective approach is to use the alkaline material as blast hole stemming (Smith and Dodge, 1995). Depending on the material being used and how well it packs, it may also result in more effectively directing the blast energy at breaking overburden. Alternately, alkaline material can be placed on the surface of the overburden where it will be subsequently redistributed following excavation and placement.

Another method of alkaline addition is to place it on the regraded spoil surface and disk it into the upper portion of the spoil. This approach is usually used either in combination with mixing in the backfill or as a remedial measure after the site has already been backfilled. Although it was originally thought that this method would take advantage of the added alkalinity in the most active zone of AMD production and create an alkaline environment, inhibiting AMD formation, most projects employing only surface application have not been successful. There are at least two possible explanations: (1) Dissolution of $CaCO_3$ and the production of alkalinity at near surface conditions is limited by the partial pressure of CO_2. Typically, the maximum alkalinity which can be achieved under thin soil cover is approximately 75 to 150 mg/L, (Rose and Cravotta, this report, Figure 1.1). This greatly limits the effectiveness of near-surface alkaline material and usually does not produce enough alkalinity to neutralize acidity generated elsewhere in the backfill. (2) Mine spoils do not transmit water as a uniform wetting front (Caruccio and Geidel, 1989). Rather, surface waters tend to preferentially infiltrate the spoils at the most conductive areas, effectively bypassing much of the near-surface alkaline material. (3) Contact of limestone with acid-producing materials is very limited in the surface environment.

The earliest alkaline addition projects spread all of the alkaline material on the pit floor, prior to backfilling, reasoning that this portion of backfill was the most likely to be saturated, allowing the alkaline material to neutralize all of the acidity produced. These sites tended to produce alkaline drainage initially, which soon changed to acidic drainage. This is presumably because the pit floor environment was not anoxic and the alkaline material became ineffective due to armoring with ferric hydroxide precipitate. Alkaline addition to the pit floor still has utility, however, when there is a need to neutralize a high-sulfur pit floor. If the pit floor was saturated, however, and iron remained ferrous, calcite on the pit floor should function like an anoxic drain neutralizing acidity. Nonetheless, the key appears to be to get the alkaline material mixed throughout the spoil and especially with the more pyritic material. Putting most of the material on the pit floor fails to take advantage of the inhibitory effect of maintaining a near-neutral pH within the spoil environment. There probably is little utility in application rates of more than 100 ton/ac (224 t/ha) to the pit floor, although at least 20 ton/ac (4.5 t/ha) should be applied to provide complete coverage.

Alkaline addition is frequently done in conjunction with special handling of high-sulfur zones, where high sulfur material is placed in pods and isolated from percolating ground waters. Alkaline material can be admixed with the high sulfur material to prevent AMD formation within the pod and it can be placed in conjunction with a cap to enhance hydraulic isolation and to help maintain an alkaline environment near the pod. Observations at the Kauffman project suggest that lime kiln dust may actually cement the material and inhibit flow through it (Rose et. al., 1995).

Recommended procedures for the handling of imported alkaline materials have undergone an evolutionary process as more is learned about AMD prevention and the interaction between acid-forming materials and neutralizing agents. Currently, the recommended procedure is to first ensure that enough alkaline material is thoroughly mixed within the backfill. Smaller amounts of imported alkaline material should be applied to the surface of the regraded backfill. Applications to the pit floor should be limited to circumstances which require isolation or neutralization of a high-sulfur pavement, and then no more than is needed to provide sufficient coverage. The use of alkaline addition as part of special materials handling has not yet been fully evaluated although some demonstration projects are underway.

Unless the remaining spoil is clearly alkaline, sufficient alkaline material should also be retained for distribution throughout the backfill.

Alkaline Materials and Verification

Although many different sources of alkaline materials may be available, most alkaline addition projects have used crushed limestone or a limestone-based waste product. Provided that the product grain size is small, the chief factor in determining its required application rate, relative to other alkaline materials, is its neutralization potential, expressed in calcium carbonate equivalence. Twice as much material with 50% $CaCO_3$ equivalent NP would be required, for example, in place of pure $CaCO_3$. Typical alkaline materials which are useful as alkaline additives include kiln dust, crushed limestone, limestone crusher waste, partially burnt lime, off-spec lime products, and fluidized bed combustion ash. Regardless of the alkaline material to be used, the application rate should be adjusted to reflect its neutralization potential as calcium carbonate equivalent. It is also necessary to periodically retest the neutralization potential of the alkaline material being used, with a frequency determined by the variability of the material.

A critical step in a successful alkaline addition project is to insure that the alkaline addition plan is properly carried out - both the amount of material to be applied and its distribution throughout the site. Because of the large quantities of materials involved, this requires careful record-keeping of each shipment of alkaline material and calculation of the quantities of material distributed. Depending on the method of mining, quantities of alkaline material distributed should be tabulated for each individual cut or phase of the operation.

Alkaline Redistribution

A practice similar to alkaline addition is the redistribution of alkaline materials to alkaline-deficient areas from areas of the same or adjacent mine sites which have more than ample alkaline strata. This procedure is practical where sufficient quantities of alkaline material are present, but their distribution is so uneven that some portions of the backfill will not receive enough neutralizers to prevent or neutralize AMD. Alkaline redistribution then becomes largely an exercise in materials handling. Alkaline stratigraphic units must be clearly identified in the field, segregated, transported to the alkaline-deficient area, and incorporated into the backfill. Depending on the quantity of alkaline material available and its characteristics, it may also be necessary to crush the material prior to redistribution. The obvious advantage to redistribution, if it can be done, is the ready availability of the material and the low or zero cost of transportation.

Michaud (1995) developed a mining plan for a proposed surface mine where alkaline redistribution was fully integrated into the operation, minimizing the need for stockpiling and rehandling of alkaline overburden. Through the implementation of a complex series of selective sequencing of cuts and multiple benches, the handling plan provided for redistribution of alkaline strata, which exists only in limited areas of the operation and in certain stratigraphic intervals, throughout the site. Through this approach, thorough mixing of alkaline material could be achieved while avoiding the need to field-identify, segregate, and redistribute specific geologic units, usually the most difficult part of a spoil redistribution plan.

Alkaline redistribution has been successfully employed on several surface mining sites, which are currently producing alkaline drainage. The Bridgeview "Morrison" site in Township, Fayette County, PA had abundant calcareous rock over most of the site with NP's as high as 700 ppt $CaCO_3$, but more typically in the 100 to 300 ppt $CaCO_3$ range. There were two areas of about 5 ac (2 ha) each which were of low cover and the calcareous rock was missing due to erosion and weathering. Alkaline material from the high cover area was transported to these low cover areas. Postmining water quality from the lobes is alkaline.

The Amerikohl "Schott" site in Westmoreland County had calcareous rock on only about 8 ac (3 ha) of the 38 ac (15 ha) site. Originally four acid-base accounting holes were drilled. These were supplemented by additional holes that were drilled to determine the lateral distribution of the calcareous rock. The calcareous rock was concurrently mined with other phases of mining and incorporated into the spoil on all portions of the mine. Waste limestone was also placed on the pit floor at the rate of 100 ton/ac (44.6 t/ha). Four years of postmining water quality monitoring shows the water to be net alkaline with alkalinity ranging from 10 mg/L to 138 mg/L (Eric Perry, personal communication, 1997). More details are available on this mine in Perry et al. (1997).

Alkaline Addition as a Best Management Practice on Low Cover Overburden

In many cases, relatively low (less than 300 ton/ac (670 t/ha)) alkaline addition rates have been employed on mine sites which indicated a relatively minor potential to produce acid mine drainage but were lacking in any significant calcareous strata. Although these sites commonly have correspondingly low sulfur contents, they frequently produce mildly acidic drainage due the lack of any significant NP. In other cases, alkaline addition was used as an added safety factor to assure alkaline drainage. Alkaline addition has proven to be an effective "best management practice" for these types of sites.

Often, mine sites with shallow (less than 40 feet (12 m)) overburden have had calcareous minerals and pyrite leached out by weathering (Brady et al., 1988). Since easily weatherable minerals have been removed, water flowing through the overburden material picks up very little dissolved solids and emerges essentially with the characteristics of rain water. In Pennsylvania, rain water does not meet effluent limits because it has a pH less than 6.0. Thus, postmining water from weathered overburden may also have a pH of 6.0 or less. The addition of alkaline material is needed to ensure alkaline postmining drainage.

Although this scenario seems logical, and general observations over the years suggest this is true, actual mine sites having adequate acid-base accounting data, water quality monitoring, and records of mining practices (including alkaline addition rates and placement of materials) are difficult to find. One such site, however, is located in West Keating Township, Clinton County. The area had been previously mined on a rider seam 10 ft (3 m) above the main bench of the middle Kittanning (MK) coal. The mined area was not reclaimed. The recent operation mined the MK coal and reclaimed the previously mined area. The total area affected by MK coal removal was 11.5 ac (4.6 hectares) and the maximum highwall height (including old spoil) was about 20 ft (6.1 m). Overburden analysis was performed on five drill holes, but only sulfur was determined. The deepest hole was 18 ft (5.5 m) to the bottom of the coal and shallowest was only 5 ft (1.5 m). The rock between the rider coal and the MK was described as "soft brown shale," indicating weathering. The coal had the highest sulfur of any of the rock encountered, ranging from 0.28 to 0.50%. Sulfur in the rest of the overburden was 0.13% or less. No NP's were determined, but it is near certainty, based on experience with other low cover sites, that calcareous minerals were not present.

Mining began in January, 1988 and was "completed" by the end of March, 1988. It is known that some alkaline material was added during mining, but we have not been able to determine the amount. A permit condition required 10 ton/ac (22 t/ha) of limestone on the pit floor, and there would have been another 5 to 10 ton/ac (11 to 22 t/ha) of limestone added to the reclaimed surface for revegetation purposes. It is suspected that the above amounts are minimums, and the actual amount added was probably several times greater.

A downgradient discharge from an unreclaimed pit, monitoring point K1, was monitored before and after mining. Following mining, the location of the discharge moved down hill to the lower seam that was mined. It is unclear why this point was not monitored during mining although it may have gone dry. Figures 13.4a through 13.4c show water quality through time for pH, net alkalinity, and sulfate. Water quality improved following mining. Because the overburden contained virtually no source of alkalinity other than what was imported, the increase in alkalinity would not have been possible without the importation of limestone. The added material has been adequate to maintain net alkaline conditions from 1990 to when it was last sampled in 1994. The sulfate concentrations, mostly less than 40 mg/L, confirm that there was little pyrite available for oxidation. These concentrations are typical of premining sulfate within the Appalachian Plateau (Brady et al., 1996). Iron and manganese data are difficult to interpret because the samples were unfiltered and many samples have elevated suspended solids.

It would have been helpful to know exactly how much alkaline material was added to this site. Comparatively small amounts (perhaps around 40 ton/ac (90 t/ha)) may have been sufficient on this site because of the small amount of overburden present and its highly weathered nature. This site illustrates that a surface mine with weathered overburden, lacking pyrite, can produce alkaline drainage with a minimal quantity of alkaline material added as a "safety factor." Without the addition of alkaline material, there would have been little or no alkalinity produced.

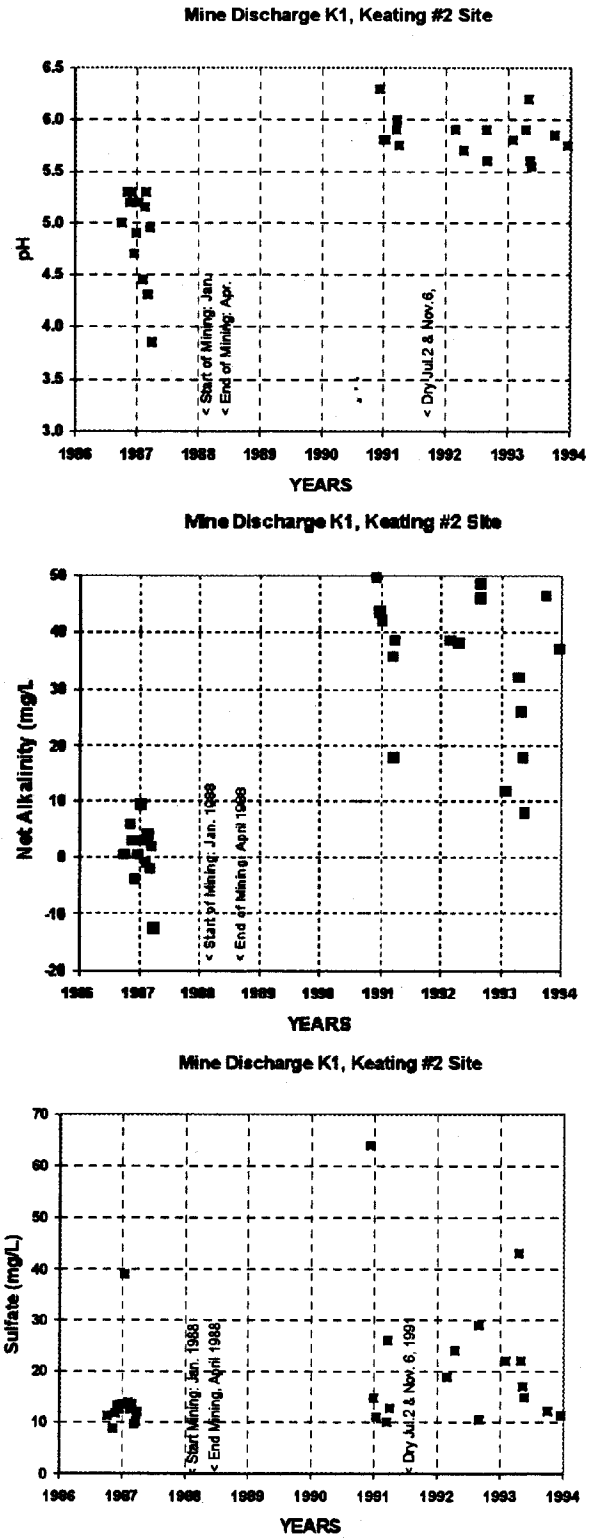

Figure 13.4 Water quality before and after mining at the Keating #2 Site, Clinton County, Pennsylvania where alkaline material was applied to the pit floor at a relatively low rate as a best management practice.

Cost Comparison

The practicality of alkaline addition, as a means of preventing AMD formation, depends largely on economics - how much alkaline material is needed, the cost of the alkaline material, transportation costs, and the added cost of incorporating the alkaline material into the backfill. These costs can vary widely from site to site. In many cases these costs can determine whether or not a site can be mined. But assuming that a site could be permitted for mining with or without alkaline addition, it is also useful to examine the costs which would be avoided if alkaline addition were used in lieu of treatment of a long-term discharge of acid mine drainage. In order to perform this analysis, several assumptions must be made about the expected postmining drainage quantity and quality, with and without alkaline addition. Costs can then be estimated for long-term treatment and for alkaline addition. The following is an example of this type of calculation for a 100-ac (40.5-ha) site which, without alkaline addition, would be expected to produce approximately 50 gpm (3.2 L/sec) of acidic drainage with a net acidity concentration of approximately 100 mg/L and Fe of 20 mg/L. The flow rate is based on expected annual recharge of 10 in (25.4 cm) / year, typical for the northern Appalachians. Acid base accounting data, however, indicate the need for 500 ton/ac (1,120 t/ha) of alkaline material.

Alkaline Addition Costs:

100 ac @ 500 ton/ac = 50,000 tons (45,455 mtons) of alkaline material	
Cost of waste lime @ $1/ton:	$ 45,455
Transportation @ $8/ton:	363,640
Materials handling @ $1/ton:	45,455
Total cost of alkaline addition:	$ 454,550

Avoided Treatment Costs:

50-year treatment costs for 50 gpm (3.2 L/sec) discharge, 100 mg/L acidity, 20 mg/L Fe estimated using REMINE computer program (U.S. EPA, 1988) and present value = 27.2 x annual cost: $1,183,445

In this particular example, and assuming that alkaline addition effectively prevents the formation of acid mine drainage which would otherwise be created, it is a far less expensive alternative than long-term (50-year) treatment of a postmining discharge. The treatment cost estimate assumed that caustic soda would be the lowest-cost conventional treatment alternative. This analysis contrasts somewhat with a site-specific analysis performed by Skousen and Larew (1995) which examined the costs of an alkaline redistribution project

and calculated treatment costs over only a 20-year term. Because of the assumptions involved, this cost-analysis should be viewed as a mechanism for comparing the relative costs of treatment versus alkaline addition and not as a reliable cost indicator for a specific mining project.

Summary

The addition of alkaline material, usually a limestone-derived waste product, to surface mine backfills can be an effective method of compensating for overburden that is naturally deficient in neutralizers. In order to successfully prevent the formation of acid mine drainage, a sufficient quantity of alkaline material must be added to the backfill. Most successful alkaline addition sites to date have used substantial application rates, exceeding 500 ton/ac (1,120 t/ha). Lower rates have only proven to be effective for low-cover overburden with very low sulfur content. Alkaline material is best applied by distributing it throughout the backfill although it may be useful to place up to 100 ton/ac (220 t/ha) on the pit floor. Surficial applications of alkaline material are less effective due to low calcite solubility and limited contact with acid-producing materials deeper in the backfill. Most failed alkaline addition sites either had used application rates that were too low or employed ineffective placement of the alkaline material.

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Chapter 14

SPECIAL HANDLING TECHNIQUES IN THE PREVENTION OF ACID MINE DRAINAGE

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Introduction

Special handling at surface mines includes the selection, handling, and controlled placement of potentially acid and calcareous rock, combined with water management, compaction or other practices to prevent acid drainage. The primary purpose of special handling is to locate acidic or alkaline strata in such a way as to minimize acid production and transport, and to maximize the generation of alkalinity within the mine soil water. Special handling is often used in conjunction with other acid mine drainage prevention techniques such as alkaline addition, water management (e.g., pit floor drains), and surface reclamation (e.g., slope grading to enhance runoff). For example, special handling, in the absence of calcareous material, cannot by itself produce alkaline drainage. Thus, where calcareous strata are absent, offsite calcareous material can be imported to offset natural deficiencies in acid-neutralizing rocks. Pit floor drains can be used, among other purposes, to engineer where the postmining water table will reestablish within the spoil, thus assuring that special handled material will be above the water table.

Typically in Pennsylvania, acidic material is placed above the postmining water table to minimize water and air contact. Calcareous materials, on the other hand, are placed such that their dissolution will be maximized. Use of special handling, alkaline addition, water management, and surface reclamation can allow the mine operator some control over acid- and alkaline-generating processes.

Incorporating special handling into the mining plan may be a difficult and costly task. However, this extra effort is invaluable if it results in the prevention of a costly postmining pollutional discharge.

Probably the first special handling concept involved the recognition of black or very dark colored rocks as potential acid formers. Initially, it was proposed that the material be buried on the pit floor. Deep burial was thought to prevent contact with oxygen, and hence shut off acid production. This approach was discussed as early as 1952 by the Pennsylvania Sanitary Water Board and is shown in Figure 14.1. The Sanitary Water Board also recommended highwall diversion ditches, pit floor drains, contemporaneous backfilling, and grading topography to limit infiltration.

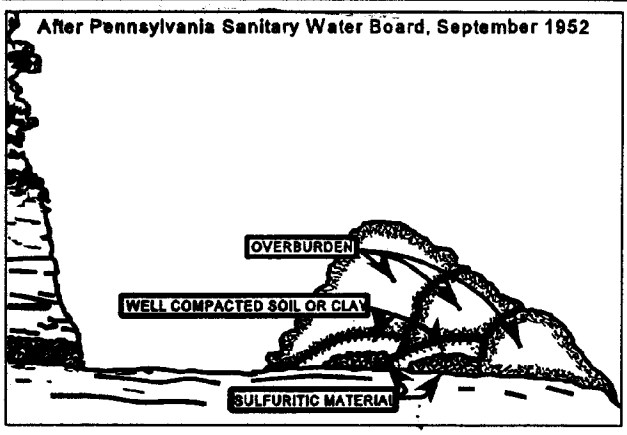
Practical experience with deep burial of the potential acid forming materials showed that water quality problems were not always eliminated and sometimes were more severe. In Pennsylvania and other Appalachian states, special handling strategies began to evolve towards isolation of material above the postmining water table and away from preferred flowpaths. This has become known as "high and dry" placement. This remains the most common special handling technique used in Pennsylvania and is illustrated conceptually in Figure 14.2.

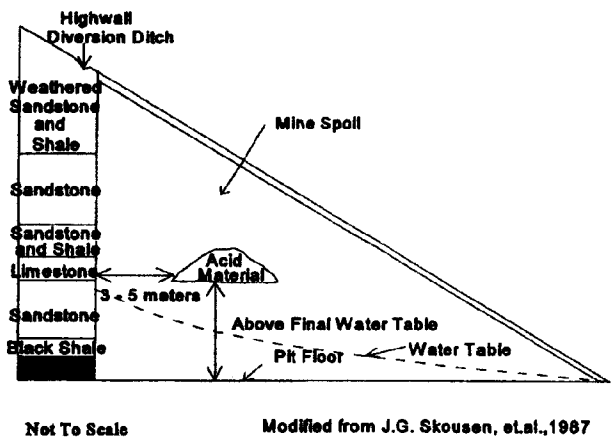
A general set of planning and handling guidelines was presented in 1979 (West Virginia Surface Mine Drainage Task Force, 1979) and later revised (Skousen et al., 1987). These publications identified some of the basic geologic, hydrologic, and mining information needed for the development of special handling plans. The Task Force guidelines emphasized placement above the water table.

Selecting a Special Handling Strategy

Special handling plans are site specific, and should include consideration of the following factors:

- Geologic and Geochemical Conditions - identifying rock types present in the overburden and the determining the distribution, location, and amount of acid and alkaline rocks in the overburden.
- Hydrogeologic Conditions - identifying the geologic structure in relationship to the area to be mined; the occurrence, quantity, and quality of surface and





Figures 14.1 and 14.2 Special handling of acid forming material evolved from placement on the pit floor to "high and dry" placement.

groundwater; and anticipated groundwater elevation in the backfill after mining.

- Operational Considerations - mining method, sequence and total area to be mined, equipment to be used, and placement and amount of alkaline materials.

Geologic and Geochemical Conditions: Acid and Alkaline Materials

The stratigraphic position, aerial extent and total volume of potentially acid-forming and alkaline materials must be known to formulate a special handling plan. A review and interpretation of the overburden analyses is used for this determination. This topic is discussed in more detail in Chapter 11.

Special handling plans must be clear, simple, and easily implemented by field personnel. Maps and cross-sections should be prepared which show the positions of the materials to be special handled, and locations where these materials are to be placed or are needed. The materials must be readily identifiable in the field, either by color or rock type. Stratigraphic intervals above or below marker beds can also be used but may be less exact. Field identification is necessary to assure implementation as a routine part of the operation, and reduces potential misunderstandings by operators or regulatory personnel.

Segregation of the acid-forming or alkaline-producing strata must also be logistically feasible. Occurrence of acid-forming material in a single or a few discrete zone(s) that can be easily identified is preferable. If blasting is used to break the overburden, then it is preferable that the material to be special handled to lie immediately above or below the coal seam.

Stratagraphic position of the material to be segregated may be a controlling factor depending upon the type of operation. When the material to be special handled lies immediately above or below the coal seam to be mined, segregation is usually not a problem. The feasibility of segregating strata located at an intermediate distance between coal seams is dependent upon the type of operation and whether or not blasting is required. In a dozer-loader operation, the overburden is ripped with the dozer and removed in layers. As long as the material to be special handled is easily recognizable in the field, the operator would have little trouble segregating this material regardless of its stratigraphic position. If blasting is necessary to break the overburden, then segregation becomes problematic if the material to be special handled does not lie directly above or below the coal seam.

Blasting usually involves the total overburden column between coal seams. However, if the strata to be segregated lies at some distance between the coal seams, blasting must be done in lifts. The first lift would incorporate blasting and removing the overburden above the unit to be special handled. The unit to be special handled would be removed separately. The remaining overburden above the coal would then comprise the second blasting lift. However, this process can easily increase blasting costs by more than 50% and may result in poor rock breakage at the top of the lift because of stemming requirements (Mike Getto, personal communication). In this case, the increased blasting costs may rule out segregation and other alternatives may have to be considered.

If the material to be special handled is dispersed throughout the highwall section in thin beds, segregation of the individual rock units may be impossible. Instead of attempting to special handle individual beds,

the entire section containing the acid- or alkaline-forming strata may need to be treated as a thick unit and the entire section special handled. Special handling such a large quantity of material will affect profitability of the operation and may be logistically difficult to achieve. In a situation such as this, other alternatives may need to be considered.

A similar problem occurs if the unit to be special handled is not of a distinct color or rock type. If the overburden analysis indicates this material to be laterally continuous across the site and located a uniform distance above a distinct marker bed, then segregation can occur with difficulty. Although fizz tests can be done in the field to identify alkaline strata, there is no comparable test for acid-forming strata. Once again, if segregation of the material is necessary, a thicker, easily identifiable sequence, which would include strata above and below the target strata, may have to be considered as the special handled unit in this situation.

When the overburden contains significant alkaline material and potentially acid-forming material, the location of these two materials relative to each other may determine the special handling plan. For example, if the alkaline section lies adjacent to the potentially acid-forming section, these two materials may become mixed without additional effort during the overburden removal operation. Separation of the potentially acid-forming strata may not be needed. Alternatively, if the alkaline- and acid-forming strata are not adjacent, but both can be segregated, a special handling plan may be implemented to place the alkaline material on top of the acidic material in the backfill as described later in this chapter.

Two conceptual overburden removal plans are shown in Figures 14.3a and 14.3b. In Figure 14.3a, acidic material is located in the upper part of the rock column and requires separate removal. In Figure 14.3b, acid material is located directly above the coal. The entire overlying rock column can be blasted and removed in one lift, resulting in a blending of the alkaline- and acid-forming material.

Hydrogeologic Conditions

The primary purpose of special handling is to control the location of acidic and alkaline strata in relationship to where groundwater enters and flows through the mine and the location of the postmining groundwater table in the spoil. The postmining water table elevation will influence placement of the potentially acid-forming material. "Rules of thumb" have evolved which recommend placement of acid-forming material at least

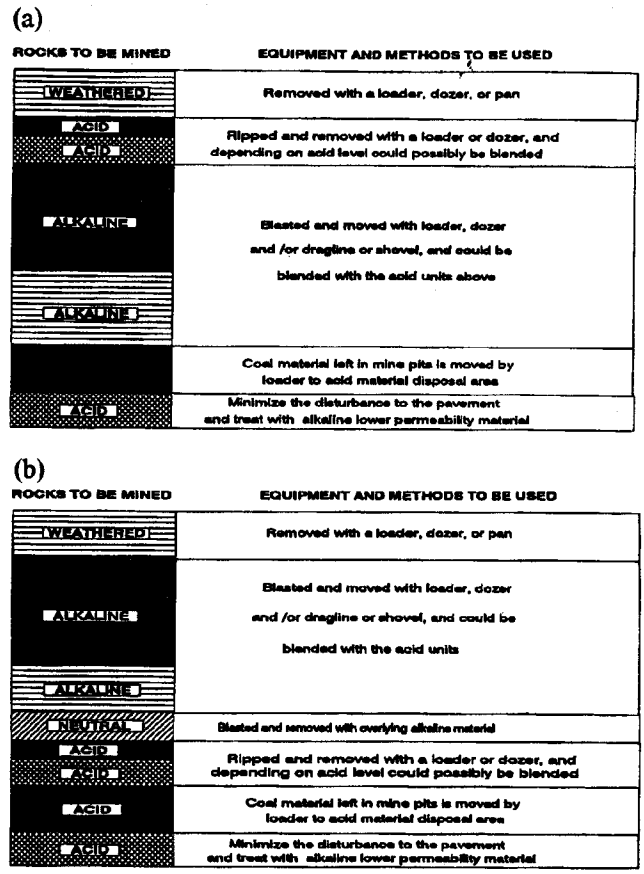


Figure 14.3a and b The positions of acid-and alkaline-forming material evolved from placement on the pit floor to "high and dry" placement.

10 to 20 ft (3.0 to 6.1 m) off the pit floor and 25 ft (7.6 m) or more away from highwalls. This is to ensure placement above the postmining water table and away from major recharge zones. This placement can be accomplished by a variety of means once the hydrologic conditions are determined. The information needed to predict the postmining water table is obtained from an analysis of the hydrogeologic setting of the mine and coal bed structure. Typically this includes a determination of the type of groundwater system, premining groundwater levels, relationship to adjacent streams, geologic structure, and mine plan.

In the situation where the operator is attempting to special handle acid-forming material by submergence, the length of time required for the postmining water table to re-establish is important. Where the operator wishes to place this material above the postmining water table, then the timing of water table reestablish-

ment is not important. However, estimates of drainage quantities can be used to design dewatering structures such as highwall or pit floor drains, or inundation structures. Additional information and discussion on spoil hydrology, postmining water tables, and anticipated groundwater volumes are contained in Chapter 3 (Spoil Hydrology) and Chapter 16 (Water Management).

Sources of groundwater recharge which the operator must consider include infiltrating precipitation, groundwater recharge through the final highwall or adjacent mined area, and upflow through the pit floor. The ability to quantify these sources allows the operator to estimate when a postmining water table will be established. The development and final configuration of the mine, along with geologic structure and pit floor characteristics, will be significant factors in determining the geometry of the postmining water table. The operator can exert some control over groundwater recharge and the configuration of the postmining water table. Once the hydrologic factors are defined, the operator can then determine where and how to place the alkaline- and acid-forming strata in the backfill to maximize alkaline water and inhibit the formation of acidic groundwater.

The contribution to the postmining water table from infiltrating precipitation during the first few years following reclamation will be less than for an unmined site. Jorgensen and Gardner (1987), Guebert and Gardner (1992), and Ritter and Gardner (1993) investigated infiltration and runoff on newly reclaimed surface mines in central Pennsylvania. They found that infiltration rates on newly reclaimed minesoils are an order of magnitude lower than adjacent, undisturbed soil. However, within four years after reclamation, infiltration rates on some mine surfaces approach premined rates (8 cm/hr). During the topsoiling operation, the soil is compacted by the equipment spreading the soil. This promotes runoff. During freeze/thaw and wet/dry cycles, macropores develop in the surface soils which promote infiltration. Warner (1987) conducting studies on reconstructed soils for landfills under a variety of cover crops, found that runoff accounted for about 5% of the precipitation, infiltration from 42 to 53% and evaporation and stored moisture 41 to 56%.

Drawdown and recharge tests of the aquifers encountered may provide the operator with information, which will allow for an estimate of groundwater recharge rates. However, since fracture flow dominates in the coalfields, wells not located in fractures may underestimate recharge rates. Perhaps a simpler and more useful technique would be to monitor the flows from cropline springs.

Reestablishment of a postmining water table will probably be most rapid for those mines where the lowest seam mined lies beneath the regional water table. In this situation, constant pumping is required to temporarily dewater the pit during mining. Once the pumps are shut off, the regional water will reestablish itself in a very short period of time. It becomes somewhat more difficult to predict the configuration of the postmining water table for those mines associated with aquifers perched above the regional water table.

The hydraulic characteristics of the pit floor will determine whether a postmining water table will be intermittent or permanent if the mine is situated above the regional groundwater table. In some cases, the pit floor might be a thick underclay which tends to serve as an aquitard. In other cases, the floor might be massive, fractured sandstone which will not inhibit the downward percolation of groundwater. The presence and character of cropline springs can provide an indication as to the nature of the pit floor. However, the pit floor should also be investigated during the drilling of exploratory holes.

Experience with postmining water tables in surface mines in similar geologic, hydrologic, and mining situations as the proposed mining operation is useful in predicting the water table location once the permit is mined. The prediction should also be based on the hydrologic properties of the aquifers to be disturbed by the proposed operation. Hydraulic properties and water levels of the aquifers that will likely recharge the site should be measured to determine the volume of groundwater to be produced by the mine.

An understanding of geologic structure is also important in the selection of special handling techniques. Structure of the lowest mined coal seam in conjunction with the area to be mined and the final highwall configuration determines the final pit floor configuration. If a down dip highwall remains after mining and the pit floor retards vertical percolation, groundwater may become impounded on the pit floor against the highwall, resulting in a higher postmining water table than in the case of an up dip highwall. A cropline barrier left in place also has the potential to impound water. In the case where a downdip highwall remains after mining and conditions are present which promote mounding of the groundwater against the highwall, then the "rule of thumb" placement of 10 to 20 ft (3.0

to 6.1 m) above the pit floor may be inadequate. It may be desirable to change the orientation and/or location of the final highwall to avoid impounding water, or to incorporate underdrains to minimize groundwater buildup in the backfilled spoil (Chapter 16).

Premining hydrologic conditions must be carefully considered in light of the experience of the permit preparer and reviewer with the development of water tables in other existing surface mines of like topographic, geologic, hydrologic, and mining scenarios.

Operational Considerations

The ability to design and effectively implement a special handling plan is influenced to a large degree by several operational considerations. These include the total area to be mined and sequence of mining, time needed to complete mining, the need for blasting, the mining method to be used, and equipment to be used.

The mining plan is often based on the area available for mining (i.e., leased) and the coal quality (need for blending), rather than the optimum configuration for overburden and coal removal. As these constraints are real, they must be considered in preparing a special handling plan. The stratigraphic and areal distribution of the acid- and alkaline-forming materials as they relate to the mining plan will determine to a large extent how these strata realistically can and will be special handled. However, several pit orientations are often possible, and the choice of a particular configuration may have different implications for special handling, especially in a multiple seam operation.

The time needed to complete mining also requires consideration in the special handling plan. When potentially acid-forming strata are exposed, rapidly covering this material helps prevent the onset of acid forming reactions (Skousen et al., 1987). Perry et al. (1997) examined seven sites with special handling and found timeliness of reclamation to have some influence on water quality. Sites where mining ceased for a period of time and then resumed generally produced poorer quality drainage than sites where mining proceeded rapidly to completion. Extended exposure of unreclaimed spoil to infiltration and circulation of water and oxygen apparently allowed more acid production. Some mine permits in Pennsylvania now include a special condition prohibiting temporary cessation of mining to limit exposure of potentially acid-forming materials.

If overburden can be removed without blasting, it is not difficult to isolate thin beds of potentially acid- or alkaline-forming materials. Where necessary for overburden removal, blasting determines the fragmenting and sizing of rocks, their position in a spoil pile, and may affect the operator's ability to selectively handle target strata. Where the target strata does not lie immediately above or below the coal seam being mined, blasting may require three steps: 1) blasting and removal of rocks above the target strata, 2) removal of the acid-forming material itself with bulldozers and highlifts, and 3) removal of the remaining overburden down to the coal. However, this approach may not be realistic considering the increase in blasting costs.

The modified block cut method of mining, also referred to as the haulback method, is used on many Pennsylvania surface mines. This entails hauling the initial cuts of overburden to temporary storage. Subsequent overburden cuts are then placed in the previously created open cut. This cycle is repeated until mining is completed. The final cut is backfilled with the overburden stored from the initial cut. Block cut mining automatically lends itself to special handling material from the operating cut into the cut being reclaimed. Usually the cuts are open for only short periods of time, and are mined with a combination of loaders, bulldozers and trucks.

Area mining, also used on some Pennsylvania mines, generally results in larger pit sizes, and a longer period of time before backfilling and reclamation begins. These often involve multiple seam extraction where it is common for the operator to use a dragline for some seams and bulldozers and loaders for other seams.

The equipment to be used for overburden removal is another important component of a special handling plan. Truck and shovel operations are able to remove distinct portions of the section and to move overburden from one pit to another. Dozers with large rippers attached can often aid in overburden removal without blasting. This can allow for separation of the potentially acid-forming material from other non acid-forming material. In general, segregation of spoil material is more difficult using a dragline. In many cases, the dragline operator does not have visual contact with the spoil he is loading. Cravotta et al. (1994a) compared the ability of dragline and loaders on two areas of the same mine to special handle acid-forming strata. Both handling methods tended to invert the original rock column. Where loaders were used, pyritic shale was placed in pods near the final surface, and only low sulfur material was near the pit floor. On the area

mined with a dragline, the overburden with the highest sulfur content was placed near the surface, but the sulfur contents for the material at the bottom of the pit were higher than they were for the area mined with loaders. A special handling study in Montana with dragline mining also reported that the overburden profile was inverted (Dollhopf et al., 1982). Both studies compared chemical and lithological properties of drillholes in minespoil to premining conditions.

The Cravotta et al. (1994a) study compared the distribution of sulfur and neutralization potential in undisturbed overburden strata (Figure 14.4) with the postmining redistribution of these parameters in the disaggregated mine spoil (Figures 14.5 and 14.6) for two mining methods. The mine site they studied was a reclaimed surface mine on two adjoining hilltops in southern Clarion County, PA. The southern area was mined with a 45 yd^3 (34.4 m^3) dragline. The northern area was mined with bulldozers and front end loaders which selectively handled the high-sulfur strata near the coal.

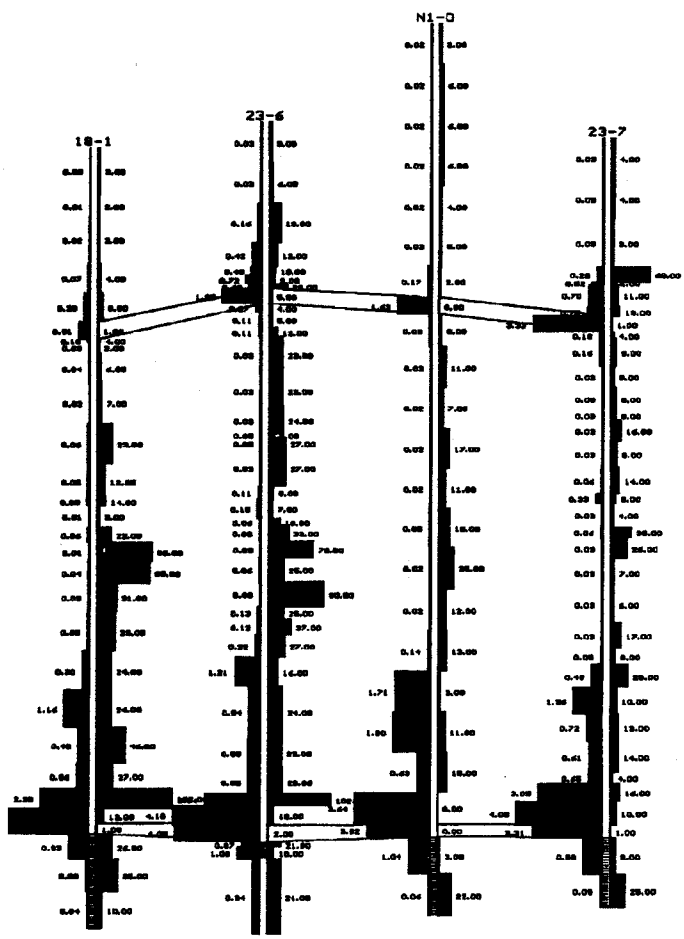


Figure 14.4 Distribution of sulfur and neutralization potential for bedrock at the special handling site in southern Clarion County, PA.

The original plan for the 16 acre (6.5 ha) northern area called for placing the high sulfur rock in pods 10 ft (3 m) above the pit floor, with low sulfur material placed between the pods and the pit floor. Drill holes N2-0 and N2-2, located 5 ft (1.5 m) apart, encountered one of the specially handled pods. The other drill logs show that mining, in general, inverted the high sulfur (>0.5%) material and located it near the spoil surface. Most logs show low sulfur (< 0.15%) material near the pit floor. Maximum saturated thickness of spoil in the northern area was 18 ft (5.5 m) and in the area of N2-0 the saturated thickness was 10 ft (3 m). The spoil sulfur data and spoil water level data suggests that the high-sulfur spoil was successfully placed above the water table within the northern area. The permit specification for placement 10 ft (3 m) above the pit floor would have been inadequate to keep the high-sulfur material above the spoil water table.

Spoil in the 34 acre (13.8 ha) southern area was also inverted, with the highest sulfur rock predominantly in the upper part of the spoil. The sulfur in the lower part of the spoil is typically between 0.25 and 0.4%. The sulfur concentrations in the lower part of the spoil are higher than what is typical on the northern area where the spoil was selectively handled. The highest saturated thickness in the spoil was about 20 ft (6 m). Thus the highest sulfur material in the southern area was also placed above the water table.

Some inferences about relative compaction of the spoil for the two mining methods can be made. Spoil handled by bulldozers and loaders would be expected to have a more uniform particle-size distribution, exhibit similar or greater compaction, and exhibit lesser hydraulic conductivity than that handled by the dragline (Chapter 3; Phelps and Saperstein, 1982; and Phelps, 1983). Air circulation commonly was lost in shallow spoil during air rotary drilling in the southern area; however, no air losses occurred in the northern area, suggesting greater compaction and more uniform particle size distribution from bulldozers and loaders than from a dragline. Nonetheless, hydraulic conductivities for saturated mine spoil were similar among the two areas. For saturated spoil, median hydraulic conductivities were $10^{-3.8}$ to $10^{-3.6}$ m/s in each area. The similarity in hydraulic conductivities could result from similar lithologies, and piping and settling processes (Chapter 3, and Pionke and Rogowski, 1982) by which

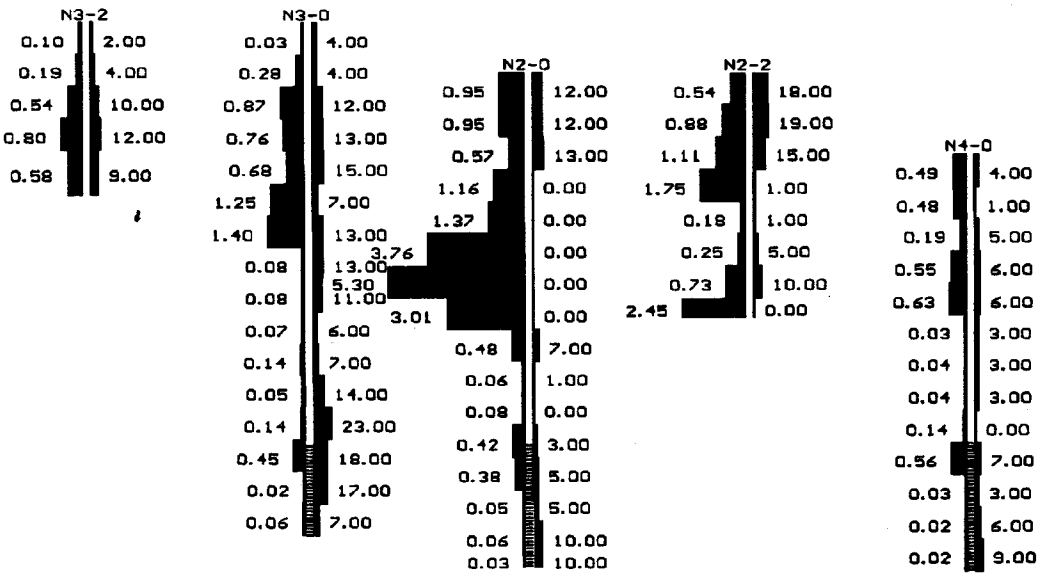
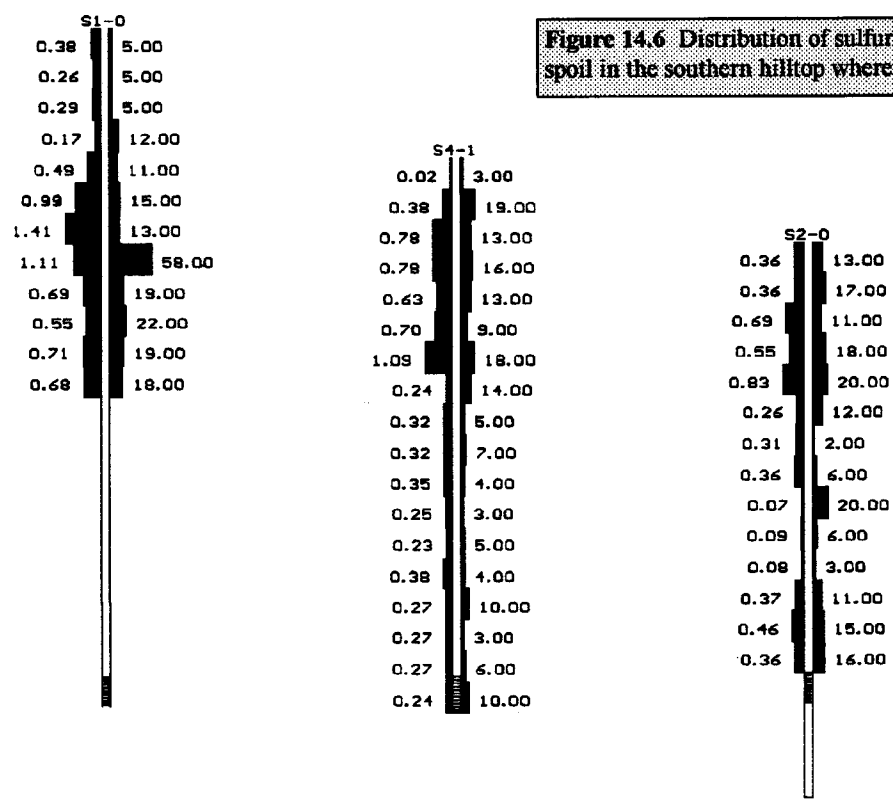


Figure 14.5 Distribution of sulfur and neutralization potential for spoil in the northern hilltop where bulldozers and loaders were used. Note the "pod" of selectively handled high sulfur material in N2-0 and N2-2.

fines are transported downward and large voids fill or collapse. Mine spoil in the southern area is several years older than that in the northern area, so a longer time has elapsed for these processes to occur.

Alkalinity, sulfate, iron, and manganese in the spoil groundwater produced by the selective-handling method was similar to that in spoil produced by the dragline method. Median values for alkalinity of groundwater in the saturated zone were between 100

Figure 14.6 Distribution of sulfur and neutralization potential for spoil in the southern hilltop where a dragline was used.



and 400 mg/L. Sulfate ranged from 600 to over 1000 mg/L (Cravotta et al., 1994b).

Design and successful implementation of a special handling plan includes understanding the limitations of mining equipment. The mine operator should have equipment appropriate to the proposed plan and site conditions. Success of a special handling technique will depend on the ability of the equipment operator to identify the acid and alkaline materials during mining, and place those rocks in the locations designated by the handling plan.

Special Handling Techniques

Several "special handling" and management techniques are used alone or in combination to dispose of acid materials on mine sites. These include:

- Relocation of potentially acid forming strata above the anticipated postmining groundwater table,
- Constructing "pods" of acid-forming materials
- Submergence or flooding;
- Blending including alkaline redistribution or alkaline addition; and
- Surface and groundwater management.

Discussion of special handling techniques includes explanation of the concept, general level of success, favorable site conditions, considerations in using the techniques, and possible field validation methods. Use of one or a combination of methods may be warranted. Overburden analysis data, hydrologic conditions and mine plan direct the best methods to accomplish this goal.

Handling Acid Materials Using Segregation and Isolation ("High and Dry") Techniques

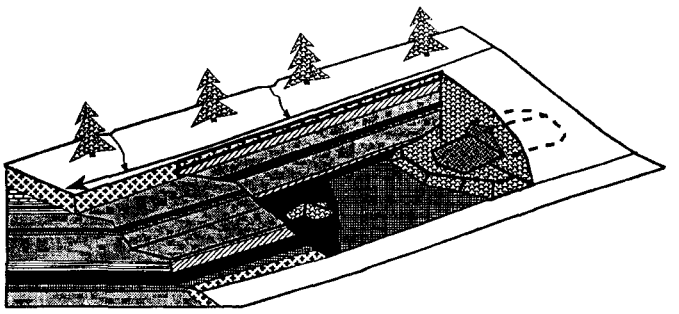
Placement of acid materials above the water table using segregation, isolation, and encapsulation techniques minimizes contact between acid-forming material and groundwater. Special placement usually occurs in "pods" or discrete piles that are located above the expected postmining water table in the backfill; hence the reference to the "high and dry" method. A few mines have constructed liners and caps to prevent groundwater contact with the acid-forming materials, a method called encapsulation.

Segregation and isolation from the groundwater system does not totally prevent pyrite oxidation. Oxygen, microbes and some water are still present in the pods. Segregation and isolation is directed at preventing downward leaching, or upward migration of oxidation products. The technique is illustrated and described conceptually in Figure 14.7.

Construction of acid-forming material pods is one of the oldest techniques used to isolate potentially acid strata. The purpose is to reduce percolation or recharge of groundwater through the potentially acid-forming strata. Pods are constructed in compacted layers, sometimes with potentially acid-forming material alternated with alkaline strata. Pods are placed above the anticipated final groundwater elevation in the backfill, and usually at least 25 ft (7.6 m) away from the final highwalls and lowwalls and 10 ft (3.1 m) from the surface. Pods are designed with a compacted sloping cap (best constructed of clay or other low permeability material), and are usually covered with and underlain by alkaline material. Potentially acid-forming material needs to be rapidly excavated and covered to prevent prolonged exposure of the materials to oxygen and water.

Improper construction of pods, especially the failure to construct an impervious cap over the top of the pod can result in conditions favorable to the formation of severe AMD. The "high and dry" burial places the pyritic material closer to the surface of the mine where oxygen is more abundant (Chapter 1). This, in conjunction with percolating precipitation and the high concentrations of pyrite, create an environment which would allow *T. ferrooxidans* to thrive. Schueck (personal communication) found severe AMD formation associated with segregated, but improperly isolated pyritic material on over a dozen mines, which were mapped geophysically. Magnetic mapping was used to locate the pods and electromagnetic terrain conductivity was used to map the pollution plumes through the site. In every case, high conductivity values were associated with and located immediately downgradient of the pods. Conductivity values decreased with increasing distance from the pod, indicating that the AMD was being diluted. Subsequent drilling and groundwater sampling confirmed that the AMD associated with these improperly constructed pods correlated with the higher conductivity values and is more severe than AMD generated elsewhere on the site. In many cases, the operator confirmed that the pods were segregated acid-forming materials, often pit cleanings, but that impervious caps were not constructed on top of the pod.

Placement of acid material into a contour surface mine backfill must fall within a projected target zone



SEGREGATION AND ISOLATION (HIGH AND DRY) TECHNIQUES

STEPS INVOLVED IN SPECIAL HANDLING ACID MATERIALS

1) Conduct drilling and blasting to expose acid materials,

2) Remove acid materials with a loader or dozer,

3) Construct the disposal site in the backfill where:
   - at least 10-20 feet from the highwall,
   - above the final water table to be developed in the post mining backfill,
   - out of the root zone probably at least 10- feet below the surface
   - away from natural drains that would flow across the post mining backfill

4) Place the acid material either in on the constructed pad in the backfill or in a in a temporary storage for transport offsite or to another part of the permit

5) Add alkaline material to acid material to reduce acid generation, and

6) Complete the reclamation and revegetation as quickly as possibleby

Figure 14.7 Three dimensional conceptual view of high and dry placement of acid-forming materials.

(See Figure 14.8). The bounds of this zone are established by the distance from the highwall, height above the pit floor, postmining water table, the depth below the root zone, the distance from the outcrop, and the distance from reestablished drainageways and various barrier areas. In the example provided in Figure 14.8, a simplistic approach is demonstrated to indicate the maximum amount of acid material that can be placed in the target zone. A further reduction to the target zone is then made based on the likely limitations of the mining equipment.

The values used for the Total Mined Area Triangle (TMAT) include:

Maximum Highwall Height ..... 60 ft/18.3 m
Coal Thickness ..... 4 ft/1.2 m
Stripping Ratio 15:1
Landslope 30%
Calculated Maximum Pit Floor Width ..... 200 ft/61 m

The values for the Acid Material Target (Area Triangle AMTAT) include:

Distance from the highwall ..... 20 ft/6.2 m
Distance above the pit floor ..... 10 ft/3.0 m
Depth below the root zone 10 ft/3.0m
Distance above the postmining water table ..... Variable
Away from re-established surface drains ..... Variable

The TMAT square footage value is 6000 ft^2 (557 m^2) using the maximum pit floor width and highwall height. The maximum height of the AMTAT to which the acid material could be placed (and still meet the segregation and isolation disposal conditions) is 34 ft (10.4 m) on the side nearest the highwall. The maximum width of the AMTAT is 112 ft (34.2 m). At most, only 32% (roughly one third) of the total mined area can be used for acid material placement. This value will change depending on highwall height, land slope and placement constraints. As a general rule, as land slope increases, the size of the target area for acid material will decrease.

Further reductions in the amount of acid material placement will result from the practicalities of handling and construction of the top portion of the AMTAT. If the material is dumped at the angle of repose (assumed to be 30°) before being compacted, the top portion of the AMTAT would not be available for use during placement. This zone (cross-hatched on Figure 14.8) represents about 5% of the fill cross section. Under these conditions, no more than about 27% of the total backfill is available for acid material placement. This target triangle area for acid material placement is not continuous around a hill (along the contour) because of the natural drainageways, which occur every few hundred feet in the Appalachian Plateau. Other obstacles such as gas wells, gas lines, power lines, and houses, etc. may further reduce available area. This further limits the lateral extent of placement. By volume, the acid material should probably represent no more than 20% of the material to be backfilled.

Meek (1994) monitored acid production on surface mined areas with segregation and several different alkaline amendments. Acid load, on an area with segregation, was reduced about 50 percent compared to a control area with no segregation or alkaline addition. The Kauffman site in Clearfield County, Pennsylvania, includes placement projected to be above the water table and large alkaline addition rates. Monitoring of Phase 1 of this site showed that a thicker than expected water table has developed in part of the backfill and is in contact with some of the acid material. This site is discussed in Chapters 2 (Groundwater) and 13 (Alkaline Addition).

Phelps and Saperstein (1982) suggested that pods should have a bulk density of 1.1 to 1.5 times the surrounding spoil to minimize infiltration. These investi-

gators also observed that the highest spoil bulk densities occurred at 50 to 80 % depth of spoil for most mining methods. They suggested that the high density spoil zones should be favorable locations for pods if hydrologic requirements are satisfied.

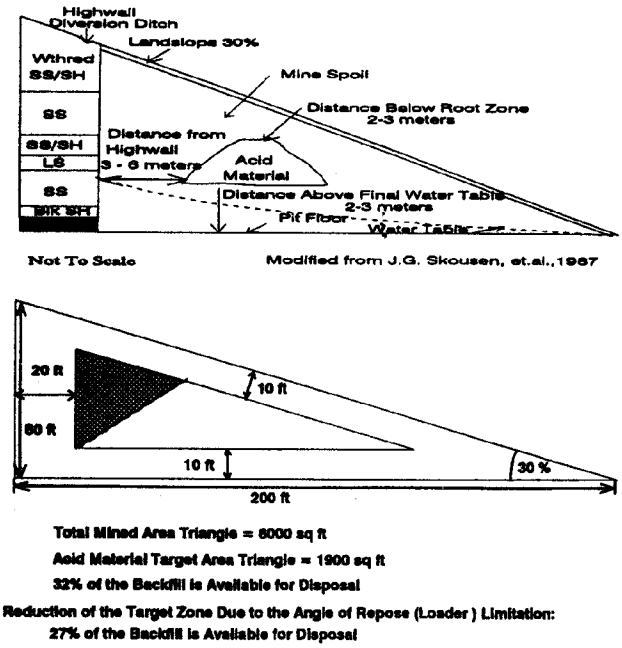


Figure 14.8 Projected target zone determination for placement of acid forming material within the backfill.

Schueck et al. (1996) reported on attempts to grout buried refuse with fluidized bed combustion ash as a form of isolating pods after the fact. This was done on a site where the lower Kittanning seam was mined and most of the overburden is apparently acid-forming. Grout was injected directly into the buried pods to plug void spaces and coat the refuse. Grout caps were also constructed over several of the pods. Combined grouting affected only 5% of the site but resulted in a 50 to 60% decrease in acid loading.

St-Arnaud et al. (1994) observed a "porous envelope" effect at a metal tailings pond in Canada. At this site, low permeability tailings have been placed within permeable soils. A large contrast in permeability promotes the flow of groundwater flow around rather than through the tailings mass, minimizing leaching of the acid material.

Short exposure time before burial and reclamation can reduce weathering and acid generation. As the acid-forming material remains exposed, weathering proceeds to produce acid products and the subsequent buildup of acid salts. If bacteria can be controlled by maintaining alkaline conditions, or through actual destruction of the bacterial population, the oxidation rates for pyrite are slower. In practice, potentially acid-forming materials are often stockpiled until enough material to start pod construction is accumulated. To reduce exposure, some mines in Pennsylvania construct temporary stockpiles covered with soil and vegetation, or cover the material with lime. The addition of lime can also inhibit the initial onset of AMD formation.

When potentially acid-forming material is removed from every cut, the best practice is to advance the construction of pods along with the mining. This ensures that acid-forming material is being rapidly buried. The Kauffman mine includes an area of test cells or pods (Rose et al., 1995). The investigators report that high-sulfur material was stockpiled for several months before construction of the pods. Some pods unexpectedly produced very acidic drainage even though they had been amended with alkaline materials. Delay in construction of the pods may have allowed acid generation to start even before the acid material was placed in pods. Rose et al. (1995) concluded that pod construction required careful implementation including prompt mixing of acid material with the alkaline amendment.

A mine in Greene County, Pennsylvania produced both alkaline and acid water on two phases (Perry et al., 1997). The two segments had similar geology and hydrology, and were mined by the same company. Alkaline drainage was produced on the segment where mining was completed without stoppage and a handling plan was followed. Acidic drainage was produced from the Phase 2 segment where mining ceased for an extended period before the site was completely reclaimed. The poor quality drainage on Phase 2 was attributed to weathering of partly reclaimed material during cessation and poor adherence to the special handling plan. Median water quality data for the two sites is summarized in Table 14.1.

Table 14.1 Summary Water Quality for Greene County Site Phases 1 and 2

Monitoring Point	pH S.U.	Net Alkalinity (mg/L $CaCO_3$ Eq)	Total Fe (mg/L)	Total Mn (mg/L)	Sulfate (mg/L)
Phase 1, Mining	6.5	176	0.3	6.5	606
Phase 2, Mining	3.6	-488	71.4	105	2233
Phase 1, Postmining	7.2	151	1.88	16.35	1197
Phase 2, Postmining	4.0	-128	18.7	62.7	1770

Capping

A cap refers to an overlying "impermeable" zone created through placement of compacted, fine grained soil material, combustion byproducts (flyash, fluidized bed wastes), kiln dust, or synthetic (plastic or geotextile) fabric. The cap is significantly less permeable (two orders of magnitude or more difference) than the surrounding material. Caps restrict or prevent the infiltration of water into acidic material from above.

The term liner is normally used in the context of an underlying "impermeable" zone created through placement of an earthen or synthetic material which is significantly less permeable than the surrounding units. However, materials used for liner construction can also be used as a cap over the specially handled pod. Liners restrict or prevent the adjacent groundwater flow system from encountering the acid-forming material. Caps and liners also restrict diffusion of oxygen; a key component of acid generation.

Acid material is isolated by construction of low permeability caps or liners. Rose et al. (1995) concluded that test pods at the Kauffmann mine were made less permeable with percolating water tending to flow around rather than through the pods. Compaction and cementation of lime layers by gypsum formation were identified as the likely capping mechanism.

A detailed study of special handling at a Montana surface coal mine included the construction of a 3 ft thick (0.9 m) clay cap over special handled material (Dollhopf et al., 1982). Construction of the cap required several pieces of equipment, including pans and bulldozers. Maintaining clay at optimum moisture content for maximum compaction was difficult; water sometimes had to be added to the clay material. Cost of special handling with the clay cap was about 1.5 times "normal" operations due in large part to idling the dragline at certain stages of cap construction. An experienced mining engineer was needed on-site to supervise operations and schedule equipment. Groundwater conditions were monitored for several years after cap construction. Special handled material was maintained in a dry state, and the investigators concluded that capping was successful.

On a larger scale, a cementitious cap constructed of fluidized bed combustor (FBC) ash mixed with waste lime is near completion on a 97 ac (39 ha) reclaimed mine site in Clearfield County, Pennsylvania. Hellier (1998) reports on the successful efforts of the operator. Surface mining on the lower and middle Kittanning coal seams began in the 1940s on this site. Upon completion of the mining, circa 1991, the operator was required to pump and treat an acidic postmining discharge. Treatment costs threatened to bankrupt the operator. Mining on the site predated special handling techniques. The operator removed the top 3 ft (1 m) of material and spread a 3 ft (1 m) layer of FBC ash mixed with 10% waste lime. Water was added to increase the moisture content. The ash/lime mixture set up to form a low strength cement. The top material was then replaced and revegetated. The cap served to inhibit infiltration, which was thought to be the primary source of water at this site. The cap would also inhibit oxygen from entering the backfill. At 80% completion, the operator no longer has to provide chemical treatment, pumps significantly less water, and the chemistry of the water remaining in the backfill has improved. A passive treatment system, which is in place, is adequate to mitigate the reduced flows of AMD.

Synthetic liners (plastic or geotextile) are a technology borrowed from the waste management industry. Thick, high-strength plastics of 20, 30, 40 or even 80 mil thickness are used to isolate acid forming material from infiltrating precipitation and groundwater interflow. The liners are designed to be resistant to a wide range of leachate conditions. They are laid in sheets with the seams heat or solvent welded or stapled.

Synthetic liners require a smooth, firm base to avoid puncture or stretching. Some plastics can also deteriorate as a result of ultraviolet radiation. A potential area of weakness is the seams which must be joined properly to avoid leakage or failure. The cost of synthetic liners is also very high, resulting in probably the most expensive technology in comparison to other methods. Refuse piles may be amenable to capping with liners, due to their engineered structure, and more controlled particle size distribution

Meek (1994) reported that a plastic cap reduced acid load about 70 percent compared to no special handling. A cap was one of the most effective treatment measures evaluated in that study.

Caruccio and Geidel (1983) used a 20 mil liner at a 40 ac (16 ha) site in West Virginia as an infiltration barrier. The acid load from two highly acidic seeps was reduced such that the liner would pay for itself in 6 years. Because of a steep outslope, the liner only covered the flatter, upper portion of the mined area. Recharge along this outslope probably accounted for most of the remaining flow to the seeps.

Earthen materials can be placed and compacted to form relatively impervious flow barriers. Cap thickness is frequently an issue, but a rule of thumb from the solid waste industry is 2 ft (0.6 m). Little information directly applied to mining is available to determine if 2 ft (0.6 m) is adequate. Permeability of a cap is affected by grain size, mineralogy, and moisture content of the earthen material, the degree of compaction, and the thickness of the lifts (lifts of 6 in (15 cm) are frequently required). Bowders et al. (1994) tested mixtures of flyash, sand, and clay as candidate hydraulic barriers in minespoil. They found that a mix of particle sizes and materials provided the highest packing density and lowest permeability, rather than flyash alone. Hydraulic conductivity varied about 2 orders of magnitude from 10^{-5} to 10^{-7} cm/sec over different mixes and moisture contents.

Design geometry of the cap may enhance or reduce the volume of water passing through the cap. A dome shape tends to "shed" water while flat caps could retain additional water. Construction of caps or liners has similar requirements to building refuse piles or other engineered disposal structures. Rubber tired equipment or a sheepsfoot roller are required for good compactive efforts. Caps constructed of earthen material can shrink and crack if allowed to dry out. Caps can also be damaged by differential settlement of spoil.

Success of segregation and isolation methods to prevent acid drainage off the mine site is directly related to proper construction of the caps and management of the hydrologic system at the site. Some documentation exists that demonstrates that this technique is effective. Rapid disposal of the material will necessitate concurrent reclamation, which may be difficult for large mining operations such as those using draglines.

Several site conditions need evaluation when using segregation and isolation disposal. Sites with small recharge areas, that are located on topographically steep slopes, and that are primarily composed of shales may pose the best conditions because higher surface water runoff and limited groundwater movement might be achieved. Within the overburden or soil material there must also be sufficient "impermeable" material to form the protective caps. The volume of acid forming material must be low enough to allow for placement of the material in the designated zone of the backfill.

Placing acid materials in a contour surface mine backfill usually invokes the following criteria:

- Isolation above the reestablished water table, 10-20 ft (3.0 to 6.1 m) above the pit floor,
- Separation from the highwall (25 ft (7.6 m)) and out of the recharge zone at the highwall-spoil interface,
- Placement below the root zone, and
- Out of surface drainage channels.

When special handling is part of the mine plan, keeping the pit clean and quickly covering acid-forming strata are simple and important activities to reduce the potential for acid production. Keeping the pit floor clean, i.e., removing pit cleanings, will ensure that any groundwater which percolates through the spoil to the pit floor will encounter minimal amounts of potentially acid-forming material. This also includes removal of ribs of coal between pits and removal of lowwalls.

Handling of Acid Materials Using the Submergence or "Dark and Deep" Technique

Submergence involves the placement of special handled material below a static water table. This method is expected to exclude oxygen from pyrite and is similar in concept to sealing and flooding of underground mines to reduce acid generation. Submergence or "dark and deep" generally requires a relatively flat area with a thick saturated zone and stationary water table to produce a near stagnant or no flow condition. The technique is not widely used in Pennsylvania or other Appalachian states because of thin and seasonally variable saturated zones. It is used in Canada and elsewhere for tailings disposal at hard rock mines (Fraser and Robertson, 1994; Robertson et al., 1997) and in the Interior coal basin of the United States where thick and stable saturated zones are more conducive to this method.

In Canada, tailings disposal in lakes usually involves water bodies with minimal circulation and anoxic conditions at depth. Tailings may also be buried on the lake floor by accumulating sediment and organic debris, providing a further barrier to oxygen. In the US midcontinent, topographic relief is low, water tables tend to be near ground surface, and flow gradients are small. Surface mining is conducted mainly by area mining methods, and the final cut is often allowed to flood at reclamation, leaving a relatively deep narrow lake incised into the terrain.

Leach and Caruccio (1991) characterized backfill materials as consisting of three broad hydrologic zones. The first zone is the vadose zone or zone of high oxy-

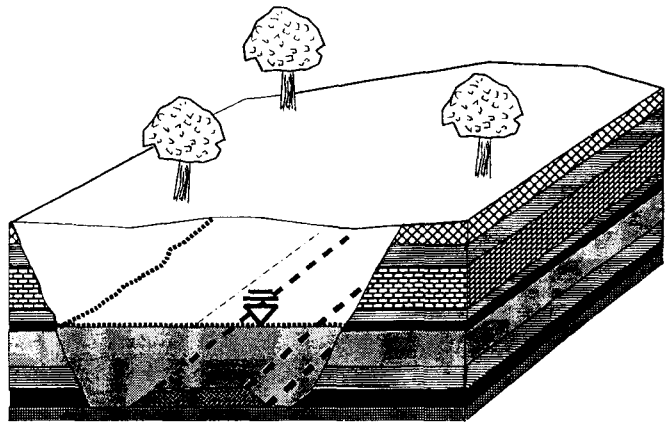
gen concentration. Next is the zone of water-table fluctuation with alternately high and low oxygen concentration. The final zone is saturated with very low oxygen concentration. Leaching experiments representing the three zones showed acid load under saturated conditions to be about 5 percent of that produced in the unsaturated zone. Acid-forming material should be in the saturated portion of the backfill to restrict oxygen diffusion. *Thiobacillus ferroxidans*, a significant factor in the acid-generation process, can remain active at oxygen levels well below atmospheric conditions.

Submergence has not been widely documented as a disposal technique in the Appalachian coalfields. Perry et al. (1997) found that submergence of acid material buried on the pit floor produced very poor quality drainage at one Appalachian surface mine. In the Interior Coal Basin of the central United States, flooding of final pits and development of a thick saturated zone occurs on many sites. The water quality of most flooded last cut lakes is alkaline; some also have elevated concentrations of dissolved solids and sulfate (Gibb and Evans, 1978). Some alkaline lakes are located in calcareous spoil derived from glacial till, loess, and shale.

Submergence requires a relatively flat area with a stable (minor seasonal fluctuations) water table in order to achieve saturated conditions. Flat topography enhances recharge, reduces surface runoff, and allows development of a low gradient water table. A "nonflowing" or stagnant (very low hydraulic gradient) groundwater regime reduces the effects of dissolved oxygen being brought into the system. Flushing, or transport of weathering products from mine spoil, can be minimized in a "no flow" regime. A typical submergence scenario for the Interior Coal Basin is shown in Figure 14.9.

Submergence entails risk. If postmining hydrology is not correctly anticipated, acid may be generated. Weathering products are leached or mobilized by flowing groundwater. Therefore, it is imperative that the site hydrology be well understood. Information necessary to characterize the groundwater flow system include:

- Estimates of available groundwater recharge to ensure a permanent water table.
- The site must be capable of being hydrologically isolated from the rest of the groundwater system.



SUBMERGENCE (DARK AND DEEP) TECHNIQUES

STEPS INVOLVED IN SPECIAL HANDLING ACID MATERIALS

1) Conduct drilling and blasting to expose acid materials,
2) Remove acid materials with a loader or dozer,
3) Construct the disposal site in the backfill at a location:
   - on the mining pit floor,
   - below the final water table to be developed in the post mining backfill,
   - within a hydrologic "no flow" (very low) zone,
   - out of the root zone probably at least 10- feet below the surface
4) Add alkaline material to acid material to reduce acid generation, and
5) Complete the reclamation and revegetation as quickly as possible.

Figure 14.9 Schematic of special handling acid-forming materials by the submergence technique.

- Backfill must be constructed to produce a reservoir containing the acid-forming material.
- This type of disposal during the mining operation should involve handling the acid-forming material only one time before permanent placement (probably on the pit floor of a previously excavated pit). Material handling for submergence is not as complex as segregation and isolation methods.

Some disadvantages to this method are that pyrite oxidation may have already begun before material is submerged, forming ferric-sulfate salts. Upon dissolution these salts release ferric iron that can oxidize pyrite and sustain acid generation. If material handling is unsuccessful; i.e., the water table is not stagnant or thick enough, resultant drainage problems will be large scale. This technique might require a relatively long lag time before success/failure can be determined and large areas can be impacted before the results are known.

Handling of Acid and Alkaline Materials Using Blending Techniques (Including Alkaline Redistribution)

Blending is the mixing of rocks on a mine site to promote the generation of alkaline drainage. Blending maximizes the contribution of carbonates by mixing them with acid-forming rock to inhibit the oxidation of pyrite. In theory, it is possible to blend rocks from virtually any position in the overburden column, but the actual practice is dependent on the mining method and spoil handling equipment. A spoil mixing experiment with dragline mining was conducted in Montana where saline or "toxic" overburden was present in varying amounts across a mined area (Dollhopf et al., 1982). Premining distribution and properties of the "toxic" material were determined from overburden analyses. Systematic drilling and sampling of the reclaimed spoil after mining showed:

- When the "toxic" material constituted about 5 % or less of the overburden, the material was undetectable in the regraded spoil.
- When the "toxic" material constituted 5 to 15 % of the overburden, partial to complete mixing occurred.
- At concentrations greater than 15% "toxic" material, partial mixing occurred.

Special handling and spoil mixing were conducted on this mine to protect both root zone material and groundwater quality.

Alkaline redistribution is special handling of alkaline material that is subsequently disposed of with the acid material. Alkaline redistribution uses material that frequently is from a different portion of the mine site, thus requiring haulage from one part to another. Skousen and Larew (1994) describe the redistribution of alkaline material from separate but adjacent mine sites. Calcareous rock was hauled from a mine extracting Bakerstown coal to a mine on the upper Freeport coal. Alkaline redistribution consisted of placement of about 3 ft (0.9 m) of calcareous shale on the pit floor, partial backfilling, then placement of acidic material about 20 ft (6.1 m) high in the spoil, followed by capping with more calcareous shale. A pre-existing mildly acidic discharge (acidity about 75 mg/L $CaCO_3$) was ameliorated and is now alkaline.

The term "blending" has been used widely in the past to refer to the mixing that occurs during the routine mining process. This technique has been recognized since at least the mid 1970s. Anecdotal information exists to suggest that it is an effective practice.

General considerations for use of alkaline redistribution include :

- Position of alkaline materials within the overburden section and volume present at the mine site:

  Position and available volume of alkaline material largely determine the feasibility and effectiveness of alkaline addition or redistribution. If the material is present as a discrete identifiable unit, it can be moved as such. However, if the alkaline material is laterally discontinuous, or dispersed through the column, a plan to isolate and move this material will be difficult to implement.

- Cost, availability, volume, and quality of off-site alkaline materials:

  Off-site alkaline materials sometimes are imported to a site deficient in alkalinity. These materials may consist of limestone, bag-house lime, or alkaline flyash. These materials all have different costs, availability, and quality, and it may be necessary to cost examine several options. The evaluation includes factors such as particle size, neutralizing value, and the reactivity of the material. In some cases, even though on-site alkaline material may be present, it may be more economical to import material than to redistribute the on-site alkaline material. Alkaline addition is discussed more completely in Chapter 13.

- Mining and equipment:

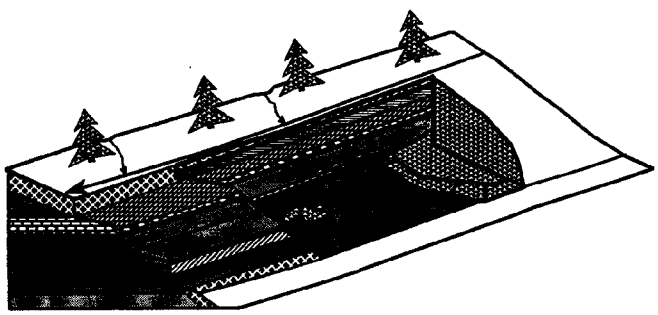
  Equipment availability to add or redistribute the alkaline material is an important consideration in the development of the special handling plan. If the proposal is to move discrete units of alkaline material, a truck-shovel operation may be necessary. In addition, if two pits are open at once, a truck-shovel operation facilitates the movement of overburden from one pit to another. However, if large sections of strata are to be removed, a dragline with a skilled operator may be adequate.

An important aspect of the mining plan is a reasonable estimate of the minimum and maximum final highwalls expected. A special handling plan may require that alkaline material, which is present at high cover, be recovered. If economic conditions change, it may be impossible to continue mining if the alkaline

material needed to fulfill the special handling plan is present only at higher cover.

When the overburden contains significant alkaline material and potentially acid forming material, the location of these two materials relative to each other may provide conditions favorable to alkaline redistribution. For example, if the alkaline section lies adjacent to the potentially acid-forming section, these two materials may become mixed without additional effort during the overburden removal operation, and separation of the potentially acid-forming strata may not be needed. If the alkaline material is located near the upper seam to be mined, and the potentially acid-forming material is located near the lower seam in a two seam operation, a special handling plan can be implemented to place the alkaline material on top of the acidic material in the backfill.

An excess of neutralizers inherent to the site and dispersed throughout the overburden profile is generally necessary to offset both acid production and imprecise mixing. Mixing alkaline strata should balance or exceed the potential acidity. The acid producing rock should be present in discrete and defined zones because this favors effective mixing with a larger volume of calcareous rock. A simple blending plan is shown in Figure 14.10



BLENDING AND ALKALINE REDISTRIBUTION TECHNIQUES

STEPS INVOLVED IN SPECIAL HANDLING ACID AND ALKALINE MATERIALS

1) Conduct drilling and blasting to expose acid and alkaline materials,

2) Remove acid and alkaline materials with a loader or dozer,

3) Blend (mix thoroughly) the acid and alkaline materials, and

4) Complete the reclamation and revegetation as quickly as possible.

Figure 14.10 Blending and alkaline redistribution does not require the isolation of acid-forming materials in isolated pods.

Handling Alkaline Material for Addition and Redistribution

Alkaline addition/redistribution strategies can include:

- Determining the proportions of alkaline material to be placed on the pit floor, mixed into the spoil, and added to the spoil/soil interface,
- Determining the methods for incorporating the alkaline material into the backfill,
- Choosing the best pit orientation to minimize haulage of the alkaline material,
- Designing a multiple pit operation to facilitate redistribution of alkaline material, and
- Ripping the pit floor to expose alkaline material beneath the coal.

These techniques are discussed below:

Placement of Alkaline Material in Mine Backfills

Once a choice has been made to add alkaline material from off-site sources or to redistribute on-site material, the mode of material placement within the backfill must be determined. Past alkaline addition plans focused on placement of alkaline material largely on the pit floor (Surface Mine Drainage Task Force, 1979).

Recently, alkaline addition has focused on the placement of alkaline material at three locations within the backfill; on the pit floor, mixing into the spoil, and placement at the soil/spoil interface. Field evidence suggests that the best chance for the production of alkaline drainage exists when the bulk of the alkaline material is mixed into the spoil. It is believed that infiltrating precipitation will become buffered alkaline water by the time it reaches the pit floor, leaving little opportunity for acid mine drainage production to begin.

Pit floor liming is useful as best management practice and to supplement alkaline addition to the backfill, particularly where the pit floor is composed of high-sulfur material. For complete coverage of the pit floor, at least 44.8 mt/ha (7 t/ha) must be applied. Higher application rates may be appropriate provided that sufficient alkaline material is applied within the backfill. Similarly, supplemental alkaline material can also be placed at the spoil/soil interface. However, because of solubility constraints, this should constitute a relatively small proportion of the total alkaline material to be

applied. Placement of alkaline material in backfills is covered more fully in Chapter 13 (Alkaline Addition).

Methods for Incorporating the Alkaline Material into the Mine Backfill

Deposition of the alkaline material onto the pit floor can be accomplished by the use of trucks or by a dragline. The materials are then spread to cover the pit floor by dozers or loaders. Redistribution of the material into the spoil is more difficult, but can be accomplished by several techniques.

Blasting can be used to help mix the alkaline material into the newly created spoil. One method is to spread the alkaline material around the blast holes so that when the blast is set off, the alkaline material mixes directly into the spoil. This may be especially useful if the operator is using blast casting to facilitate overburden removal. An operator in Lycoming County, Pennsylvania, uses waste limestone, sized at approximately ¼ inch as stemming in the blast holes. The blast holes drilled are 9 inches in diameter and, for the blast pattern used at the site, limestone was added at a rate of 165 mt/ha (27.2 t/ha) for each of the three coal seams removed (Smith and Dodge, 1996). The main benefit of this method is that the alkaline material is thoroughly mixed into the spoil.

Alkaline material can also be added to the blasted rock and spoil. Alkaline material can be dumped onto the spoil by a truck and distributed on the spoil surface by a dozer. This can be done at different depths in the spoil to ensure that the alkaline material is spread throughout the backfill. This method can also be used for a site with blasting to avoid double handling the alkaline material.

A dozer can spread the alkaline material that is to be located at the spoil/soil interface during the rough grading of the backfill.

Operational Constraints Involving the Location of the Alkaline Materials

Several operational constraints arise as a result of the location of the alkaline materials. The orientation of the pit has an important role where alkaline material is located under high cover in the overburden section and is missing or minimal under low cover. In general, the block cuts need to be oriented perpendicular to the slope to intercept both high and low cover overburden sections. Using this method, within each cut, alkaline material is available for placement in the backfill. If the mining were conducted along the contour, the lower cover mining would result in alkaline deficient spoils.

A coal mine operator in Clearfield County, Pennsylvania, approached the high alkalinity/high cover problem in a slightly modified manner. The first cut was taken along contour. Spoil from the cut was stockpiled near the final highwall. The ensuing mining was done with block cuts oriented perpendicularly to the contour. Spoil generated from these cuts contained the alkaline material present at higher cover as well as some lower cover overburden deficient in alkalinity. A portion of this spoil was then used to fill that part of the initial contour cut located below the block cut, as well as the first block cut. A portion of the spoil from the contour cut was used to fill the higher cover part of the block cut, thus effectively spreading the alkaline spoil throughout both the block cut and the contour cut, with the added advantage of producing low cover coal on the first cut.

A second operational constraint arises when multiple mining pits are used to blend spoil. Use of multiple pits is an integral part of a special handling plan when the alkaline unit must be mined separately from the coal. This may occur during single seam mining if an alkaline zone is isolated and will be excavated and redistributed throughout the site. It may also occur on a multiple seam operation, where it is necessary to move alkaline material associated with the overburden of one or more seams to another pit or pits where mining is being conducted on a seam with no alkaline strata.

A mine in Westmoreland County, Pennsylvania used alklaine redistribution to amend carbonate deficient rocks. Acid-forming materials were laterally continuous and had 0.5 to over 2% total sulfur. A zone of calcareous materials, with carbonate content exceeding 20% was present in a few acres at the updip end of the site. The calcareous materials were absent or thin elsewhere. Two of the four acid base accounting drillholes included acidic strata and had NNP's less than zero. Special handling consisted of moving excess calcareous strata from the upper end of the mine and redistributing it in the alkaline deficient areas. Three pits were operated simultaneously. Operations were timed so alkaline material was available and cut and fill balances could be maintained. Material placement and backfilling included crushed limestone on the pit floor, "neutral" spoil backfill, placement of potentially acid material in lifts covered by more "neutral" spoil, and finally topsoil.

Wells and springs have been monitored for four years after reclamation at the alkaline redistribution site (Table 14.2). In Well MW-6, located downgradient of the site, median sulfate concentration decreased about 70%, and net alkalinity rose above zero after reclamation was completed. MP-10, a spring located downgradient of the mine, is representative of shallow groundwater conditions and contains negligible alkalinity. Overburden rocks in the recharge area for MP-10 and well MW-6 were likely acid formers. Postmining water quality for MP-10 and MW-6 show a small but significant increase in net alkalinity. Sulfate concentrations indicate some oxidation and leaching is occurring within the spoil.

Key factors influencing postmining water quality are the redistribution of calcareous rock to alkaline deficient areas, and rapid completion of mining and reclamation. Responses in water chemistry are attributed to placement of acid forming materials above the water table to minimize leaching, while the calcareous rocks are dissolving and producing alkalinity.

Table 14.2 Summary of Water Quality Conditions, Alkaline Redistribution Site

Monitor Point	pH (S.U)	Net Alkalinity (mg/L, CaCO3)	Sp. Conductance (umhos/cm)	Sulfate (mg/L)	Total Fe (mg/L)
MW-6(mining)	6.1	-8	855	398	0.15
MW-6 (postmining)	6.1	24	404	115	1.5
MP-10 (premining)	6.5	6	N/A	19.5	0.04
MP-10 (postmining)	7.1	20	280	90	0.09

Another operational constraint occurs when the alkaline material is located beneath the coal being mined. Ripping the pit floor can be done to incorporate alkaline material into the mine backfill at sites where alkaline strata exist below the lowest coal seam to be mined. This method involves removing the coal and ripping the pit floor to expose the alkaline strata for contact with groundwater on the pit floor. It is a suitable practice if the pit floor or underclay is not acid forming. The operator must have equipment capable of ripping the pit floor to the needed depth and sufficiently breaking up the alkaline zone. Typically an average size dozer can rip to a depth of about 3 ft (1 m), while a D-11 dozer is capable of going to greater depths. If the alkaline material is at a depth greater than the depth accessible by ripping, the overlying material may need to be removed prior to ripping.

Limestone is generally a durable rock and is resistant to abrasion. When ripped, the rock tends to be of a much larger size than that normally associated with alkaline addition or redistribution. Therefore, this method is adequate for mines where alkaline deficiencies are small, as it may have a limited effect on groundwater quality when compared to alkaline addition of fine-grained material or its redistribution in the spoil.

Conclusions

Special handling is one of a group of tools for managing acid materials, and is often used in combination with alkaline addition and water management practices. Placement above the postmining water table is the predominant special handling practice on Pennsylvania surface mines. Plans are site specific. Key concepts include:

- Special handling practices used in Pennsylvania include: blending of acid and alkaline materials, the segregation and isolation of acidic materials (high and dry), management of groundwater, and alkaline addition. Submergence (dark and deep) is seldom used in Pennsylvania.
- Special handling in the absence of alkaline materials cannot produce alkaline drainage.
- Special handling usually involves **both** acid and alkaline materials and may also include clay materials for capping and lining pods of acidic materials, and boulders for use in drains, trenches, and ditches.
- Special handling is most effective in conjunction with alkaline addition, surface and groundwater management, and other techniques.
- The volume of the material to be special handled should generally be less than 20% of the mine backfill volume because of the need to keep acidic materials away from the surface, water table, highwalls, etc.
- Special handling is not necessary on all mine sites.
- Identification and segregation of acid material is extremely difficult if multiple zones exist in the stratigraphic section unless: 1) blasting is not used to remove the overburden, 2) the acid zones are persistent (laterally and vertically), uniform in thickness, and distinctive in appearance.
- Special handling requires that the proper equipment be used at the mine site.

- Monitoring during and after mining is necessary to evaluate special handling techniques

Effectiveness of special handling has been evaluated in a few case studies and the results are frequently beneficial. Special handling may not totally prevent postmining water quality impacts, however. Special handling cannot be relied upon by itself to prevent acid generation, but should be used as one of a collection of best management practices. Many questions remain as to the effectiveness of special handling, the most advantageous placement of materials, how to best isolate acidic materials, how to best promote dissolution of calcareous materials, and so forth.

Appendix

INDUSTRY EXPERIENCE WITH MINE PLANNING AND SPECIAL HANDLING

David Maxwell

Introduction

This section describes the approach of one mining company to management and prevention of acid materials and drainage, from exploration through mine planning and operating procedures.

Exploration and Planning

Premining determination of groundwater and surface water quality and quantity, and overburden quality are the most important factors in determining a site's mineability and potential production of AMD. Each of these items can be documented and understood prior to mining. A special handling program that addresses these factors can be designed and implemented during mining. The result should be a successful surface mined site with no adverse affects to the environment.

After each potential mine site is core drilled and the coal has been determined to be marketable, an extensive amount of engineering is done to determine groundwater and surface water quality and quantity and overburden analysis. To expand on these three factors, the following sections look at how each is handled premining and followed up in the field for implementation.

Groundwater

In order to form AMD in minespoil, groundwater must be present. Therefore, it is important to determine the amount and chemical composition of groundwater that exists prior to mining an area. This step is simply accomplished through measuring static water levels, and drawdown and recovery testing of core holes. Certain holes are left open and capped after the initial drilling has taken place. These holes are then pumped completely dry and then measured for the time it takes to recharge to a static water level. If a hole recharges quickly, it can be assumed that there exists a good possibility of appreciable groundwater inflow during mining and reclamation on the site. Likewise, if a hole takes much more time to reach its equilibrium, if at all, then little or no groundwater inflow may occur during mining and reclamation.

One must also take note that drawdown and recovery tests are indicators and not full scale aquifer tests. Strike and dip of the formation, stratigraphy, and the presence of fractures affect the magnitude and direction of hydraulic flow and head pressures.

It is also important to know the groundwater quality prior to mining. Water in the open core holes can be sampled after pumping, and tested for its chemical composition. The presence of alkalinity in premining groundwater can be useful for indicating the presence of "neutralization potential", or carbonate minerals, in the overburden.

As stated previously, groundwater can be handled during mining to help prevent the formation of AMD. Highwall drains and anoxic drains can be constructed to carry groundwater safely away from mine spoils to natural surface drainage ways. This must first be accomplished prior to mining by determining the strike and dip of the coal seam to allow for the engineering of the drains for easy construction during mining. Once the mine site is laid out, the actual construction of the drains should be a simple procedure.

After all coal is loaded away from the highwall and the coal waste is cleaned up from the pit floor, an impervious barrier is placed on the pit floor. The area against the highwall is then lined with 4 in (10.2 cm) limestone approximately 6 to 10 in (15.2 to 25.4 cm) thick, which will act as a french drain. A 4 to 6 in (10.2 to 15.2 cm) flexible perforated pipe can also be used in conjunction with the aggregate. This procedure is carried out throughout the life of the mine site in each successive block cut to insure the groundwater draining from upslope areas will be safety conveyed through an alkaline drain past the mine spoils and discharge to a natural drainageway without encountering acid-forming materials.

Another procedure Amerikohl has concluded to be effective in preventing AMD has been the elimination

of coal crop barriers. Contrary to past industry standards, the elimination of crop barriers allows free flow of water from mine spoils, preventing "pooling" in the backfill, thus preventing chemical reactions in the spoil.

Surface Water

As with groundwater, the more surface water which can be redirected from the mine spoils, the better chance you will have in elimination of postmining AMD. At Amerikohl mine sites, the field personnel try to redirect as many natural springs and wet weather drainage courses as possible. This is simply done by constructing upland diversion ditches and redirecting the water, which would normally flow into our mine sites, away from the site and to a natural drainageway. Not only are upland diversions beneficial in the reduction of surface waters influencing the mine spoils, but they are also relied upon to reduce the erosion, which can take place after reclamation.

Overburden Quality

Finally, another important step in prevention of AMD is the determination of overburden quality, the recognition of acid bearing rock strata, and the special handling of those strata.

During initial core drilling operations, strategically placed overburden holes are drilled to collect one-foot intervals of rock chips using an air rotary drill. In addition, Amerikohl likes to core the areas above and below the coal seam to further define the thickness of possible acid-forming rock and to prevent contamination of those units by coal chips. These overburden chips are then logged and sent away for lab analysis. Using this lab work, mass balance computations can then be made through the recognition of acidic and alkaline rock formations. For the most part, if the mass balance ratio of alkaline material to acidic material does not come out to a 2 to 1 ratio, the site most likely will no longer be evaluated as part of Amerikohl's future mine plans. If you cannot predetermine potential AMD through the accumulation of strong data, then the site is without merit regardless of the economic value of the coal.

Special Handling Implementation

Once a proposed site is deemed minable based on analysis of good data; the implementation of the site specific special handling plan becomes important. While there have been a few different special handling techniques used at various Amerikohl mine sites to be discussed later, there still exists many commonplace procedures at each site which contribute to the overall success of a mine.

Mining Methods

Amerikohl employs the modified block cut method of mining at its mine sites. This entails simply hauling the initial two cuts of overburden from the coal outcrop to final highwall away to a place where it will be deposited in the final open pit. Subsequent overburden cuts are then placed in the open cut created before it, and so forth. Topsoil and subsoil are saved for final reclamation. The benefit of block cut mining is it automatically lends itself to concurrent reclamation. This ultimately helps prevent the generation of AMD and promotes environmental protection.

Normal equipment fleets located on each site consist of no less than one Caterpillar DION dozer, one Caterpillar 988B front end loader, two 40 to 50 ton rock trucks, and various coal loading, coal crushing, and grading equipment.

After the coal is mined from each block cut, the operators take special care to make sure that all coal waste and inferior or "boney" coals are either trucked or carried out of the pit area to a location high in the backfill, but away from the final highwall. This eliminates the possibility of the coal waste coming in contact with groundwater. The cleaned pit area is then lined and compacted with an impervious material such as clay. Anywhere from 6 in (15.24 cm) to 5 ft (1.5 m) of material is placed on the pit floor depending on the quality and availability of the material on site. Once the pit floor is sealed off from water contact, a limestone waste or other calcareous material is then placed at an average rate of approximately 448 mt/ha (73.4 t/ha) of 100 % $CaCO_3$ equivalent.

As with the coal waste, potentially acidic rock strata and alkaline strata as documented by the overburden analysis, are also special handled. These overburden zones are recognized in the field by highwall observation in relationship to the drill log data, and also by field fizz testing of the alkaline zone with the use of 10 % HCl acid. When those mine sites with special handling procedures are being developed, extra care is taken to educate the mine supervisor and equipment operators on their awareness of those zones to be special handled. Without exception, acidic materials are trucked or carried high in the backfill for much the same reasons as the pit cleanings are hauled. This procedure allows for the potentially acidic mate-

rial to be placed at a location high in the backfill away from surface and groundwater infiltration. In conjunction, the alkaline material, if present, is also trucked or placed in lifts with the acidic materials.

The typical Amerikohl surface mine has a job life of approximately 5 months from initial development through final reclamation. Within this average there have been mine sites which have lasted less than 1 month, to an uncommon 18 months. This type of short lived mine site lends itself to a continuously aggressive acquisition and development program to find not only coal which is of economic value, but also a site which is environmentally conducive to surface mining.

Concurrent Reclamation

One of the most beneficial of all the procedures at an Amerikohl mine site in the prevention of AMD is its concurrent reclamation process. Never is there a time when an area which has been mined and reclaimed to approximate original contour, gone past a growing season without the placement of subsoil and topsoils, then seeded and mulched. This simple and necessary function helps to eliminate and seal off surface water infiltration in addition to the reduction of liability.

Finally, while the logic behind the special handling of acidic and alkaline material seems to be a constant, the varying techniques implemented at Amerikohl mine sites differ with the location of each area as it relates to the regulated receiving stream classification. The three specific special handling techniques for alkaline materials have been:

- Alkaline amendment (purchased)
- Alkaline amendment (within overburden column)
- Alkaline redistribution

Alkaline Amendment (Purchased)

Certain times when the overburden indicates that the mass balance equation would show that the mine site would be capable of alkaline post mining discharges, it is still a good idea to provide alkalinity to the backfill to ensure positive results. Therefore, in those cases it is necessary to incorporate alkaline material in the mine spoils which is purchased and brought into the mine site. At a few Amerikohl mine sites, an alkaline amendment has been trucked in and incorporated in lifts within the mine spoils.

Alkaline Amendment (Within Overburden Spoils)

Some sites possess the ability to produce alkaline waters through their own inherent overburden characteristics. In these cases, there exists certain zones of alkaline material within the rock strata which will be mined as a course of uncovering the coal.

In these cases, operator awareness is necessary due to the importance of singling out the alkaline rock to segregate and special handle. The operator is first given a general location of the alkaline rock based on the overburden analysis, then a field fizz test is administered to tie down the location. Then the alkaline rock is segregated and trucked to the area where it is to be placed in lifts within the backfill and incorporated with the acid bearing materials.

Alkaline Redistribution

The final and certainly the most broad-minded approach to special handling is alkaline redistribution. In simple terms the redistribution of alkaline material is no more than special handling alkaline material within the permit area, but not an actual part of the coal removal area, to a place where coal overburden is taking place for use as an alkaline amendment. In this particular case, the alkaline material can originate from below the coal seam to be mined, or from an area above the final highwall.

Using a more specific description; alkaline redistribution consists of incorporating alkaline material within mine spoils to meet or exceed a minimum mass balance ratio or 2 parts alkaline material to 1 part acidic material.

Actual implementation of alkaline redistribution is impossible without the use of rock trucks, since the alkaline amendment is not an integral part of coal overburden removal. Once the amount of alkaline amendment per acre affected is calculated via overburden analysis and mass balance equations, it is important that a sufficient stockpile is maintained. Once a stockpile has been built, the actual implementation of alkaline redistribution is the same as all of the special handling techniques (i,e. place alkaline material in lift with acid bearing material).

In conclusion, past experience with the success of the mine sites Amerikohl has completed has brought the realization that as much homework that can be completed prior to a particular property being surface mined, the better chance that site has to produce alka-

line, low metal discharges. That is, after all, what everyone involved in the industry is striving to achieve.

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Chapter 15

BACTERICIDAL CONTROL OF ACIDIC DRAINAGE

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Introduction

As previously discussed in Chapter 5, iron-oxidizing bacteria can play a critical role in determining the rate of pyrite oxidation. The kinetics of acid formation are dependent on the availability of oxygen, the surface area of exposed pyrite, the activity of iron-oxidizing bacteria, and the chemical characteristics of the influent water. *Thiobacillus ferrooxidans* is generally regarded as the principal iron-oxidizing bacterium involved in pyrite oxidation (Leathen et al., 1953; Kleinmann and Crerar, 1979). Acidification progresses in a three-stage sequence dependent upon the activity of *T. ferrooxidans* and solution Eh and pH (Kleinmann et al., 1981). The bacteria serve as a reaction catalyst.

During the first stage of this process, fine-grained pyrite can be directly oxidized by *T. ferrooxidans* or can be abiotically oxidized by air, with equal amounts of acidity produced by the oxidation of sulfide to sulfate and by the hydrolysis of Fe^{3+}. During this stage, it is possible to forestall acidification by adding alkalinity (lime, limestone, etc.) to the reaction system; if alkalinity exceeds acidity, the only major downstream effect is an increase in sulfate concentration. As the pH declines, abiotic oxidation of Fe^{3+} slows as much as 100-fold for each pH unit, and *T. ferrooxidans* takes on its primary role of oxidizing Fe^{2+}. This transition stage is referred to as stage 2. Stage 3 begins when the decreased rate of $Fe(OH)_3$ precipitation results in increased Fe^{3+} activity. The Fe^{3+} rapidly oxidizes the pyrite, producing Fe^{2+} that is then oxidized by the bacteria to Fe^{3+}. This cyclical reaction series greatly accelerates the rate of acid generation at many mine sites.

The importance of oxygen availability is illustrated in Fig. 15.1. At oxygen concentrations above 14%, the rate of abiotic pyrite oxidation is essentially equivalent to what is observed when the bacteria are present and active. However, at lower oxygen levels, the bacteria assume greater importance. For example, at 1% oxygen, the rate of reaction is over seven times faster if the bacteria are active (Hammack and Watzlaf, 1990).

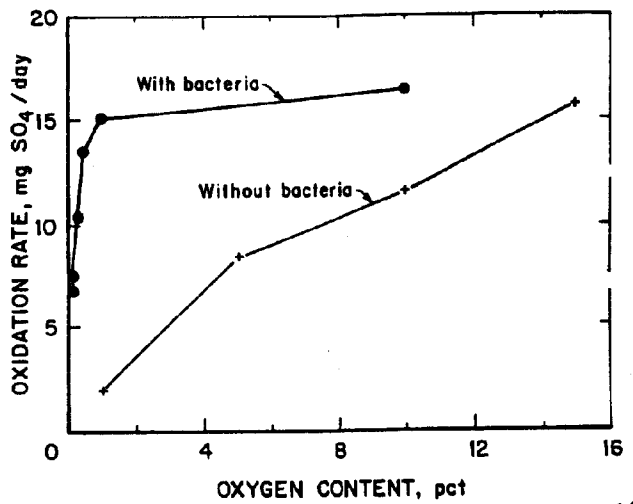

Figure 15.1 Rates of pyrite oxidation with and without iron-oxidizing bacteria in small columns maintained at different oxygen partial pressures (Hammack and Watzlaf, 1990).

Thus, bacterial catalysis is probably not critical in well-ventilated sections of active underground mines but could be very important once the mine is abandoned. In unconsolidated, highly permeable mine spoil, oxygen concentrations often exceed 15%, but in coal refuse piles and low-permeability, shaly spoil, oxygen concentrations decrease dramatically with depth, effectively limiting abiotic pyrite oxidation to a thin near-surface layer less than a meter thick (Erickson et al., 1982; Guo and Cravotta, 1996).

In mine environments where bacterial activity determines the rate of acid generation, inhibition of these bacteria can prevent acidification or greatly reduce the acidity that is produced. This possibility was first considered in 1953 but was rejected as probably impractical (Leathen, 1976). Unsuccessful attempts followed in the 1960's (Barnes and Romberger, 1968; Shearer et al., 1970), followed by successful efforts over a decade later (Kleinmann, 1979; Kleinmann and Erickson, 1982).

The biological literature contains numerous studies of *T. ferrooxidans* that indicate a vulnerability to

certain metals (such as mercury, tellurium, and molybdenum), thiocyanate, organic acids, anionic surfactants, and food preservatives (Schnaitman et al., 1969; Tuovinen et al., 1971; Imai et al., 1975; Dugan, 1975; Tuttle et al., 1977; Onysko et al., 1984; Sobolewski, 1993). Only anionic surfactants and a food preservative have warranted field testing, and only the surfactant approach has been shown to be cost effective (Kleinmann and Erickson, 1982; Watzlaf, 1986).

Use of Anionic Surfactants

Surfactant Solutions

Anionic surfactants are commonly regarded as good cleansers but poor bactericides (Walters, 1965), as opposed to the germicidal cationic surfactants commonly used in hospitals. However, it has been shown that anionic surfactants are markedly more inhibitory at low pH (Dychdala, 1968). The various means by which surfactants affect microorganisms have been summarized by Hugo (1965), who concluded that alteration of the semipermeable properties of the cytoplasmic membrane is the most typical mode of inhibition. *T. ferrooxidans* possesses a multilayered cell wall, which allows it to maintain an approximately neutral internal pH despite the extremely acid environment in which it lives (Howard and Lundgren, 1970; Adapoe and Silver, 1975; Langworthy, 1978; Ingledew, 1982). At low concentrations, it appears that anionic surfactants induce seepage of H^+ into the cell, which slows Fe^{2+} oxidation by decreasing the activity of pH-sensitive enzymes. Higher concentrations of the surfactant kill the bacteria, presumably by causing permanent damage to these enzymes and the membrane material (Hotchkiss, 1946; Lundgren et al., 1974; Dugan, 1975; Kleinmann, 1979).

Figure 15.2 shows the effect of three anionic surfactants on acid generation in the laboratory. Sodium lauryl sulfate (SLS) was the most effective, killing *T. ferrooxidans* at 25 mg/L; alkyl benzene sulfonate (ABS) and alpha olefin sulfonate (AOS) required somewhat higher concentrations.

Based on these laboratory results, field tests were initially conducted using SLS as the inhibitory agent. Five hundred and fifty gallons of a 30% solution of SLS was diluted 175:1 with water and applied with a hydroseeder to an 11 ac (4.4 ha) inactive coal refuse pile. Water quality improved after a 3 month lag period, with a 60% decrease in acidity, sulfate and manganese and a 90% decrease in iron concentrations

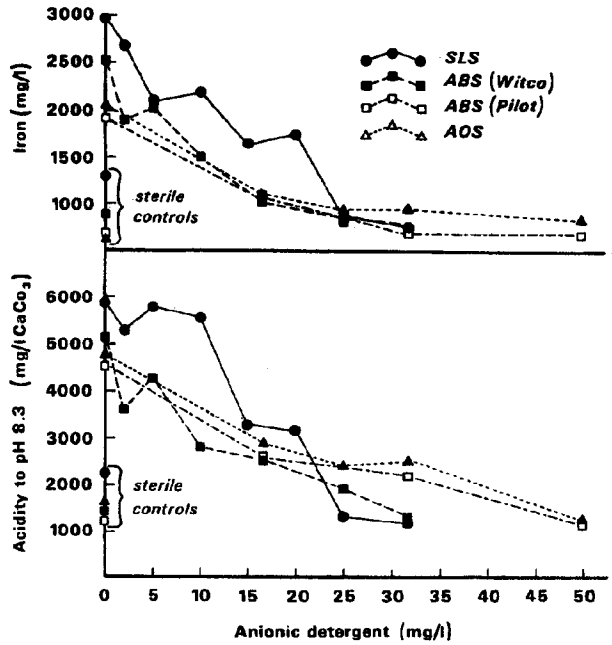

Figure 15.2 Effect of anionic detergents on acid production from pyritic coal. SLS = sodium lauryl sulfate, ABS = alkyl benzene sulfonate, AOS = alpha olefin sulfonate (after Kleinmann, 1979).

(Kleinmann and Erickson, 1981, 1983). The lag period was presumably caused by the time required for infiltration to flow through the old pile, but stored acidity in the form of sulfate salts was probably also a factor (see Chapter 1). The magnitude of the improvement was greater than any change observed over the prior 10 years, and seasonal effects can be discounted, since in previous years the contaminant concentrations peaked in winter.

Figure 15.3 illustrated the results of a similar application to an active refuse pile in northern West Virginia. Runoff water quality improved dramatically within a month of the SLS application. Acidity, sulfate, and iron concentrations were reduced by more than 95% and remained low for about 4 months after treatment.

Effluent concentrations of surfactant were extremely low at both sites. Except for one measurement of 0.6 mg/L shortly after application of the SLS to the inactive pile, SLS concentrations were consistently less than 0.1 mg/L; no SLS was detected in the stream at the discharge point of either treatment plant.

As a result of these tests, mining companies began to apply surfactant solutions at active refuse and coal storage piles. Initially, SLS was used, but it was subse-

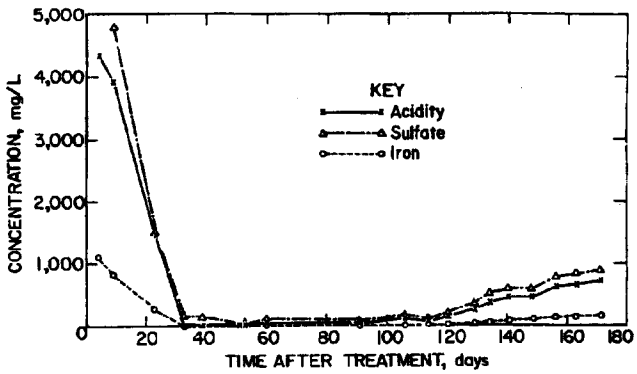

Figure 15.3 Effect of sodium lauryl sulfate on runoff water quality at 8-acre active coal refuse pile in northern West Virginia. Application rate: 55 gal/ac (93 L/ha) of 30% solution, diluted 50:1 (Kleinmann and Erickson, 1983).

sequently found that ABS, which is a common ingredient in many laundry detergents, was more cost effective. At such sites, the surfactant solution is either diluted and applied to the pile periodically (3-4 times a year) or sprayed onto fresh refuse just before it is added to the pile (Rastogi, 1996). Either approach avoids the problem of bacterial reestablishment, which can be observed occurring 120 days after initial treatment in Figure 15.3.

It should be noted that the U.S. EPA regulates the use of bactericides under the Federal Insecticide, Fungicide and Rodenticide Act (FEFRA). Therefore, only those surfactant or bactericide formulations that are registered under FIFRA can legally be used to avoid or abate acid generation.

Slow-release Formulations

Periodic or continuous application of surfactant solution can be appropriate at an active site where new pyritic material is always being added, but cannot be continued after the pile is completed and revegetated. The surfactant would be adsorbed by the soil and never reach the pyritic material. If pyrite oxidation is allowed to proceed unchecked beneath the soil cover, the roots of the vegetation will be exposed to acidic water and will wither away; soil erosion will soon follow.

To counteract this problem, slow-release surfactant pellets that could be applied before the soil cover were developed (Kleinmann, 1982). The surfactant migrates from the interior of the pellet to the pellet surface to replace the surfactant that is dissolved each time the pellet gets wet. Initial formulations used a rubber matrix and lasted about 2 years. Subsequent formulations made of polyethylene and developed for commercial applications have release lifetimes of 6 or more years (Splittorf and Rastogi, 1995), assuming that a soil cover is applied and revegetation commences soon after the surfactant application. The release lifetime is intended to allow time for vegetation and normal soil bacteria to become established in the topsoil layer, consuming the oxygen that would otherwise fuel pyrite oxidation.

Based on a recent revisit to a ten year old field test, it appears that this premise is valid (Splittorf and Rastogi, 1995). The 1984 field test was conducted by the Ohio Department of Natural Resources using an early slow-release formulation: SLS in a rubber matrix. SLS was applied in solution (at the rate of 225 kg/ha) and as pellets (575 kg/ha, containing 16-28% SLS) to a 1.0 ha section of a regraded refuse pile. An adjoining 0.9 ha section received no surfactant and served as a control. Both areas were then covered with 15.2 to 20.3 cm of topsoil, fertilized, limed, seeded and mulched.

Water quality, vegetative cover and activity of normal soil bacteria were all markedly improved by the bactericidal treatment (Sobek et al., 1990). These improvements were sustained long beyond the 2 year lifetime of the pellets. Five years after reclamation, biomass production was nine times greater (2915 kg/ha vs. 315 kg/ha) and acidity in the vadose zone was 80% lower in the treated area than in the control plot. After 10 years, 35-40% of the control area is barren and eroding; the treated area has no significant erosion and 4,118 kg/ha of biomass, including extensive volunteer vegetation (Splittorf and Rastogi, 1995).

The only published results of the first field trial of the ABS polyethylene pellets indicated a similar level of success after 3 years. Acidity was reduced by 96%, sulfate concentration was reduced by 91%, and total iron concentration was reduced by 97%. Biomass production totaled 1,604 kg/ha in the surfactant-treated area, compared to 1,033 kg/ha on the control area (Sobek et al., 1990). Subsequent field applications have no control area for comparison but appear to be effectively preventing or delaying acidification of selectively handled mine spoil and improving water quality by 82-90% at active coal refuse areas (Parisi et al., 1994).

Procedural Recommendations

Surfactants have proven to be cost effective when applied directly to highly pyritic material. Since the

surfactant must reach the pyritic material to be effective, sites that have been reclaimed with topsoil or backfilled with non-pyritic overburden are generally not appropriate for surfactant treatment. The surfactant will absorb onto the intervening material and never reach the pyrite.

Another factor to be considered is the response time before a surfactant application has an effect on site effluent water quality. Response time is determined by groundwater flow-through time and stored acidity. Groundwater flow-through time is the time it takes for rainwater to infiltrate through the mine material and emerge in a spring or seep. This can vary tremendously from site to site but improvement in water quality at the discharge point cannot occur faster than groundwater flows through the material.

Acidity can be stored as metal sulfate salts that dissolve over time, or ponded as acidic water on the old mine floor or in a refuse area. Such stored acidity retards or masks the effect of reduced acid production. The presence of substantial amounts of stored sulfate salts is indicated if high flows are accompanied by high concentrations of contaminants. The presence of acidic groundwater can sometimes be surmised by a steady acid load in the base flow during dry periods and only slight changes in the acid load during higher flows. If the stored acidity is significant, it could be several months before a decrease in acid production is reflected by more than a gradual improvement in water quality. If faster results are desired, alkalinity must be added to the site in sufficient quantities to neutralize the acidity.

Application rates are largely site-specific, and are heavily dependent on the adsorptive capacity of the material being treated. Laboratory tests have been developed to evaluate this aspect (Kleinmann and Erickson, 1983). However, if one is trying to evaluate the potential cost-effectiveness of applying a bactericidal treatment, consider setting up pilot-scale field tests in well-washed, plastic 55 gallon drums. Rastogi et al., (1995) have shown that small test piles do not accurately simulate larger sites, presumably due to the fact that oxygen concentrations are unrealistically high in the small test piles.

Both hydroseeder and road-watering trucks have been used by mine operators for application of the surfactant solution. With either machine, it is important to add the water to the tank at the bottom (using a hose) to avoid excessive foaming. For the same reason, agitation should be avoided as much as possible. Care should be taken when dealing with the concentrated surfactant; gloves should be worn to avoid "dishpan hands," and contact with the skin and eyes should be avoided. Finally, it is recommended that the tank and hoses be thoroughly rinsed of all surfactant after the application is completed, as the concentrated solution can cause pitting if allowed to remain.

Controlled-release pellets should be applied along with a surfactant solution to pyritic material just before the material is covered with soil or clay. A hydroseeder can be used. The surfactant solution satisfies the adsorptive capacity of the pyritic material; without it, the surfactant released by the pellets will reach very little of the reactive material. Alkalinity can be applied along with LAS (an important advantage over SLS) if needed to neutralize already-formed acidity.

Ongoing Research

Researchers periodically evaluate alternative bactericides for potential cost effectiveness or extended duration of treatment relative to anionic surfactants. Recently, thiocyanate was investigated in the laboratory; unfortunately, it proved to be effective for only 30-60 days. Apparently, it was converted to ammonia (Sobelewski, 1993).

An earlier laboratory study, evaluating alternative antibiotics and antibacterial agents, identified nitrapyrine as an effective inhibitory agent. Nitrapyrine is the active agent in a commercially-available nitrification inhibitor. However, the nitrapyrine did not appear to be as cost effective as the less expensive anionic surfactants (Sherrard et al., 1990).

Researchers are beginning to evaluate the role that bacteria play in catalyzing acid generation in underground mines and whether it is possible to control their activity in such an environment. Due to the high oxygen concentrations in an active, ventilated mine, the bacteria may be less critical in such an environment; however, they are probably very important in unflooded or partially flooded abandoned underground mines. Inhibitors applied in solution would not be appropriate in such an environment. An inhibitory gas or vapor that can permeate into rock fractures, or a fine mist or aerosol of one of the established inhibitors, may be better. Alternatively, potentially inhibitory compounds with low vapor pressure could be effective; acrolein (2-propanol) for example, kills *thiobacilli*, though the possibility of groundwater contamination may preclude its use. Another option is to alter the

environment so as to ecologically favor bacteria other than *T. ferrooxidans*.

Summary

At present, anionic surfactants are the only appropriate means to directly inhibit the iron-oxidizing bacteria that catalyze acid generation. Surfactants have proven to be cost effective when applied directly to highly pyritic material; they delay or prevent acidification and reduce pyrite oxidation rates 60-95%. They are most effective when applied to compacted or fine-grained material, where most of the pyrite oxidation is occurring near the site of treatment. Dilute surfactant solution can be applied to exposed pyritic material 3 to 4 times a year or can be applied to fresh waste material as it is being transported for disposal. Controlled release of surfactants is appropriately used just before the pyritic material is covered with non-pyritic material; such an application has been shown to have long term benefits with respect to water quality and revegetation.

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Chapter 16

WATER MANAGEMENT TECHNIQUES ON SURFACE MINING SITES

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Introduction

Water plays a key role in the formation and transport of mine drainage. It is an essential part of the pyrite oxidation process and necessary for dissolution of neutralizing minerals such as calcite and dolomite (see Chapter 1). It is also the transport medium for pyrite oxidation and neutralizing products. Although water is an integral part of the mine drainage process and has been extensively studied in the context of mine drainage prediction and prevention, limited research has been done on the subject of water management techniques on surface mining sites. This chapter will examine the available literature and discuss water management case studies.

There are three primary means by which water enters surface mine spoil (Figure 16.1). These are surface infiltration (from precipitation and/or snowmelt), groundwater inflow from the highwall, and upward leakage from underlying aquifers (in groundwater discharge areas). All three can be important although the two primary players are surface infiltration and groundwater inflow from the highwall.

There are at least four means of managing water on surface coal mines. The first is to minimize infiltration into the spoil surface. A second is to minimize the contact time between groundwater and acid-producing mine spoil. A third is to promote the contact of infiltrating water with calcareous materials in the mine spoil. The fourth is to submerge acid-forming materials below the water table (flooding).

Examples of the first method include highwall diversion ditches and final surface grades which promote surface runoff. An example of the second method is spoil drains, which will be discussed in detail in this chapter. The third method usually employs trenches filled with alkaline materials strategically positioned to receive surface drainage from the mine before the drainage infiltrates into the backfill (Caruccio and Geidel, 1984). This method is designed to enhance the dissolution of calcareous minerals by promoting water contact with these minerals. Wirem and Naumann (1996) used a variation of this concept when they constructed alkaline material-filled trenches on top of highly permeable "chimney drains." In some ways this third method is a variation on alkaline addition, which

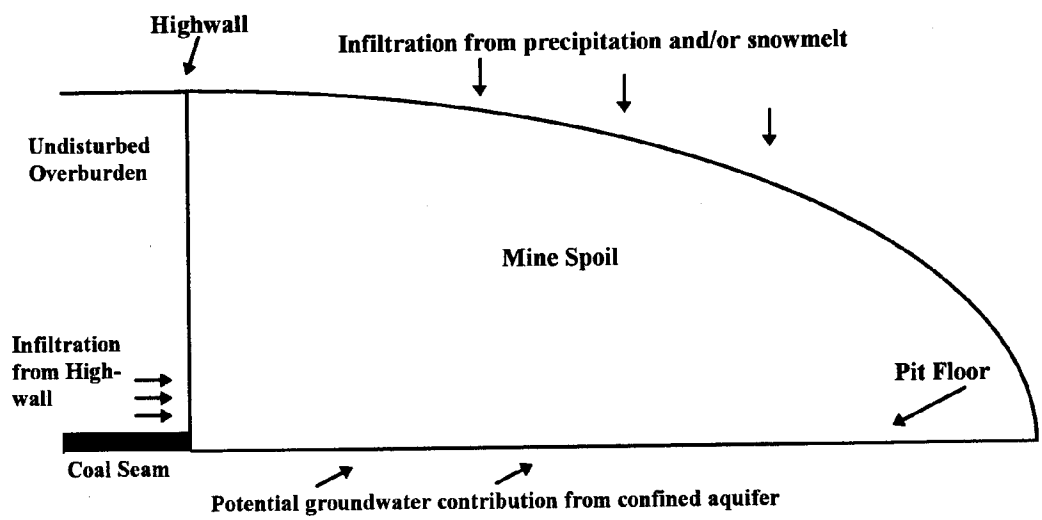


Figure 16.1 General schematic of mine site hydrology.

is discussed in Chapter 13. The fourth method, flooding, takes advantage of the limited amount of oxygen that can be dissolved in water. This topic is discussed in more detail in Chapter 14 which deals with special handling of acidic overburden.

Some of the earliest research pertains to the fourth method. Leitch et al. (1930) found that acidity concentrations from flooded deep mines were generally lower than in water from up-dip mines. Additional research in the mid-1930s revealed that flooded deep mines had 60 percent lower acid loads than non-flooded mines (Mihok and Moebs; 1972). Studies show that atmospheric oxygen, which is needed for pyrite oxidation, is greatly reduced under submerged conditions (Singer and Stumm, 1970; Watzlof and Erickson, 1986). Flooding, however, is generally impractical for surface coal mines. Most surface mines are located in groundwater recharge areas and spoil hydraulic conductivity is often too high to maintain a thick saturated zone. Additionally, the water table can experience short-term fluctuations due to precipitation events and can fluctuate seasonally. Thus portions of the spoil may be alternately saturated and unsaturated Perry et al. (1997) discuss two sites in the Appalachians where attempts at submergence failed because of an inadequately thick saturated zone and/or a fluctuating unsaturated zone.

The water management practices discussed below focus on the control of surface water runoff and infiltration, and groundwater management. Groundwater management is emphasized in this chapter and several case studies illustrate the use of highwall drains.

Management of Surface Water

Erosion and Sedimentation Controls

Although relatively simple, an adequate erosion and sedimentation plan is an essential component of water management on surface mines. Well designed and constructed erosion and sedimentation controls can prevent a significant amount of infiltration into a mine site. Poor controls may add to the problem. The use of erosion and sedimentation controls has been a recommended practice since the mid-1950s (Braley, 1954; Brant and Moulton, 1960).

An erosion and sedimentation control plan generally consists of sedimentation ponds and a network of associated collection and diversion ditches. Specific erosion and sedimentation features used to minimize surface water infiltration on a surface mining site include:

Diversion ditches: These features are positioned where they will divert surface water away from a surface mine site. They are usually located above the final highwall or in areas where it is necessary to divert surface flows away from spoil material. Diversion ditches may not be needed on all mine sites due to topography or the presence of highwall berms or topsoil piles. Nevertheless, their function to prevent excessive infiltration of surface water into backfilled spoils is often overlooked and should be considered in mine planning.

Collection ditches: The purpose of collection ditches is to collect runoff (mostly from precipitation) from active or recently backfilled areas and convey it to sedimentation ponds in a non-erosive manner. Collection ditches are normally located in undisturbed ground below the mining area; however, they may at times need to be constructed in relatively permeable spoil material. When constructed in spoil, collection ditches may direct large quantities of water into the backfill. To prevent this, ditches in spoil should be lined with impermeable material to prevent infiltration. Additional factors to consider are: (a) the elimination, where possible, of cross-site ditches; and (b) removal of ditches once vegetation is fully established. Promoting rapid reclamation and revegetation of the site will allow for rapid removal of these features.

Sedimentation and treatment ponds: As with collection ditches, ponds should be located with regard to possible infiltration of water. If constructed in spoil material and not lined properly, large amounts of infiltration are possible. Ponds should be located in original ground where practical or lined with impermeable material. Experience has shown that it is better to construct ponds in original ground rather than attempting to line them. Ponds to be left as permanent features or in acid mine drainage (AMD) prone areas should not be constructed in spoil.

Control of Surface Water Infiltration

Reclamation and revegetation can reduce the production of AMD by promoting surface runoff and evapotranspiration, thus minimizing infiltration into the backfilled spoil. The effect of reclamation and revegetation on mine drainage production is discussed in Chapter 12. Another method to reduce surface water infiltration is the construction of a low-permeability barrier immediately below the topsoil and subsoil. This barrier can be composed of clay or other suitable material such as a fly-ash cement (Sheetz et al., 1997). Barriers to infiltration can be constructed using con-

ventional mining equipment but can significantly increase the cost of reclamation. Also, other considerations such as slope stability and soil suitability for reclamation must be taken into consideration. Although a promising technique, this approach has been used sparingly and mostly as an abatement technique for sites that already have poor quality discharges. In one documented case (See Case Study 2), normal postmining flows were decreased by two-thirds after application of a three-foot compacted clay cap.

Speed of Reclamation

AMD problems may decrease significantly when sites are mined and reclaimed quickly (Perry et al., 1997). Rapid reclamation reduces the amount of available water as well as its contact time with acid-forming materials and limits the time available for pyrite oxidation, two important items in acid production (Chapter 1). One method to help insure rapid reclamation is to limit the total surface area disturbed and unrevegetated at any one time. Another is to minimize the temporary cessation of backfilling. Although Pennsylvania's mining regulations (25 PA Code, Section 87.157) do allow for suspension of mining, recent research has indicated that this can be the catalyst for AMD problems, especially on marginal sites (Perry et al., 1997).

Case Study 1 substantiates this point. The site was mined such that no vegetative cover was present over the winter season which resulted in combined flows of over 100 gpm (378 lpm) from the site. Once vegetation became established the following spring, the combined flow decreased by more than 80 percent.

Groundwater Management

Control of groundwater flow is not a new water-management technique. Several other disciplines use varying techniques such as grout curtains, interceptor trenches and rock drains to control surface and/or groundwater. For the most part, these have been fairly successful and have resulted in numerous articles including those by Atwood and Gorelick (1960), Gilbert and Gress (1987), Zheng, Bradbury and Anderson (1988), Das, Claridge and Garga (1990), and Duchene and McBean (1992). What is relatively new, however, is the application of these techniques to the surface mine backfill environment in order to prevent or minimize AMD formation.

Highwall Drains

Mining operators through the years have used various forms of drains in controlling water on surface mining sites. Some examples are rock drains under spoil piles and the establishment of first (or last) cut drains through the lowwall. Although very little literature is available on this subject, it is discussed in PA Department of Health (1958), Brant and Moulton (1960), and Perry et al. (1997).

In the last few years, however, the Pennsylvania DEP has conducted field studies on highwall drains on several mine sites. The idea behind highwall drains is quite simple; collect groundwater entering a mine site

Table 16.1 Highwall drain water quality from 5 Pennsylvania mining sites.

Site	Drain #	N	pH	Alkalinity mg/L	Acidity mg/L	Fe mg/L	Mn mg/L	Al mg/L	SO_4 mg/L	Location
1	1	26	6.49	228	0	5.26	8.55	0.42	122	Westmoreland County
1	3	16	6.63	273	0	18.4	6.92	0.47	160	
1	6	7	6.48	330	0	4.75	6.61	0.44	107	
1	7	9	6.34	226	0	14.5	7.85	0.77	72	
1	8	10	6.59	274	0	6.52	13.1	0.47	188	
2	1	82	6.9	280	0	5.85	19.5	0.79	945	Greene County (BOY)
3	1	12	6.48	200	0	1.54	5.49	0.89	571	Highwall Drain
3	2	10	7.36	151	0	1.07	1.02	1.07	369	Lowwall Drain
4	1	41	6.43	79	0	15.4	6.63	0.5	459	Raw Water
4	1	20	6.55	43	0	0.44	0.86	0.25	342	Bog Discharge
6	1	10	6.84	408	0	0.47	1.51	0.53	499	Greene County (BAL)

before it comes into contact with mine spoil and convey it rapidly through the site with minimal contact with spoil. In this manner, groundwater largely unaffected by mine drainage will "bypass" most potentially acid-forming material (i.e., pit cleanings and pyritic spoil) and exit the site with minimal chemical change.

The study sites fall into two categories: those that exhibited marginal overburden quality characteristics (i.e., near neutral or slightly acidic), or those where hydrologic conditions such as impounded groundwater in the spoil increased the potential for AMD. No sites with substantial negative net neutralization potentials were examined in these studies.

This study examined six surface mining sites with highwall-drain systems. Permits for these sites were issued over the past eight years. At the time of this report, five of the six sites have been completed. One site is still active. With the exception of one drain, water quality is within effluent standards when it leaves the permit boundary (Table 16.1). From this study, it appears that highwall drains can reduce the potential for AMD on sites with marginal overburden quality or can reduce the quantity of AMD which is generated.

Design and Installation of Highwall Drains

The design and installation of a highwall drain system must be tailored to each specific site. Some design parameters to consider include: (1) where to place the drains, (2) what materials to use, and (3) how to construct them. Although most designs are fairly simple and installation is inexpensive, one should expect minor revisions during construction due to subtle geologic changes discovered during mining.

The placement and number of drains are probably the most important items to resolve early in the design stage. To determine this, one must first review the mining plan and hydrologic data and predict the post-mining hydrologic regime. Items such as structural dip, amount of recharge, and configuration of mining will reveal, among other things, the amount of groundwater expected and where groundwater is likely to be impounded in spoil. It may not be unusual to have more than one drain on a site especially if the site is large or irregularly shaped.

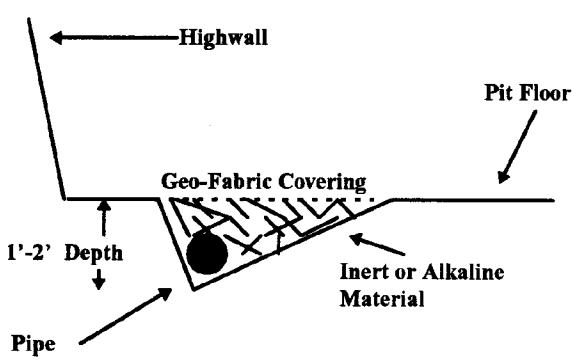


Figure 16.2 Example of drain in pit floor.

It is important to insure that drain systems are designed such that all groundwater is collected where it enters a mine site. This may be at the highwall, endwall or even the lowwall. Of equal importance is ensuring that drains are constructed such that positive drainage results. Surveying may be necessary in some instances.

The drain discharge location is also important as high sediment loads can be present during active mining. The most practical approach is to design the drains to discharge to a collection ditch, allowing any sediment-laden water to be transported to sedimentation ponds prior to final release. Discharging to a collection ditch may also be advantageous if treatment is needed. If circumstances prevent constructing the drain outlet into a collection ditch, thought must be given to providing sufficient sediment control at the drain outlet. Alternatives include the construction of sump areas and/or the use of filter fence or hay bales.

Drain installation must consider: (1) the construction method, (2) the transport medium (i.e., pipe or rock), and (3) protection of the drain, ensuring it is not crushed during backfilling. In this study, three different methods of pit floor drain construction were used. However, other techniques may also be appropriate.

The first drain construction technique starts with the excavation of a small channel in the pit floor with a backhoe or similar equipment to a depth just sufficient (about 1 ft (0.3 m)) to capture groundwater from the highwall. A pipe (4 or 6 in (10-15 cm)) is then placed in the bottom of the channel and covered with gravel or coarse-grained material. Finally, to prevent infiltration of sediment which could plug the pipe, filter fabric is installed over the ditch. (See Figure 16.2)

The second method is to install pipe at the low spot of each pit and allow water to naturally flow into it. This second method does not include any disturbance of the underclay. In the one instance where this method was used, an inert 2 ft (0.6 m) compacted clay

seal was placed on the pit floor under and on either side of the pipe. This permitted groundwater flow along the top of the inert clay rather than on the acidic underclays. Both Methods 1 and 2 involve the installation of a pipe to collect and transport groundwater.

The third procedure is generally the same as the first but does not use pipe. Using this approach, groundwater flows into a channel along the highwall (constructed similar to Method 1) and flows down-dip through a porous gravel (or on-site rock) medium. Whichever method is utilized, it is critical that positive drainage results. Surveying is usually necessary.

Although all three methods have resulted in satisfactory water quality, Method 1 is preferred. This allows for the capture of groundwater within a small area (ditch and pipe) and provides for rapid groundwater transport and little chance, barring plugging of the pipe, that groundwater will contact significant volumes of spoil.

To facilitate rapid transport of groundwater, operators have used flexible 4 in (10 cm) plastic pipe, Schedule 40 PVC pipe and, in one case, no pipe at all (i.e., ditch only). In the author's opinion, flexible pipe is a better choice as it is pliable and fits better in ditches which have undulations. Sturdy PVC pipe does not conform well to an uneven pit floor and can lead to groundwater flow under, rather than in, the pipe. It is important that the ditch be constructed such that it is has a gentle 1-2% slope and is free of rolls.

A potential problem is that the flexible pipe will be compressed by the weight of the backfill. Operators experienced with drain installation indicate that the potential for this is greatly reduced if the drain is covered properly. The best method appears to be to cover the pipe with 4 in (10 cm) diameter stone to a depth of approximately 2 ft (0.6 m) using a backhoe or small front end loader. If done properly, this will not compress or crush the pipe, especially if it is in a ditch similar to that shown in Figure 16.2. After that, normal backfilling can resume.

Normal mining operations must provide for the installation and covering of drains on a pit-by-pit basis, especially if the contour block mining method is used. Mine operators must also insure that the discharge end of each drain segment can be located. Methods of identification include the use of brightly colored 55 gal drums, spray painting of the spoil, or placement of easily identifiable material (such as limestone or red clays) over the end of each drain section.

Pit floor drain pipes have been perforated in two different styles to allow for groundwater infiltration: one is the construction of ½ in (1.27 cm) holes situated around the diameter of the pipe while the other uses much smaller perforations (Figure 16.3) (Duchene and McBean, 1992). Field experience has shown that the smaller perforations (Figure 16.3a) are preferable as they reduce the potential for plugging from sediment. The placement of filter fabric directly over the pipe can also help to reduce sediment inflow.

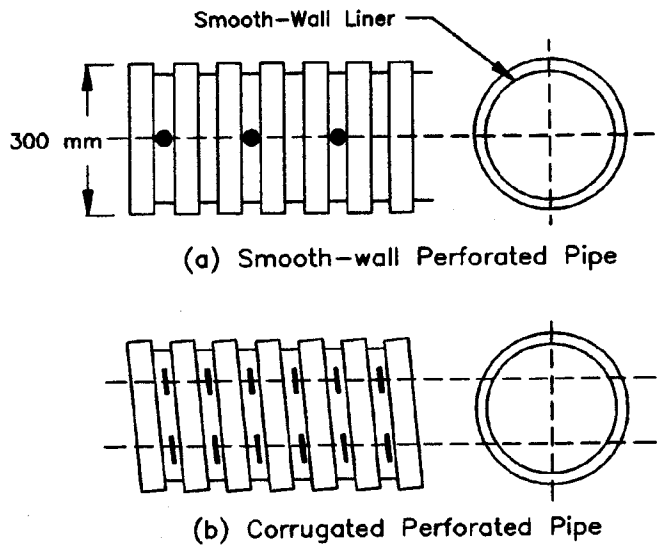


Figure 16.3 Pipe details used for pit floor drains.

Other factors which should be considered for sites where drains are proposed include the following:

1. All drain outlets should be designed with a "water trap" near the outlet to prohibit oxygen from entering the site via the drains. This can be done with a simple "U" joint or other type of apparatus. Although simple, the trap can be very effective. In Case Study 1, the installation of this feature decreased the dissolved oxygen in several drain discharges by approximately 50% and correlated to a major decrease in iron levels.
2. At a minimum, the discharge from drains should be monitored quarterly for quantity and quality. This will indicate how much groundwater is being intercepted and whether or not the intercepted water is being influenced by mine spoil.
3. Since sites with highwall drains often have marginal overburden quality (near neutral or slightly acidic), it is important that reclamation be conducted as rapidly as possible. Failure to accomplish this can lead to potential problems (See Case Study 1).

4. For large sites with significant infiltration from precipitation, it may be useful to construct dual highwall drains as shown in Figure 16.4. The primary drain along the highwall is slotted but connected to a solid pipe which allows for the rapid migration of unaffected groundwater through the site Additional groundwater resulting from infiltration is then captured by the slotted second pipe. Although infiltrating surface water does contact spoil as it migrates downward through the backfill, the overall contact time is reduced due to the presence of the second drain pipe.

The Pit Floor

The pit floor should also be considered in the management of groundwater to minimize AMD formation. This is the surface over which most groundwater eventually travels within the backfill and can be a likely source of contact with pyritic material. Pyritic material associated with the pit floor can come from coal cleanings, high-sulfur reject material, or the strata comprising the pit floor itself (i.e., the underclay).

Some coal remnants are found on the pit floor once the main coal seam is removed. Often this is just a result of normal mining operations but can also be associated with that portion of the bottom coal which does not meet market specifications. Barring the presence of substantial pit water accumulations, most operators will remove as much of this material as possible and "special handle" it prior to backfilling. This process can be time consuming and expensive to complete as it can easily take several hours to "clean' a 150 by 150 ft (30 by 30 m) pit. However, failure to remove this acidic material can lead to water quality problems later.

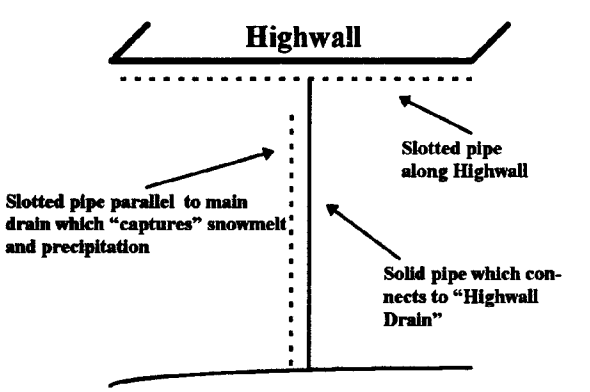


Figure 16.4 Schematic showing parallel drains.

Underclays can also be highly acid-forming, commonly having total sulfur contents in excess of 1.0%. If high-sulfur underclays are present, care should be taken to develop a mining plan which minimizes contact time with groundwater. This can be done by removing the high-sulfur material, by sealing off the high-sulfur zone (with clay), by liming the pit floor, or through the construction of drains to promote free flow conditions. Removal of high-sulfur underclays should be done with care so as not to cause additional AMD through the handling of the acidic material. It can also allow the downward migration of AMD or, if confined aquifers are present, the potential for increased groundwater into the backfill.

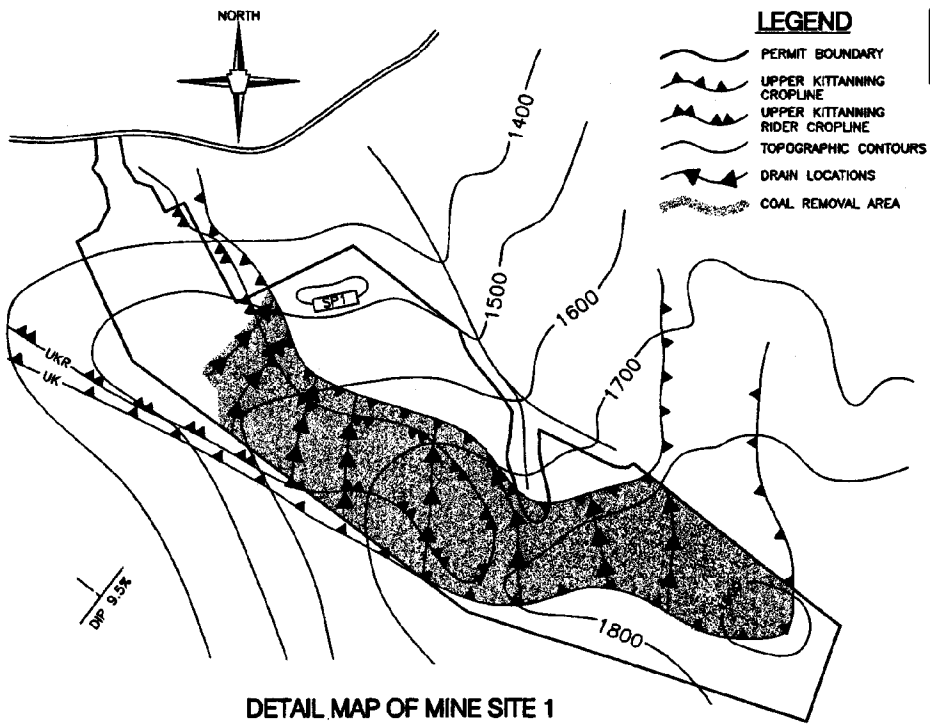
Water Management Case Studies

Case Study 1

Site 1 is a 170 ac (68 ha) site on a high quality stream in Westmoreland County, Pennsylvania. It is located in an upland area on the western flank of Chestnut Ridge. Over 100 ac (40 ha) of the upper Kittanning coal seam were mined and reclaimed over a 10-month period in 1995. The topography and general dip of the coal were both to the northwest at about 10% (Figure 16.5). The highwall height did not vary substantially during the life of the mine and was never over 50 ft (15 m).

Overburden data indicated near neutral conditions with little in the way of acidic or alkaline strata. Volumetrically, the site exhibited a NNP deficiency of approximately 0.9 ppt $CaCO_3$ due to sulfur in the coal and a 1 ft (.3 m) shale zone immediately above the coal. Pre-mining ground water levels and well yields were low, indicating that the pit would not encounter a large amount of water. The adjacent area had been previously mined on the same coal seam without creating any discharges. Mining was permitted following the submission of a detailed operations plan which included, among other things, a highwall drain system.

As can be seen in Figure 16.5, the configuration of the mining area was rectangular and required several drains. The drains were constructed per Method 2, above, and all outlets, except one, discharged into collection ditches. As expected, minimal flows occurred during active mining. Drain 1, structurally the lowest, was the only one which exhibited nearly constant flows and these were minor, ranging from 1 to 2 gpm (3.78-7.5 lpm). Flows from almost all drains, however, increased substantially beginning in December, 1995 due to a lack of vegetative cover and above average mid-



DETAIL MAP OF MINE SITE 1

Figure 16.5 Drain locations on mine site in Case Study 1.

winter precipitation and snow melt. At its peak, the combined flow of the drains was over 100 gpm (378 lpm).

Table 16.3 shows that initial water quality results were very good and all parameters were well within permit effluent guidelines. The relatively low sulfate concentrations are especially significant, indicating minimal spoil/groundwater interaction and confirming rapid groundwater movement through the drainage system.

Subsequently, water quality deteriorated in late winter as concentrations of metals increased. Iron and manganese levels rose to 40 and 20 mg/L, respectively. This deterioration was probably due to two processes. First, a lack of vegetative cover coupled with the seasonal reduction in evapotranspiration allowed large amounts of precipitation and snow melt to infiltrate into the mine spoil. Second, the resulting groundwater interacted with pyritic pit cleanings and siderite ($FeCO_3$). The presence of siderite was confirmed by x-ray diffraction The result was high flow discharges with elevated metals. By June, 1996, however, early spring re-seeding succeeded in substantially increasing vegetative cover, reducing infiltration into the backfill and decreasing metal concentrations.

Another factor which appears to have helped to abate the elevated metals problem was the addition of air traps at the ends of the drain to prohibit the influx of oxygen into the site. The combined effect of surface vegetation and the addition of the traps resulted in nearly a 50% reduction in dissolved oxygen levels at the discharge outlets. Field results such as these show the advantage of "air traps" and demonstrate the need for concurrent reclamation and revegetation.

Case Study 2

Site 2 is a 48 ac (19 ha) surface mine located in Green County, Pennsylvania. Mining began in early 1985 but was not completed until September, 1991 due to the suspension of mining from mid 1985 to late 1988. During this period, an 850 ft (255 m) open pit remained. The Waynesburg coal seam was the only seam mined. Due to its upland location, minimal groundwater was present in the pit. Initially, no overburden analysis was performed.

Shortly after mining was suspended, a series of three discharges formed at the toe-of-spoil just above the sedimentation pond (Figure 16.9). Combined flows were approximately 5 gpm (19 lpm.). In addition, runoff from a spoil pile indicated severely degraded AMD as shown in Table 16.2.

Table 16.2 Water quality from mine site 2.

DATE	pH	Alkalinity mg/L	Acidity mg/L	Iron mg/L	Manganese mg/L	Aluminum mg/L	Sulfate mg/L
July-1987	2.5	0	7,400	>300	>300	>500	13,209

Table 16.3 Water quality from highwall drains on mine site 1.

DRAIN #	Date	Flow	pH	Alkalinity	Acidity	Fe	Mn	Al	SO_4	Comments
		gpm		mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	
Drain 1	5/16/96	1.0	8.0	117	0	0.28	0.8	0.4	28	First Sample
	3/26/96	13.5	6.1	168	36	23.4	15.2	0.5	181	Site Unvegetated
	9/11/96	3.0	6.7	266	0	0.69	9.2	0.5	331	Good Growth
Drain 3	5/16/95	0.4	7.7	188	0	0.3	0.99	0.5	36	First Sample
	3/26/96	3.0	6.2	280	0	33.9	13.5	0.5	169	Site Unvegetated
	9/11/96	1.0	6.8	312	0	34.5	10.9	0.5	218	Good Growth
Drain 6	9/26/96	1.0	7.2	173	0	0.05	2.2	0.1	53	First Sample
	3/26/96	18.0	6.3	270	0	5.7	9.3	0.5	113	Site Unvegetated
	9/11/96	1.25	6.6	480	0	0.36	9.04	0.5	156	Good Growth
Drain 7	12/6/95	3.0	6.5	190	0	49.3	16.7	0.5	98	First Sample
	3/26/96	19.5	6.1	242	0	8.59	8.21	0.5	84	Site Unvegetated
	9/11/96	1.25	5.9	226	0	3.5	4.96	0.5	80	Good Growth
Drain 8	10/19/95	1.0	6.9	452	0	1.63	2.99	0.29	123	First Sample
	3/26/96	13.5	6.2	182	146	7.28	18	0.5	205	Site Unvegetated
	9/11/96	0.12	7.7	366	0	0.3	12.6	0.5	170	Good Growth

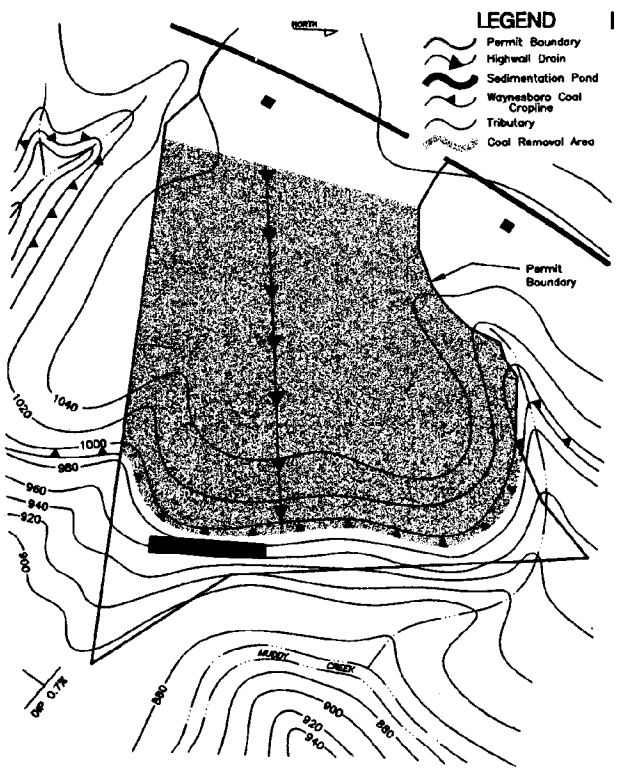


Figure 6.6 Drain installation schematic at mine site in Case Study 2.

A hydrologic evaluation was conducted which included acid-base accounting overburden analysis. Results indicated a lack of alkaline overburden and the presence of a high-sulfur shale interval immediately above the coal. This unit was variable in thickness and ranged from 5 to 8 ft (1.5 to 2.4 m). Volumetrically, the overburden results indicated a net neutralization potential deficiency of over 1,500 tons $CaCO_3$ per acre (551 t/ha).

A decision was made to allow continued mining with a revised mining plan. The revised plan included the establishment of a highwall drain, a 3 ft (1.0 m) compacted clay cap over the site, clay sealing of the first cut spoil, addition of alkaline material, and implementation of a revised special handling and blasting plan.

The highwall drain was installed using Method 1 as above and was installed at the lowest elevation of each cut. Due to structure, however, the pit floor at the highwall was about 8 to 10 ft (2.4 to 3.0 m) lower than at the outcrop. It was therefore necessary to breach the pit floor along the length of the drain in order to promote positive drainage. Due to the acid-forming nature of the underclay and the potential for the next lower aquifer to be contaminated, an inert clay seal was placed in the channel along the length of the drain. Slotted 4 in (10 cm) flexible pipe was then installed.

The operator chose not to extend the drain along the entire length of the final highwall in a "T" fashion (Figure 16.6). It was only extended 50 ft (15 m) to either side.

Once mining resumed and the initial section of the drain was installed (late 1988), water quality improved dramatically. Highly acidic water with elevated metals concentrations changed to alkaline water having low iron concentrations. Sulfate levels, although still elevated, decreased substantially after installation of the drain. Table 16.4 shows a compilation of water quality results from the drain.

In the author's opinion, the main factors in the substantial water quality improvement were the alkaline supplement and the establishment of the highwall drain and clay cap. This combination effectively supplied alkalinity to the ground water and provided for rapid flow of groundwater through the backfill while decreasing surface water infiltration by about two thirds. Gradual thinning of the highly acidic shale layer as mining progressed was also a significant factor.

It is interesting to note that many of the water quality problems on this site may have been avoided if the site would have been mined expeditiously and mining would have extended to the cropline on the southwest side of the permit 200 ft (60 m) away from final highwall. Mining to this cropline would have allowed for the free flow of groundwater off the site without creating a pooling effect. Unfortunately, this was not possible because of adjacent property interests which prevented mining.

The overburden on this site (high sulfur/low neutralization potential) represents conditions that today would be unlikely to meet the standards for permit issuance, even considering alkaline addition and the addition of a highwall drain/clay cap system. It was used here in an attempt to abate an existing acid mine drainage problem.

Case Study 3

Site 3 is a 60 ac (24 ha) site located in southern Armstrong County, PA (Figure 16.7). Approximately 20 ac (8 ha) of the upper Freeport coal were mined beginning in June, 1995 with final backfilling occurring in June, 1996. The site was seeded a month later and good growth is present.

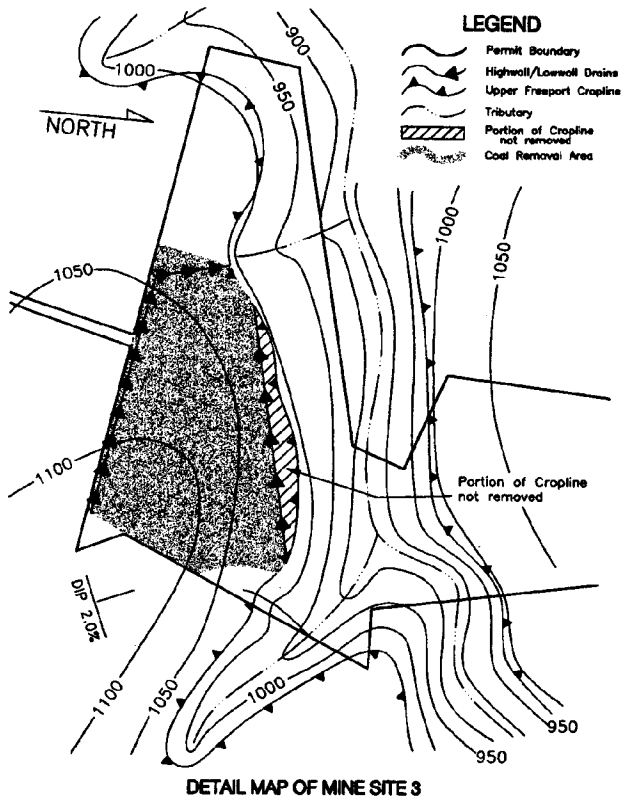


Figure 16.7 Drain installation schematic at mine site in Case Study 3.

An adjacent pre-act mine on the same seam had resulted in an alkaline discharge with high metals concentrations. Overburden analysis on Site 3, although indicating high sulfur coal (4 to 5%) and 2 to 4 ft (0.6 to 1.2 m) of moderately acidic overburden over the

Table 16.4 Water quality from mine site 2.

Sample point	Date	pH	Alkalinity mg/L	Acidity mg/L	Fe mg/L	Mn mg/L	Al mg/L	SO_4 mg/L	Comments
Discharge	6/88	3.7	0	386	123	48.3	20.6	1445	Last sample of discharge before drain installed
Highwall Drain	1/89	7.1	158	0	5	22.2	0.6	1218	First sample once drain installed
Highwall Drain	12/91	6.9	214	0	4.68	15.9	0.5	750	Highwall Drain completely installed
Highwall Drain	6/92	6.9	382	0	3.82	19.4	0.5	774	Site revegetated
Highwall Drain	9/96	6.6	296	0	5.7	25.3	0.5	1099	Latest sample

coal, also indicated a large net excess of alkaline material in the range of 3,000 tons $CaCO_3$ per acre (1102 t/ha). A moderate amount of groundwater was expected due to the number of springs in the area and the quantity of water encountered in exploratory drill holes.

Both the topography and the coal on the first phase of the operation dipped to the north, allowing unrestricted groundwater flow through the spoil along the base of the pit floor (Figure 16.7). However, a permit condition precluded coal removal in the area of the outcrop. Because of the adjacent mining problems, a highwall drain system was suggested as a means of minimizing the contact of groundwater with the backfill and of facilitating rapid groundwater flow through the outcrop coal barrier.

In this case, both a highwall and lowwall drain were constructed. The purpose of the highwall drain was to intercept the inflow of groundwater at the highwall and transport it down-dip. The intent of the lowwall drain was to prohibit any water from building up behind the portion of the coal cropline which would remain. Prior to constructing the lowwall drain, the exposed crop coal was sealed with clay to further minimize the chances of groundwater migration through this area.

Both drains were constructed without pipe per Method 3. A D9 dozer constructed a V-shaped channel along the highwall to a depth of 1 ft (0.3 m) and filled it with permeable low- sulfur sandstone from the mine site. Filter fabric was used to cover the drain prior to backfilling.

The drains have been in place since July and November, 1995 and both have discharged fairly continuously. Water quality parameters have been well within permit standards since installation as can be seen in Table 16.5. Interestingly, sulfate levels are elevated which may be linked to sandstone in the trench (instead of a pipe) resulting in slower groundwater flow and increased contact time or it may be due to the ability of groundwater recharge from surface water infiltration to enter the open trench system. No air traps were constructed for this site primarily due to the lack of any pipes in the drain. However, it would be fairly easy to include this feature as only a small area would need disturbed in order to install a 30 to 40 ft (10 to 12 m) solid section of pipe with a trap near the end.

Table 16.5 Water quality from drains at mine site 3.

Sample Location	N	pH	Alkalinity mg/L	Acidity mg/L	Fe mg/L	Mn mg/L	Al mg/L	SO_4 mg/L
Highwall Drain	12	6.48	200	0	1.54	5.49	0.89	571
Lowwall Drain	10	7.36	151	0	1.07	1.02	1.07	369

Summary

The use of water management techniques to prevent AMD on surface mining sites can be divided into three main practices: (1) erosion and sedimentation controls, (2) controls on surface water infiltration, and (3) groundwater controls. All three relate to the control of water on, around and within the mine. Key principles include the use of highwall drain systems to minimize contact between groundwater and acid-forming materials and rapid reclamation and revegetation to help prevent AMD formation.

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Chapter 17

REMINING

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Introduction

In general, remining is defined as any operation where additional mining occurs subsequent to the original mining or site abandonment regardless of the existence or quality of mine discharges. However, the term remining as it is used in this chapter, primarily refers to surface mining of abandoned surface or underground mines or reprocessing of coal refuse piles where pre-existing pollutional discharges will be affected by remining under Pennsylvania's Subchapter F and Subchapter G (anthracite) program. Site-specific effluent standards are established based on loading rates rather than conventional concentration-based BAT effluent standards. Mine drainage prediction of remining sites where the discharges are required to meet conventional effluent standards is covered by standard prediction techniques discussed in the preceding chapters of this manual.

Prediction of additional mine drainage from remining sites is distinctly different compared to normal mine drainage prediction at previously unmined sites. Instead of contaminant concentration (e.g., mg/L) levels and pH of the effluent, prediction of contaminant load (e.g., lbs/day or kg/day) levels become the primary objective for remining mine drainage prediction. Discharge flow rate is used to determine contaminant load and becomes a primary determinant of the reviewed effluent standard. There is a direct positive correlation between discharge rate and pollution load. Smith (1988) and Hawkins (1994a; 1994b) have observed that discharge flow rate is a major element of contaminant load. Therefore, the physical hydrology of the mine becomes a larger component of mine drainage prediction than overburden geochemistry in remining situations compared to mining virgin sites.

Historical Impacts of Remining

Remining in the bituminous coalfields of Pennsylvania has, at the majority of sites, resulted in no change or an improvement in the water quality in terms of contaminant (acidity, iron, and sulfate) loads (Hawkins, 1994b). Analysis of 24 reclaimed western Pennsylvania remining sites illustrated that a large majority of the sites either did not change or significantly reduced post-remining acidity, iron, and sulfate loads. For that study, data were analyzed from remining sites in the bituminous coal fields of Pennsylvania that had been reclaimed (backfilled to rough grade) for one year or longer.

The study determined changes in the post-remining contaminant load data using the methodology employed by the Pennsylvania Department of Environmental Protection and two other applicable analytical methods (Mann-Whitney U test and nonparametric upper prediction limits). All three of the methods indicate that remining either successfully reduced or did not significantly change the contaminant loads for at least 20 of the 24 sites. More sites (8) exhibited a significant reduction in acidity, iron, or sulfate load than the number of sites that exhibited a significant load increase (3 or 4) (Hawkins, 1994b).

There were a few cases where the post-remining water quality was significantly improved in terms of contaminant load and began to meet the concentration-based statutory effluent standards (25 PA. Code 87.102). This situation usually occurred on sites where surface mining daylighted (i.e., remined abandoned underground mines by surface mining methods) a substantial area of abandoned underground mines. Figure 17.1 illustrates an example of acidity concentration meeting 25 PA. Code 87.102 standards approximately 900 days after backfilling. The water quality improvement appears related to the presence of significant amounts of alkaline material (e.g., limestone or calcareous shales) in the overburden. Removal of the coal itself and redistribution of roof material that collapsed in the open voids may have contributed to the water quality changes. Before the underground mine was daylighted, the groundwater had limited and transient contact with this alkaline material. Groundwater passing through the underground mine had prolonged exposure to the floor rock, coal and roof rock, all of which are commonly acid-forming materials. Additionally, roof falls and pillar weathering continue to add new

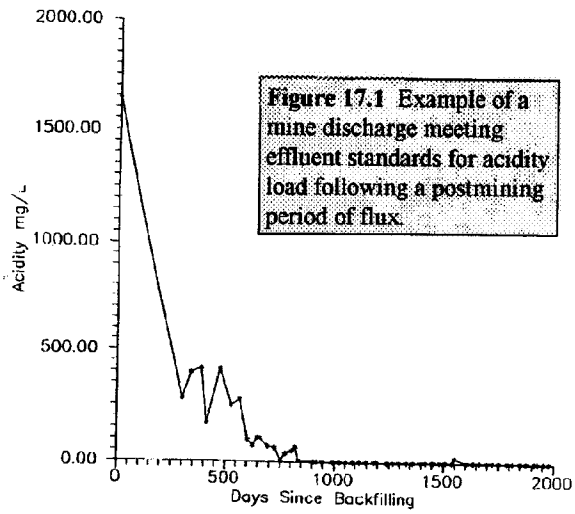

Figure 17.1 Example of a mine discharge meeting effluent standards for acidity load following a postmining period of flux.

sources of acidity from the freshly exposed rock material. Daylighting radically alters the groundwater flow regime, the rock material contacted, and greatly increases the rock surface area and groundwater contact time. Therefore, when limestone in the overlying strata is removed and backfilled, it has the potential to yield substantially more alkalinity to the groundwater, which can significantly improve the groundwater quality.

In the cases where the remining increased pollution loads there are several possible causes. The first reason may be that remining has created additional pollution. However, short-term changes in flow and/or contaminant concentration that commonly occur during the initial 1-3 years after backfilling is another possible cause. The first 1-3 years after backfilling is a period of substantial physical and chemical fluctuation within the spoil aquifer. During this period, the water table is reestablishing and the spoil is undergoing considerable subsidence, piping, and shifting. The sulfate salts, created by oxidation when the cast overburden was exposed to the atmosphere during mining, are flushed through the system (Hawkins, 1995). Figure 17.2 is an example of a discharge acidity load during this transient period. If the data for that discharge were analyzed after only 1000 days, the remining would appear to have failed because the acidity load frequently exceeds the upper bound of the 95% confidence limits. However, when the post-remining sampling period is extended to over 1800 days, that conclusion is no longer valid. Therefore, the true impact of remining on pollution loads may require monitoring beyond 3 years after backfilling and short-term degradation may not be unexpected. Figure 17.2 is an extreme example of water quality changes that can occur during this transient period. The majority of discharges exhibiting water quality changes during this period are usually less extreme.

Daylighting of underground mines does not necessarily improve the discharge water quality. Reed (1980) analyzed the impact of daylighting an abandoned 850 ac (344 ha) underground mine in Tioga County, Pennsylvania. He observed that the daylighting, still active during his study, was increasing the acidity concentration of the discharges. A direct relationship between the amount of daylighting and the acidity concentration increase was noted. Concentration is frequently a function of discharge rate (an inverse relationship), therefore load is a better assessment of water quality improvement. However, the impact of the mining on the acid load was not determined. The cause of the apparent acidity increases is not known. However, it is possible the overburden may have had significant amounts of acid-producing strata, or it may have been a case of temporary degradation, as previously discussed. Subsequent analysis of the acid loading data from the three main discharges, after reclamation of the corresponding recharge area, showed no statistically significant changes from pre-remining levels. Although, the acid loads may have lowered from the levels recorded during the active daylighting phase (Meiser, 1982). Daylighting on the same coal seam at a near-by site also resulted in degraded water quality, due to the substantial high-sulfur strata and the lack of significant alkaline strata overlying the coal (Naylor, 1989).

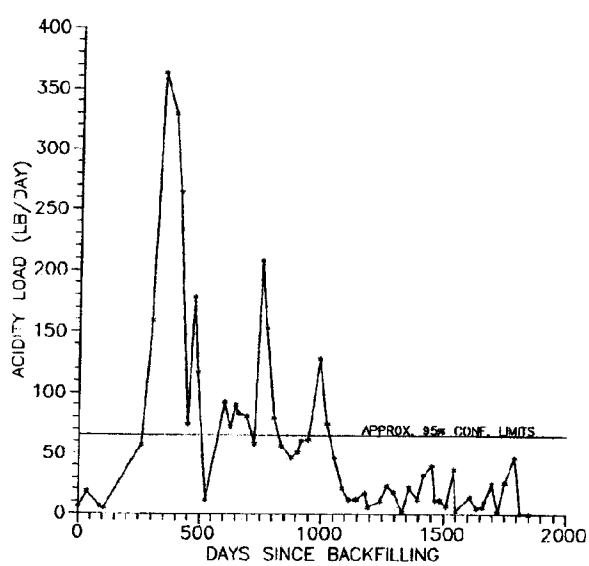

Figure 17.2 Example of a mine discharge meeting acidity concentration statutory effluent standards after remining.

Similarly, Ackerman and others (undated) evaluated the impact of daylighting an abandoned underground mine in Garrett County, Maryland. They observed that the post-remining pollution loads did not significantly change from pre-remining levels. However, a slight improvement in pollution load may have occurred shortly after reclamation. They also observed that the pollution load seasonal fluctuations were greater than pre-remining levels.

Remining Techniques

An important aspect of remining is determining what elements of the original mining caused the degradation. This "post mortem" analysis performed on the abandoned mines will indicate what, in terms of past mining practices, geology, hydrology, or other factors caused or contributed to the production of acid mine drainage (AMD). This analysis will identify what abatement procedures, implemented during the remining operation, will preclude further degradation and possibly ameliorate the existing pollution problem. The causes of AMD formation at abandoned surface mines generally differ from that of abandoned underground mines, because their groundwater flow systems are substantially different (open conduit vs. a double porosity system).

In conducting this post mortem evaluation, several possible reasons why abandoned surface mines will produce AMD can be considered. In some cases, overburden quality is such that AMD formation is inevitable, even if the operation was conducted entirely within the existing regulations and prevailing best mining practices. In those cases, the original permit probably should not have been issued, and, with the advances in mine drainage prediction in Pennsylvania in the last 15 years, it probably would not now be issued. In other cases, older mining methods and practices (or lack thereof) may have caused or accentuated AMD production. For example, the mine may not have been backfilled in a timely manner or never completely reclaimed. Improper disposal of acid-forming materials (pit or tipple cleanings) with respect to the postmining water table may have caused or increased AMD formation. At a few sites, additional acidic materials may have been brought to the site and disposed in the backfill. It is possible the overburden was slightly alkaline or neutral, but the addition of the acid-forming materials overwhelmed the modest amount of natural alkalinity available. Certain hydrologic conditions within the mine, such as pit water accumulations unchecked during the original mining, can also contribute to AMD formation. The abatement plan will outline how the remining operation will be conducted differently from the original mining as well as what additional measures will be taken in an attempt to improve the water quality.

Abandoned underground mines are commonly ideal environments for the formation of AMD. Therefore, a post mortem of these environments is generally simpler than that for abandoned surface mines. AMD formation is facilitated by the normal configuration of the mine which permits groundwater to preferentially encounter acid forming materials. Subsidence can route surface water that normally runs off the surface directly into the mine workings. Even properly sealed mines commonly continue to have significant oxygen content, often approaching atmospheric levels in the unflooded sections and the open entries permit periodic unrestricted flushing of the substantial amounts of sulfate salts during flooding episodes. Roof falls and pillar deterioration continue to introduce additional acid-forming materials into the system. AMD abatement procedures conducted during remining of underground mines is primarily just the process of daylighting. The act of daylighting is radically different than the mining processes that caused the underground mine to create AMD, because the coal, mine entries, and gob are eliminated. The post-remining configuration of the daylighted sections is similar to a reclaimed surface mine. Although, because of roof falls and pillar deterioration, there may be a higher amount of unrecoverable coal mixed in with the spoil associated with daylighting than with remining surface mines. After daylighting and in the absence of selective spoil handling, groundwater flowing through the reclaimed portions should encounter acidic, alkaline, or relatively inert spoil materials at a frequency based on the volumetric content of the spoil and the groundwater flow regime.

Impact of Discharge Flow on Contaminant Loading

Previous studies (Smith, 1988; Hawkins 1994a; Hawkins, 1994b) have illustrated that the discharge flow rate is a strong determinant of contaminant load. The strong influence of flow on load is illustrated by figure 17.3, which compares acid load, acid concentration, and flow data from a remining discharge in western Pennsylvania. Not all discharges show this strong of a relationship between flow and load, but significant

positive correlations are extremely common (Hawkins, 1994a). Smith (1988) stated that "Proper flow measurement is of overriding importance in monitoring pollution load." He also observed that flow changes dominate baseline acidity load variations.

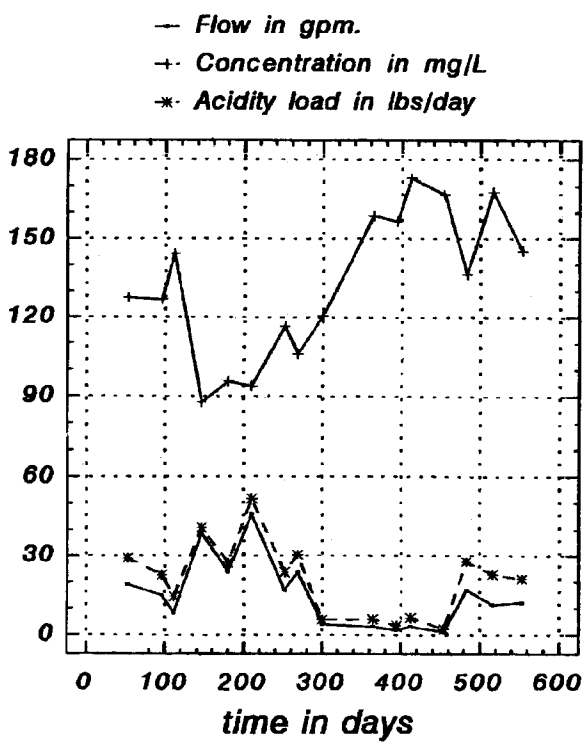

Figure 17.3 Example of the strong influence of flow on contaminant load.

Hawkins (1994a) analyzed pre- and post-remining hydrologic data from 24 remining sites in Pennsylvania using normality testing (skewness and chi-square), exploratory data analysis techniques (notched box-and-whisker plots), and correlation analysis (Spearman's rank correlation). All three types of analyses illustrated that flow dominates acidity, iron, and sulfate loads before and after remining. Hawkins (1994b) observed that when a significant load change (increase or decrease) occurred after remining, a flow rate change was the most common cause.

Concentration was found to be subordinate factor in some instances; therefore, the role of contaminant concentration in load determination cannot be completely discounted. Hawkins (1994b) noted that 71% of the excursions above the 5% significance level were accompanied by "substantial concentration level changes." With this in mind, overburden analysis is still necessary to determine the potential impact of remining on the contaminant concentration levels.

Discharge Flow Rate Reduction

The aforementioned studies have shown that if the discharge flow rate can be controlled (decreased), a reduction in the load is highly likely regardless of fluctuations in contaminant concentration. Reductions in the flow from the mine site can be achieved by controlling recharge to the spoil through the implementation of the pollution abatement plan. Decreasing surface water infiltration as well as lateral recharge from adjacent mined and unmined areas is required to diminish the discharge rate from remining sites. The control of groundwater and groundwater recharge is discussed in detail in Chapter 16. However, there are several reclamation techniques that can be applied to remining sites to reduce the discharge rate. Flow reduction is achieved by diverting or excluding ground and surface water from the backfill.

The exclusion of surface water from the backfill includes installation of diversion ditches, capping the site with a low-permeability material, spoil regrading, and revegetation. Diversion ditches prevent surface water from entering backfilled areas or facilitate rapid drainage away from the surface of the backfill. A seal covering the backfill reduces or prevents surface infiltration. This cap can be comprised of a variety of materials such as on-site clays, self-cementing coal ashes, or a geotextile. Abandoned surface mines, prior to remining, commonly have unreclaimed pits and other closed contour depressions in poorly sorted spoil that act as recharge areas. Regrading these areas significantly increases runoff and reduces surface water infiltration by eliminating surface impoundments and rapid infiltration zones. Revegetation with certain plant types further reduce infiltration by facilitating runoff or retaining and using infiltrated water at the soil horizon. The water held in the soil is subsequently transpired or evaporated.

There are several methods for decreasing lateral recharge to the backfill from adjacent or underlying sources including the installation of highwall and lowwall drains, floor drains, grout curtains at the highwall and lowwall, sealing the pit floor, horizontal free-draining or vertical dewatering wells in adjacent strata, and sealing of exposed underground mine entries with low-permeability materials. Groundwater drains intercept groundwater prior to entering the backfill or rapidly remove existing groundwater from the spoil and then divert it off site. Optimally, highwall, lowwall, and floor drains should be installed while the operation is active, prior to reclamation. Drains that collect and

route water from underground mines through (by-passing) the backfill are becoming increasingly common. Grout curtains and sealing the pit floor precludes lateral and vertical groundwater flow into the backfill from adjacent and underlying strata. Grout curtains can be installed after reclamation, whereas the pit floor is must be sealed as mining progresses. The dewatering wells prevent a positive hydraulic gradient in adjacent areas toward the backfill by suppressing the water levels in the adjacent or underlying strata. These wells can be installed at anytime during the operation. Sealing of exposed mine entries with a low-permeability material is very important in preventing lateral movement of groundwater from flooded mine workings into the backfill. They should be sealed while the site is open at the final cut, although they can be sealed later by back-stowing and grouting via large drill holes.

Proven Track Records and Experience-Based Rules-of-Thumb

Within Pennsylvania there are certain areas, coal seams, and mining situations (e.g., abandoned underground mines, surface mines, or coal refuse piles) that are known to mining professionals to have either a good or bad track record when disturbed by remining. Some regions and coal seams are known to yield greatly improved water quality after remining virtually regardless of how the operation is conducted. Other areas and coals seams are notorious for producing worse quality discharges, regardless of how well the operation was conducted.

Experience has shown that daylighting of Pittsburgh coal underground mine workings in Washington, Beaver, and Allegheny Counties, Pennsylvania substantially yields improved water quality over pre-remining conditions. When the daylighting is substantial, the discharges change from being strongly acid to being significantly alkaline. This change in water quality is illustrated by figure 17.1. Some acidic mine discharges improve somewhat after remining, but do not become alkaline. An example of this situation was an operation in Washington County, where there were 5 pre-existing acidic mine discharges. Some of the discharges went from being acid to alkaline (acid loads went from 75.6 lb/day (34.3 kg/day) to no acid load), while others exhibited reduced acid loads, but remained acidic. The degree of change of the discharges appeared to be related to amount of the recharge area that was daylighted. The water quality changes appear to be directly related to both the removal of the coal, which has sufficient sulfur content to be acid producing, and breakup of the overburden, which possesses a significant amount alkaline material. Entire streams, such as Potato Garden Run in Beaver County, have recovered because of nearly complete daylighting of abandoned underground mine working in that area.

Examples exist where complete daylighting of an underground mine will eliminate or nearly eliminate the discharges through substantial changes to the groundwater flow system. At a 43 ac (17 ha) mine in Clinton County, the underground mine workings were completely daylighted. Subsidence and collapse features that facilitated recharge to the mine were removed. The postmining recharge rates through the spoil were significantly below pre-remining levels (See Chapter 3 for a discussion on recharge to mine spoil). Three years of postmining data seldom showed any measurable flow at the one discharge point. It is unlikely that the discharge was completely eliminated, because some of this monitoring was conducted while the water table was reestablishing. However, the data indicate that the flow was and will continue to be substantially lower than pre-remining levels.

There are coal seams in parts of the coalfields where remining is known to leave discharges unchanged from pre-existing levels. Examples of this are the Freeport coal seams in northern Armstrong County, which are known to have marginal overburden quality, yet remining seldom increases the pollution loads. The pre-remining acidity loads (the discharges are slightly acidic) are generally low and the metals (iron, manganese, and aluminum) commonly at times meet Best Available Technology (BAT) (87.102) effluent standards. The overburden is characterized by low amounts of alkaline material coupled with low sulfur values. Both of these constituents appear to have been leached from the strata by weathering, leaving little to react (Michael W. Gardner, personal communication).

There also are certain seams and areas within Pennsylvania where remining without additional abatement measures such as alkaline addition, typically increases the pollution load for acidity and/or metals. For example, commonly remining on the Waynesburg coal seam in Greene County increases the pollution load. Manganese and iron loads are frequently observed problems associated with the Waynesburg coal (Michael W. Gardner, personal communication). The Waynesburg sandstone is thought to be the main AMD producing unit. Remining on the Lower Kittanning or Clarion coal in northcentral Pennsylvania generally increases

acid loads unless flow reduction measures are taken and alkaline materials are brought to the site (Michael W. Smith, personal communication).

Recommendations

Mine drainage prediction for remining sites must be viewed differently than for virgin sites. Discharge contaminant loads instead of concentrations are regulated and forecasted. Because of the dominance of flow in contaminant load determinations, abatement and reclamation plans should stress the implementation of flow reduction techniques. Abatement practices to reduce recharge to the spoil aquifer should yield a predictable (within a range of projected values) decrease in flow using known site conditions along with standard geologic and hydrologic techniques. The flow reduction will subsequently yield a predictable contaminant load reduction.

Given the track record in Pennsylvania and the observed benefits that reducing flow has on contaminant load, remining can be a viable means of abating or diminishing AMD discharges in many areas. This may be the only economically viable solution for reducing some of the highly-degraded/high-volume underground mine discharges. Long-term discharge treatment is typically not viable and in many instances cost prohibitive.

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Chapter 18

APPLICATION OF THE PRINCIPLES OF POSTMINING WATER QUALITY PREDICTION

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Introduction

The previous chapters of this document present in detail the individual predictive tools necessary to determine if and how a site can be surface mined without an unacceptable risk of pollution. This chapter will summarize the key principles from the previous chapters and will show how those tools are synthesized into a prediction of whether pollution will occur. The process is not always straightforward nor simple.

Historically, there has been some skepticism surrounding predicting postmining water quality, especially the heavy use of overburden chemical analysis. Apparent reasons for this skepticism include:

- Any decision making which relies heavily on the professional judgment and experience level of the decision maker is typically subject to question.
- The number of factors which must be considered and the potential for those factors to sometimes contradict one another provide an opportunity for even experienced data interpreters, looking at the same data set, to reach somewhat differing conclusions.
- To interested parties not closely familiar with the geologic and chemical science behind the data interpretation, the decisions may appear virtually random. It may be completely reasonable in terms of the potential for pollution why one property may be mineable and an adjacent property may not be. However, it is easy to understand how the affected property owners and mining companies may find such a decision incomprehensible.
- The legacy of polluted streams left behind by mining operations that took place prior to modern understanding of the mechanisms of mine drainage formation has convinced much of the general public that any mining will lead to acid mine drainage pollution and that efforts to prevent it are fruitless.
- The science of predicting acid mine drainage is fairly young, and as is always the case when the experience level is low, there were notable early predictive failures.

Despite the skepticism, much progress has been made in the science of predicting postmining water quality over the past ten to twenty years, and a significant majority of the sites permitted and mined in Pennsylvania today produce acceptable postmining drainage quality. A recent informal survey (Gary Byron, PA DEP, personal communication, 1997) of surface mining permits issued in Pennsylvania between 1977 and 1992 showed that 344 permits out of a total 3710 permits issued, or 9.3% resulted in discharges which failed to meet effluent limits and which required permanent treatment. (See table 18.1 for data.) However, the average failure rate for predictions during the first 8 years of the period examined was 14.7 %, while the failure rate for the final 8 years (1985-1992) improved to 2.9%. The data in Table 18.1 should be viewed with some caveats in mind: the predictive success for sites, which due to hydrologic conditions, do not produce a discharge is really an unknown and not necessarily a success; not all the sites surveyed have been completed to date, which is one reason why data for sites permitted after 1992 were not considered here; other factors such as market conditions (the demand level for certain coal seams) and changes in inspection frequencies and sampling intensity may also have some influence on these data. A comprehensive study (Hawkins, 1995) of Pennsylvania's program (subchapter F) for remining sites with poor quality discharges revealed that the acidity and iron loads were either unchanged or declined at 21 of the 24 sites studied for an 87% success rate. Acidity rates actually declined significantly at nearly one-third of the sites. A recent survey conducted by the Department (Michael Smith, PA DEP, personal communication, 1997) revealed that, of 260 subchapter F permits issued up to

1997, only 5 have caused statistically significant long-term degradation of the pre-existing discharges; an additional 6 sites required treatment of discharges at some point during operation, but the water quality on those sites eventually returned to baseline conditions. The data from the remining studies are especially notable since such sites are generally very well-monitored.

Table 18.1 Total number of surface mining permits issued in PA per year and the number of those permits resulting in discharges requiring treatment. (Please see caveats in text regarding these data.)

Year	Total Permits Issued	Permits With a Discharge Requiring Treatment	Percentage of Permits Requiring Treatment
1977	341	54	16
1978	265	35	13
1979	212	50	24
1980	230	36	16
1981	245	51	21
1982	228	37	16
1983	185	25	14
1984	300	7	2
1985	300	13	4
1986	250	2	1
1987	260	5	2
1988	221	7	3
1989	181	8	4
1990	183	5	3
1991	167	5	3
1992	142	4	3

The importance of adequate water monitoring both during and after mining is emphasized here for two reasons. First, accurate predictions of postmining water quality depend on accurate input data, and water quality from adjacent mined sites is one of the most useful predictive tools. Second, such monitoring can serve as an early-warning system for active sites that unexpectedly develop problems. If the problems are discovered early enough, it is possible that one or more of the management tools discussed in other chapters of this document can be employed to correct the problem or lessen its severity. While traditional stream monitoring is useful, the monitoring of pit water, mine discharges, downgradient springs and monitoring wells best document water quality directly associated with a mine site. Inadequate monitoring hampers both the mining industry and regulators in making appropriate decisions about how and where to mine.

The findings in this document are based upon research and experience largely applicable to the northern Appalachian coal fields. Geochemical and climatic differences found in other regions of the country, especially in the arid West, must be understood and factored in by water quality predictors in those regions.

Complicating Factors

There are several potential complications which confront those who attempt to predict postmining water quality. In some cases information is not available on all the factors which may affect postmining water quality. Perhaps there is little pertinent mining history to evaluate, or the site's hydrogeological setting may make it difficult to discover background groundwater quality. A decision must nonetheless be made. Sometimes the predictive factors point the data interpreter in opposite directions: site-specific overburden analysis may suggest alkaline drainage will result, while adjacent sites have produced acid mine drainage. More commonly, the factors may present seemingly ambiguous results, not pointing strongly toward any one conclusion. Complicating factors exist not only between the predictive tools but within each one. Probably the most notorious is the "gray zone" in acid-base accounting results, wherein the rate of predictive failure can still be significant despite the advances in understanding which have shrunk that zone over the years. Another complicating factor is how to assess the array of possible management practices which a mine operator may suggest to counter problems with overburden quality. Will alkaline addition work and how much is enough? What are the benefits of special handling of overburden materials and what specific plan is best for the site under consideration?

Risk Assessment

The need to consider the risk level associated with a prediction that proves to be incorrect is interwoven with the complicating factors which must be weighed when predicting mine drainage quality. The reality, which applies to any type of predictive endeavor, is tied to the need to consider risk: there will always be a certain percentage of failures, although under some conditions the risk of predictive failure is extremely low. Common sense and legal and regulatory requirements affect the level of certainty acceptable for a given prediction. For a mine site proposed on a pristine stream that serves as a public water supply, the level of certainty required of the prediction is much

higher than that required for a proposed remining site (one involving abatement of existing environmental problems) on a degraded stream. In the latter case it may be acceptable to permit a site where the predictive tools provide somewhat contradictory guidance. This action may be justified because of the potential benefits of remining the site, and the possibility of less stringent effluent limits - which for some pre-existing discharges may be equal to background polluted water quality. However, for the case of the pristine stream serving a public water supply, the requirement for stricter effluent limits, tighter in-stream standards, and the need to protect public health and safety suggest that all the predictive tools must provide strong evidence of acceptable postmining water quality to support a decision to approve mining on the site.

Each proposed mine site presents a different scenario of potential risks and benefits, usually not as clear-cut as the two just described. There are also risks associated with decisions, which err on the conservative side: property owners and society as a whole suffer economically if a site which can safely be mined is not permitted because of a misperceived risk level. While there has historically been little formal discussion of risk analysis as it applies to mine-site permitting, it nevertheless has been, and will continue to be, a factor weighed by permit applicants, technical consultants and regulators, who all naturally and inevitably consider the potential consequences of their decisions.

The Best Tool

Those who must predict postmining water quality sometimes debate which of the predictive tools should weigh the heaviest. An appropriate answer to the debate is "all of them." Some critical cases may require that all the factors point solidly in the same direction. However, more frequently, they do not, nor is it usually necessary that they do.

Water quality data from adjacent completed mining operations on the same coal seams are often cited as the most reliable of the predictive tools. This may be true as a generality, because such water quality data are direct empirical evidence. However, site-specific exploratory drilling and overburden chemical data should be used to evaluate lithologic, stratigraphic, and geochemical differences between the sites being compared. If these differences are significant, predictions based solely on adjacent mining can be completely wrong. For example, a completed site on which the overburden was primarily a channel sandstone without significant neutralization potential may have produced an acidic discharge. However, data from a proposed adjacent site may show that, due to facies changes, the overburden is primarily shale that is relatively high in calcium carbonate content. In that case it may be appropriate to weigh the water quality results from the adjacent mining less heavily than some of the other factors. In situations where well-documented historical data has proven that surface mining operations on certain seams consistently produce good quality water, site-specific overburden analysis may not even be required to make a correct prediction, and the requirement for overburden analysis may be waived.

Even when data from adjacent mining and site-specific overburden analyses are in complete agreement, serious prediction errors can occur if factors such as the extent and depth of weathering and the mining plan are not considered. For example, a completed site may have been mined to a ninety-foot highwall height and produced an acceptable quality discharge; the overburden analysis may show units high in sulfur but also may include a thick, consistent high-carbonate shale unit located forty feet above the coal. However, if the proposed site mining plan is to take only fifty to sixty feet of cover, perhaps due to thinning of the coal between the sites or the existence of a deep mine under higher cover, then it is doubtful that a significant amount of the high-carbonate shale unit will be encountered in a unweatherd state. Without consideration of weathering and the mining plan, a prediction based on historical water quality and a site-specific overburden analysis, which are in complete agreement with one another, could still be wrong.

In summary, the best predictions are those that weigh all the predictive factors, and serious errors can result from predictions that fail to consider less than all of the available data. Or, in the words of two noted researchers in the field of predicting volcanic eruptions: "Predictive capability is best achieved by using a combination of data sets and methods, rather than by reliance on any single procedure," (Voight and Cornelius, 1991).

Key Principles from Previous Chapters

The correctness of any prediction is dependent on the validity of the information considered. The following key principles from the previous chapters of this document must be understood and considered by

those who attempt to predict postmining water quality. As noted earlier in this chapter, information is not available on all the predicative factors all the time, nor is that always necessary. But the best predictions make use of the largest amount of scientific data available.

1. Not all mine sites in Pennsylvania make acid. Mine drainage quality can vary widely from waters that are highly acidic to waters that are highly alkaline. The metals concentrations found in mine drainage can also vary greatly. Tables 1 and 2 of Chapter 7 show the wide range of possible water qualities from mine sites by presenting the worst-case and best-case water qualities that the Department has documented from mine sites in PA. The presence or lack of carbonates strongly affect shallow groundwater chemistry.

2. There is no such thing as a "dry" mine site in the humid East where in any year precipitation always exceeds evapotranspiration. Every mine site contributes groundwater flow to lower strata and to downgradient discharge points, although in some geologic settings, the effects of the mining may be difficult to document. Sites located in groundwater discharge areas have the potential to create much larger problems in terms of the volume of water discharged through and from the site. However, water quality problems cannot be completely avoided by selecting "water-free" sites; they do not exist in the Appalachian coal fields.

3. Groundwater flow in mine spoil occurs in a "dual-porosity" system, as defined in Chapter 3. The hydraulic properties of spoil are difficult to predict. Porosity, hydraulic conductivity and transmissivity of mine spoil are much higher than in the undisturbed surrounding rock.

4. The environmental, economic and social consequences of incorrect mine drainage predictions are considerable.

5. Obtaining representative samples for overburden chemical analysis is critical. The importance of a well-planned sampling regimen following proper protocols is imperative. No prediction can be better than the quality of the underlying data.

6. Laboratory personnel and data interpreters must be aware of aspects of the acid-base accounting (ABA) test which can affect the reliability of the results. The fizz test is subjective. Since it determines the volume and normality of acid used in the neutralization potential (NP) digestion, it affects NP results. Siderite, a common mineral in Pennsylvania coal overburdens, can interfere with NP determinations. The addition of a hydrogen peroxide step seems to reduce this interference. Presently, using total sulfur values leads to more reproducible and accurate maximum potential acidity (MPA) values than does using forms of sulfur data.

7. Kinetic tests could be a valuable tool in the mine drainage prediction toolbox, because they factor in several variables found under field conditions but not reproducible by static tests. However, the large variation in the test methods used and the lack of standardization has made interpretation of kinetic test results quite challenging. There are specific physical, chemical and biological factors which should be included in any kinetic test.

8. In a general sense water quality can be correlated to the geologic units affected by mining, so proper understanding of the geologic section and of controls, such as depositional environments, can serve as a first-cut predictive technique. However, there can also be considerable regional and local variation in water quality generated from mines in the same geologic section. Tables 1 and 2 of Chapter 8 show how variable mine drainage quality can be and how the quality relates to the stratigraphic section being disturbed. The distribution of carbonates in the geologic section is critical to predicting mine drainage quality, because without carbonates significant alkalinity will not be produced. Site geology must be thoroughly understood to ensure representative overburden sampling and to develop appropriate mining and special handling plans.

9. Water quality from adjacent mining in the same strata can be a powerful predictive tool. However, site-specific data must be carefully analyzed to ensure that lithologic, geologic, geochemical, and hydrogeologic differences between sites do not negate the validity of the comparisons being made.

10. If the groundwater flow systems are properly understood, background water quality data from a proposed mining site can help confirm overburden analysis data and the presence of carbonates. This

background groundwater quality will not help significantly in identification of sulfur-bearing strata however, and it is possible to be misled by shallow flow springs, which typically do not reflect the chemistry of unweathered rock. The presence of alkaline water on a site can be helpful, even if the carbonates that generated it are located off site. Sites with natural groundwater quality low in buffering capacity due to an absence of carbonates can be prone to acid production.

11. Acid-base accounting has proven to be a valuable and reliable tool in predicting whether a mine site will generate acidic or alkaline water. The key to proper interpretation is to understand that a clear excess of carbonates is necessary to ensure alkaline drainage: predictions based on the assumption that NP need only equal or slightly exceed MPA will fail. Mine water chemistry is controlled by the typically small fraction of the overburden with significant carbonate and sulfide mineral content; as little as five percent of the rock on the site can control postmining water quality, while the remaining 95 percent of rock is essentially inert in terms of its effects on postmining drainage quality.

12. Proper reclamation and revegetation of a site can help reduce the potential for pollution by preventing excess infiltration. However, infiltration cannot be eliminated and even exceptional quality reclamation will not prevent acid mine drainage in an otherwise poor setting.

13. Alkaline addition can change the geochemical balance of a site and can produce alkaline drainage where acidic drainage would have otherwise occurred. However, on a typical site the amount of carbonate which must be imported to change the geochemistry, while small compared to the total overburden mass, is large when considered in terms of logistics and economics. The minimum amount needed is often cost prohibitive. Due largely to economic considerations, alkaline addition presently remains most viable on remining sites where lesser water quality standards, and therefore lesser amounts of carbonate addition may be acceptable. Alkaline addition may also be viable on sites with largely weathered overburden.

14. The effects of overburden special handling are not completely understood. On Pennsylvania surface mines, keeping the material well above the water table and limiting infiltration into it seems best. Continuous submergence has been shown to limit pyrite oxidation by limiting exposure to oxygen. However, hydrologic conditions are not conducive to continuous submergence on most Pennsylvania mine sites which are frequently located in upland recharge areas with highly fluctuating water tables.

15. The use of bactericides is a management technique presently best suited to limiting water quality problems, not preventing them. As with other management techniques, using bactericides may reduce the severity of a problem but is unlikely to prevent a problem in a setting with a high acid mine drainage potential. While bactericides can reduce bacteria catalysis, the presence or lack of carbonates controls whether a site produces alkaline or acidic drainage.

16. Water management is another technique that can be used to limit the potential for mine drainage problems, but which cannot completely prevent problems on a site otherwise likely to produce acid mine drainage. The emphasis should be on keeping the quality of water coming into the site good through the use of tools like surface water diversions and highwall drains. While capping of a site with ash or clay may be a helpful abatement technique once mine drainage pollution has developed, it is not generally possible, nor desirable, to completely eliminate infiltration into a site.

17. Remining can be an effective way to simultaneously develop energy resources and to reclaim previously abandoned mine lands. Reducing pollution loads by reducing flow can be an effective abatement technique on sites with pre-existing poor quality discharges. Implementing a combination of the management techniques described in this document can also provide positive results. Certain sites with particularly negative conditions may not be successfully rehabilitated by remining.

Data interpreters that approach the prediction of mine drainage quality and the prevention of mine drainage pollution with the preceding key principles in mind will make the right decisions most of the time.

Examples of Predictive Decisions

Examples of sites for which permits were requested from the PA DEP are presented in this section. The goal here is to illustrate the thought process that was

used to make a decision - sometimes in the face of somewhat conflicting evidence - not to establish whether the decision was right or wrong. The examples were chosen because of the points which they illustrate about the principles found in the other chapters in this document, and not because they necessarily are representative of permits that are either issued or denied. The reader is cautioned that these examples should not be applied directly to other sites, rather, all the information presented in all the other chapters of this document must be used to make predictive decisions about postmining water quality.

Site 1

Site 1 is located in Cambria County, PA. The operation proposed removing coal from 69.7 ac (28.2 ha), primarily on the lower Freeport coal (LF) with some upper Freeport coal (UF) to be encountered incidental to the LF mining. The operator also proposed mining 11.5 ac (4.6 ha) of upper Kittanning coal (UK).

The overburden includes the entire Freeport Formation of the Allegheny Group rocks and the lowermost part of the Glenshaw Formation of the Conemaugh Group, all of Pennsylvanian Age. At this locale these rocks are freshwater deposits with plant fossils common. The sediments typically include a significant amount of carbonate-bearing rock, suggesting that mine drainage associated with these strata should be alkaline. There are exceptions where the shales and fresh water limestones are replaced by channel sandstones and under low cover conditions where the carbonates have been removed by weathering. On Site 1, there were no significant channel sandstone formations present, so the overburden was comprised of the typically expected thin interbedded sandstones, shales and limestones.

Previous mining on these coal seams in Cambria County has generally led to alkaline water, typically with low metals concentrations. Some discharges from these seams may meet drinking water standards, with the possible exception of sulfate concentrations.

Drilling on the site confirmed the expectations about overburden quality formulated from a basic knowledge of the site geology. The data from the individual overburden holes will not be presented here in the interest of brevity. However, Table 18-2 displays a summary of the overburden geochemical data for the site. The data for each drill hole were weight averaged based on the acres and total mass of overburden represented by each drill hole. In Table 18-2 the overburden for both the UF seam and LF are combined into the "L. Freeport" category because the UF was to be mined only where encountered in the course of mining the LF. The UK seam was to be mined separately; consequently, it was considered separately in the overburden calculations.

Table 18.2 Overburden analysis data summary for Site 1. Calculated without thresholds from five drill holes on the LF seam and three drill holes on the UK seam.

COAL SEAM	MPA	NP	NET NP
L. FREEPORT (total tons)	68748	412772	344024
L. FREEPORT (ppt $CaCO_3$)	9.68	58.09	48.42
U. KITTANNING (total tons)	4118	45395	41277
U. KITTANNING (ppt $CaCO_3$)	2.61	28.8	26.19

The data show a compelling excess of carbonates in the LF overburden. The net NP of 48.42 ppt $CaCO_3$ is well above the 12 ppt $CaCO_3$ identified by Brady et al. (1994) as necessary to ensure alkaline drainage. A similar case can be made for the UK mining where the net NP is 26.19 ppt $CaCO_3$. The net NP for the UK overburden takes into account a plan presented by the mine operator to scour the proposed pit floor, which was composed of approximately 0.7 ft (0.2 m) of low-sulfur clay to expose the top of the Johnstown limestone to any water on the pit floor. When analyzed using threshold values of 30 NP, 0.5% S, and a 1 fizz rating, the LF overburden showed a calcium carbonate equivalent of 6724 t/ac excess while the UK overburden showed a 3289 t/ac excess.

Row 1 of Table 18.3 represents premining quality of a spring/headwater tributary whose entire potential recharge area lies within the mining area. The premining spring quality is typical for shallow groundwater flow springs in the Appalachian Plateau except that the pH is higher than expected, probably due to the carbonates in the overburden. Note that the alkalinity is low, demonstrating a point made in Chapter 10 that, as expected, shallow groundwater springs often do not reflect groundwater and overburden quality under higher cover. The site geology, acid-base accounting overburden analysis data, and mining plan seems to indicate that this site could be mined with little threat of a problem.

There was one other significant factor to consider. The site is located on a relatively undeveloped watershed which is classified as High Quality and which supports a wild brook trout population. The receiving

stream has very little buffering capacity and is only marginally supporting the trout population because of elevated acidity and aluminum concentrations. The acidity and aluminum come from natural weathering of Pottsville Group rocks in the headwater areas of the stream and from acid precipitation. Given the stream conditions, even a relatively minor acid mine drainage discharge could eliminate the aquatic life in downstream areas. These facts raised significant public opposition to the proposed mining. This was a very high-risk site where even a partially wrong predictive decision could have caused significant downstream impacts.

Site 1 is typical of those where all, or nearly all, of the predictive factors need to point strongly toward alkaline drainage, because of the unusually high degree of risk. In this case, because the major predictive tools did point strongly toward alkaline low-metals drainage, the mining was approved. It was also thought that in-stream alkalinities could even be raised by accelerated weathering of the carbonate-rich overburden. Mining of this site is nearing completion as of the date of this writing. Row 2 of Table 18.3 shows the postmining quality of the headwater stream which originates within the mining area. Both alkalinity and sulfate have increased substantially. The sulfate levels should have no negative impacts on aquatic life, while the alkalinity increases in this small tributary should help buffer the natural acidity in the main stream to which it discharges. (Note that had a public water supply intake been located in close proximity downstream of the site, the potential sulfate increase was another risk factor which would have to be considered.)

Table 18.3 Median water quality at the mouth of the headwater stream emerging within Site 1, based on the first five premining samples and the last five postmining samples collected.

Date	Flow (gpm)	pH (su)	Alkalin. (mg/L)	Fe (mg/L)	Mn (mg/L)	Al (mg/L)	Sulfate (mg/L)
Premining	41.0	6.88	9	0.05	0.02	<.10	10
Postmining	15.0	7.92	159	0.06	0.03	0.11	327

Site 1 illustrates several of the key principles from the previous chapters. The key to interpreting acid-base accounting data, and the geologic setting, is to evaluate the amount of carbonates on the site (Chapter 11). Background groundwater information can be useful, but shallow groundwater springs may not fully represent site geology (Chapter 10). Not all surface coal mining sites make acid mine drainage, and high levels of alkalinity can be produced (Chapter 1). Special care must be taken in high-risk areas, but when the scientific data clearly shows that the risk of a problem is remote, the decision making should follow the lead of the data.

Site 2

Site 2 is also located in Cambria County, PA. Mining was proposed on 25.5 ac (10.3 ha) of lower Kittanning coal (LK), 28.8 ac (11.6 ha) of middle Kittanning coal (MK) and 8.6 ac (3.6 ha) of upper Kittanning (UK) coal.

The overburden on Site 2 includes all the Allegheny Formation and the lowermost section of the Freeport Formation in the Allegheny Group. In the area of this site, the LK and MK overburden rocks are generally brackish water deposits. Channel sandstone deposits frequently exist within a framework of finer-grained sediments such as shales and mudstones. Within the Allegheny Formation in this area, the only significant zone rich in carbonates is the Johnstown limestone horizon (freshwater) which is typically located at or a few feet below the bottom of the UK coal. The shale units, especially those which directly overly the LK and MK coals frequently include significant amounts of sulfide minerals. With the lack of carbonates in the overburden and the high sulfur shales located around the coals, one would expect LK and MK mining to produce poor quality water, although the role of the Johnstown Limestone has to be considered in that conclusion.

Surface and deep mining on the LK and MK seams in the area of Site 2 generally has resulted in acid mine drainage. Because of its persistence, thickness and quality, the LK seam has been extensively deep mined, so is generally available for surface mining only under lower cover. The MK seam, while usually of good quality, is usually not thick enough for deep mining and often occurs in multiple benches. Surface mining on these seams, therefore, often cannot take place to a high enough cover to encounter much, if any, of the Johnstown limestone. This is a case where the mining plan must be accounted for in interpreting the overburden analysis data. Holes drilled at high cover through the Johnstown limestone may indicate an ample excess of carbonates, but mining may be limited to low cover. While the overburden for these seams can be problematic, the previous mining that has occurred and the resultant unreclaimed spoil, deep mines and discharges

present remining opportunities at locations where appropriate mining plans can be developed.

The exploratory data on Site 2 confirms what is known about the regional geology. Over most of the site, the LK coal is directly overlain by a shale of 0 to 12 ft (0 to 4 m) in thickness. Above that is a thick channel sandstone, which cuts down to the top of the coal in places. There is a thin clay layer beneath the MK coal. The MK overburden over most of the site is shale, with minor sandstone units in places. The Johnstown limestone is not present on the site, but at the horizon where it would be expected, there is a shale unit which contains significant amounts of carbonate, as high as 27 % (NP = 270 ppt $CaCO_3$). Unfortunately, the high-carbonate shale exists only at the highest cover in an unweathered state and only a limited amount of it will end up in the backfill. The UK coal would be mined incidental to the MK on this site, and due to its thinness and weathering, it is doubtful that much of it is actually recoverable.

Table 18.4 displays a summary of the overburden data for the site. These data show a probability for the site to produce acid mine drainage. The LK overburden has a net NP of -5.80 ppt $CaCO_3$ and the MK has a net NP of -0.66 ppt $CaCO_3$. The positive NP for the MK overburden is from the carbonate in the Johnstown Limestone horizon. In terms of calcium carbonate equivalence, the LK overburden showed a deficiency of 653 t/ac and the MK overburden showed a deficiency of 65 t/ac.

Table 18.4 Overburden analysis data summary table for Site 2. Calculated without thresholds. Represents six drill holes on each coal seam.

COAL SEAM	MPA	NP	NET NP
L. KITTANNING (total tons)	**14514**	**0**	**-14514**
L. KITTANNING (ppt $CaCO_3$)	**5.8**	**0**	**-5.80**
M. KITTANNING (total tons)	**15310**	**13433**	**-1876**
M. KITTANNING (ppt $CaCO_3$)	**5.4**	**4.74**	**-0.66**

Table 18.5 shows the water quality associated with Site 2. MW-2 is a monitoring well drilled into the Kittanning sandstone of the Clarion Formation, but the recharge area for the well includes the area being mined. MD-1 is an abandoned LK deep mine discharge which is of acid mine drainage quality. The premining data from MW-2 represents natural background quality in an area of the site not substantially affected by previous mining. Note the low pH and natural acidity of the water reflecting the lack of carbonates in the overburden.

Table 18.5 Median water quality data from Site 2. MD-1 data represents the median values from 21 samples. MW-2 data represents the first 4 and last 4 samples collected

Sample Point	Date	pH (su)	Acid. (mg/L)	Fe (mg/L)	Mn (mg/L)	Al (mg/L)	Sulfate mg/L)
MW-2	**Premining**	**5.3**	**8.5**	**2.06**	**0.26**	**0.30**	**48**
MW-2	**Postmining**	**3.5**	**150**	**16.80**	**14.40**	**6.92**	**427**
MD-1	**Premining**	**2.6**	**570**	**66.86**	**5.47**	**34.14**	**790**

Mining on Site 2 included a proposal to daylight some of the abandoned deep mines, and to reclaim old spoil and an abandoned highwall on the site. The mining plan also proposed alkaline addition in the form of ash from a circulating fluidized-bed combustion boiler power plant, which burns coal refuse to generate electricity. The proposed ash had a NP of about 240 ppt $CaCO_3$ and the proposed ash addition rate was 2160 t/ac (4850 t/ha) averaged over the site, which equates to approximately 500 tons of calcium carbonate addition per acre (1,123 t/ha). The ash was to be added to the pit floor, mixed with the spoil, and added to special-handled material at different rates for each coal seam being mined. Effluent limits for two preexisting discharges on the site, including MD-1, would be determined by the baseline pollution load for the discharges under the Department's Subchapter F program.

The receiving stream at this site was already degraded by the past mining. However, approximately 4 to 5 miles (6.4 to 8 km) downstream, it does improve enough to allow for stocking of brook trout.

In this case a decision was made to permit the site. While many of the predictive factors indicated that there was a risk of mine drainage production, the benefits of the reclamation which would be gained were also weighed. Other mitigating factors were the alkaline addition proposal and the effluent limits equal to baseline conditions for the existing discharges.

Shortly after the permit was activated problems developed. Mining began in an area upgradient of MW-2. The postmining data for MW-2 in Table 18.5 showed that the character of the groundwater in the area began to change to one representative of acid mine drainage. A spring downgradient from the site showed similar changes. Factors considered as possible causes for the changes were an alkaline addition rate which may not have been high enough and rerouting of water from the existing deep mines along flow paths which could not be anticipated. Because the problems were identified early in the operation, changes were made to

the mining plan in an attempt to salvage the situation. At the time of this writing, these changes are being implemented. A series of anoxic limestone pit floor drains are being installed as mining progresses to route the deep mine water through the site without contacting additional acid-forming material. The operator is trying to obtain additional amounts of ash so the alkaline addition rate can be increased. Passive treatment systems may eventually be added to the end of the pit floor drains, depending on final postmining water quality. Mining at the site is on-going so the final outcome is unknown at this point.

Site 2, although its final results are unknown, illustrates several key points. The site geology (Chapter 8), premining groundwater quality (Chapter 10) and the acid-base account overburden analysis data (Chapter 11) were all in agreement as to the lack of carbonates on the site. That, along with the previous history of mine drainage (Chapter 9), indicated the potential for problems. Because the risk factors were relatively low in terms of direct in-stream environmental impacts and because of mitigating factors like reclamation work (Chapter 17) and a substantial alkaline addition proposal (Chapter 13), a decision was made to approve mining on the site. The problems that did develop illustrate the need to ensure a clear excess of carbonate on a site when alkaline addition is proposed (Chapters 1, 8, and 11); it also illustrates the need to understand and consider to the extent possible groundwater flow systems (Chapter 2) in and around the site, especially when there is pre-existing pollution present. The fact that adjustments could be made to the mining plan relatively early in the operation, with some hope of salvaging the situation, illustrates one of the benefits of a good groundwater monitoring plan and demonstrates the applicability of mitigation tools such as pit floor drains (Chapter 16).

Site 3

Site 3 is located in Somerset County, PA. The mining plan proposed the removal of 65.2 ac (26.4 ha) of upper Freeport coal, so the overburden to be disturbed was the lowermost portion of the Glenshaw Formation of the Conemaugh Group. As noted in the discussion of Site 1, in Cambria County, these sediments are typically freshwater shales and limestones, and significant amounts of carbonate can be present. However, as one approaches the Maryland border in southwestern Somerset County, conditions change.

Drilling data from Site 3 revealed that much of the overburden was a thick sequence of massive sandstone, although a shale unit did directly overlie the coal in some holes. On a mass-weighted basis across the site, sandstone represented 64% of the overburden, but in some locations comprised up to 90% of the overburden.

A monitoring well was installed on the site to determine background groundwater quality. However, the well was constructed with portland cement grout. When sampled during pump tests, the well would initially produce highly alkaline water, but the alkalinities would decline with time. It was apparent that the grout was affecting the well quality to an extent that the data from the well could not be reliably used, so background groundwater quality was an unknown for the site. The hydrologic setting for the site was such that there were no springs or discharges which could be reliably used to determine background quality. The UF seam had been mined on areas adjacent and near to the proposed mine site, resulting in acid mine drainage discharges.

Table 18.6 summarizes ABA overburden analysis data for Site 3. When analyzed without using thresholds the site has a positive net NP of 3.80 ppt $CaCO_3$. When examined using thresholds, there are no individual sampling units with a significant NP (>30 ppt $CaCO_3$), and very few units with >0.5% sulfur; the average calcium carbonate equivalence of the entire overburden column is -36.0 t/ac (-80.8 t/ha). This is a classic example of the low NP/low sulfur site that falls into the difficult gray area of interpretation for ABA data.

Table 18.6 Overburden analysis data summary table for Site 3. Calculated from six drill holes without using thresholds.

COAL SEAM	MPA	NP	NET NP
U. FREEPORT (total tons)	24912	57401	32489
U. FREEPORT (ppt $CaCO_3$)	2.91	6.71	3.80

The permittee drilled an overburden hole on one of the adjacent sites which had produced poor water quality to determine if there were geochemical differences between the proposed site and the adjacent site. That hole revealed an overburden column, when examined without thresholds, with a negative net NP of -3.45 ppt $CaCO_3$. With thresholds the calcium carbonate equivalence of the adjacent site was -1695 t/ac (-3084 t/ha). The adjacent site overburden had several

zones high in total sulfur. There were also lithologic differences between the sites in that there was a higher percentage of shale in the overburden of the adjacent site. It appeared that there was some validity to the argument that the results of the adjacent mining may not fully represent what could be expected to occur on the new site.

This proposed mine site was located on a high quality stream that supported a trout fishery. The stream had suffered some degradation from the nearby mine sites, some of which had mined the UF seam, but the fishery was still viable. In addition to the risk of degradation to a valuable stream, the risk of cumulative impacts was especially important here, because the stream had already suffered some degradation from the previous mining.

In the end, Site 3 was not permitted for mining. While there was some ambiguity in the ABA data, none of the predictive tools indicated that alkaline drainage was likely, and there were indications that acid mine drainage would result. The prevalence of sandstone in the overburden was a concern (Chapter 8). There was not a clear abundance of carbonates on the site (Chapters 1, 8 and 11); in fact, there was very little carbonate present. While the comparability of the historical water quality data from previous mining (Chapter 9) was questionable, there was no evidence that previous mining had produced good quality water in the vicinity. While the UF overburden is part of a geologic section that frequently does produce good quality water, the site-specific lithologies showed that the conditions which normally generate the alkaline drainage were not present on this site (Chapter 8). Background groundwater quality was essentially a piece of missing information here (Chapter 10.) This was a high-risk site in terms of its location on a high quality stream and the potential for cumulative impacts on a fishery. There was little positive data which supported mining.

Site 4

Site 4 is located in Redbank Township, Armstrong County. Approximately 30 ac (12.1 ha) of lower Kittanning (LK) coal were proposed to be mined on this site. The overburden comprises the lowermost section of the Kittanning Formation of the Allegheny Group. On-site drilling showed that shale made up most of the strata. The two overburden analysis holes on the site contained three percent sandstone, with the remainder of the strata being fine- grained sediments, primarily shale. The rocks to be disturbed were deposited in a shallow marine environment, based on the fossils found in them. Many of the fossils appeared to be comprised of secondary calcite (Richard Beam, PA DEP, personal communication, 1997).

The site had previously been surface mined to a relatively low cover height, so that most of the background groundwater quality was at least slightly affected by previous mining. In general, that water quality was alkaline with slightly to moderately elevated sulfate concentrations and low metals concentrations. The site setting is such that, beyond the mine site, the LK coal was overlain entirely by the Allegheny Group. Groundwater coming onto the site may have been deriving some alkalinity from the limestones higher up in that group (Richard Beam, PA DEP, personal communication, 1997).

Site 4 is located on the Mudlick Creek watershed. Mudlick Creek is classified as a cold water fishery, and supported aquatic life, including fish. However, previous mining had resulted in increased sulfates in the stream. The risk factors associated with this site could best be described as moderate: the stream was not of pristine quality and did not serve as a public water supply, but was nonetheless of decent quality.

Table 18.7 summarizes the ABA overburden analysis data for Site 4. The overburden included several feet of relatively high sulfur (%S >0.5) strata and several feet of strata with significant neutralization potential (NP > 30 ppt $CaCO_3$). However, the NP values were only marginally significant and the highest in either hole was 42 ppt $CaCO_3$. The NNP for the site was 1.00 ppt $CaCO_3$, calculated without using thresholds. The overburden analysis data considered alone indicate that Site 4 has a high probability of producing acidic drainage.

Table 18.7 Overburden analysis data summary table for Site 4. Calculated without thresholds. Represents weighted average of two drill holes.

COAL SEAM	MPA	NP	NET NP
L. KITTANNING (total tons)	70284	73336	3052
L. KITTANNING (ppt $CaCO_3$)	23.02	24.02	1.00

The lower Kittanning coal has been mined throughout northeastern Armstrong County and southwestern Jefferson County. The site conditions and overburden analysis results for Site 4 are typical of the LK coal in this area. The LK mines in the area have consistently

produced alkaline drainage with low metals concentrations, despite the overburden analysis data which indicate that acid drainage will occur. Adjacent mining is frequently given precedence when prediction tools conflict and where there are not hydrogeologic or other differences between sites which may lessen the validity of comparisons made between sites. Based largely on the results of previous mining done in the area under very similar conditions, Site 4 was permitted and mined.

Table 18.8 displays water quality data from a postmining discharge that emerged when Site 4 was completed. The data in Table 18.8 are average values of 10 samples collected from the discharge. The discharge is alkaline with low metals concentrations and moderately elevated sulfate concentrations.

Table 18.8 Median postmining water quality data from Site 4. Average values based on ten samples.

Sample Point	Date	pH (su)	Alk. (mg/L)	Acid. (mg/L)	Fe (mg/L)	Mn (mg/L)	Al (mg/L)	Sulfate (mg/L)
Discharge	Postmining	6.7	68	0	0.23	0.25	<.50	267

Site 4 illustrates a problem with interpreting neutralization potential values in the range of a few tens of ppt. It is typically unknown what carbonate minerals are present. The common iron-carbonate mineral siderite frequently produces NP values in this range. Siderite, as discussed in other chapters of this document, does not generate alkalinity. X-ray diffraction analyses were performed on the overburden for Site 4. The X-ray diffraction showed that the NP present on Site 4 was from calcite rather than siderite (Richard Smith, PA Geological Survey, personal communication, 1996). It is possible that the intimate association of the calcite with the pyrite inhibits pyrite oxidation. (The overburden samples containing significant percent sulfur were typically the samples which included the highest NP values.)

Site 4 illustrates the need to understand the geologic setting of the site being evaluated (Chapter 8). On Site 4 the LK overburden is of marine origin, while on Site 3 it is of brackish origin, which is a significant factor in the geochemical differences between the sites. The results from previous mining results was the key predictive tool used here (Chapter 9). The role of siderite, as discussed in several previous chapters also is a significant consideration here. As emphasized elsewhere in this chapter, predictive decisions need to be made in the context of all the available data; it would have been easy to mistakenly assume that Site 4 could not be successfully mined, if a decision was made based solely on the overburden analysis data.

Conclusions

Much progress has been made over the past twenty to twenty-five years toward better predictions of postmining water quality. One area where some of the greatest increases in understanding have come is in the use of ABA data and the corollary understanding of the important role that carbonates play in defining mine drainage quality.

There are four areas that stand out as needing further work to continue the progress so far made, and those engaged in research concerning mine drainage prediction are urged to pursue work in these directions to further advance the science:

1. Industry, consultants, academic researchers and regulators need to take a closer look at the vast amount of data currently available, and which continues to become available, to better record and refine predictive techniques. The best way to improve predictive tools is to study completed sites to determine which factors had the most significant role in influencing water quality. To this end a sound representative monitoring program for each site should be seen as providing a future benefit to all who have an interest in understanding postmining water quality
2. Kinetic tests need to be standardized if they are to fulfill their potential role as an important tool in predicting postmining water quality. The fragmented and repetitive nature of much of the work which has been done with these tests has made the interpretation of the results quite challenging.
3. The potential value of mitigating tools such as alkaline addition, special handling, bactericides, and hydrologic controls needs to be documented and understood. It is especially important to thoroughly monitor and study sites that employ one or more of these techniques.
4. There is a need to move into the realm of quantifying postmining predictions. Today, the best that can be obtained is a determination of whether drainage will be net alkaline or net acidic. In many sensitive areas it is necessary to go a step beyond to determine what concentrations of various parameters may occur.

While much improvement has been made over the past twenty years in predicting postmining water quality, there are significant advances yet to achieve. Those engaged in making predictions must always keep in mind that the best predictions will be those using as many of the predictive tools as are available.

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Gary Fleeger - received his B.S. in geology from Bucknell University, and a M.S. in geology from the University of Illinois at Urbana-Champaign. His M.S. research involved the till stratigraphy of the pre-Wisconsin glacial episodes in western Illinois. Gary is currently a hydrogeologist with the Pennsylvania Geological Survey. Prior to this he was with the PA DEP as a hydrogeologist with the Bureau of Mining and Reclamation, and as a geologist for the Bureau of Oil and Gas Management . Previous employers include the Colorado Department of Health (drinking water program), the oil and gas industry in Colorado, coal consultant in Pittsburgh, PA, and the Illinois State Geological Survey.

Michael D. Gardner - has been a hydrogeologist with the Greensburg District Mining Office of PA DEP since 1983. He was previously employed by the U.S. Bureau of Mines and the U.S. Army Corps of Engineers. Mike has a B.S. from the University of Pittsburgh in earth and environmental sciences with geology being his area of concentration. He also holds an Associate Degree from the Community College of the Air Force in Weather Technology (Meteorology). His research interests and publications encompass water management, special handling techniques, and mine drainage prediction on surface coal mines in Pennsylvania.

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Tim Kania - is a hydrogeologist in the PA DEP's Ebensburg District Mining Office. He has worked for DEP since 1982. His experience and professional interests lie in the areas of predicting postmining water quality and other aspects of mining hydrogeology. Tim holds a B.A. in journalism and a B.S. in earth sciences, both from Pennsylvania State University.

Robert L. P. Kleinmann - received his Bachelors Degree in geology from Penn State in 1974, and his M.A. and Ph.D. in geology (Water Resources Program) from Princeton University in 1976 and 1979 respectively. He was hired by the U.S. Bureau of Mines in 1979 to establish an acid mine drainage research team at the Pittsburgh Research Center, and served as a group supervisor until promoted in 1984 to Research Supervisor for the Environmental Technology Division. When the Bureau of Mines was abolished by Congressional action in 1995, Bob and his group were transferred into the US Dept. of Energy, where he currently serves as Director of the Environmental Science and Technology Division. He serves as editor of the international journal, Mine Water and the Environment.

David Maxwell - has worked for Amerikohl Mining, Inc. since 1987. He has held positions as lease manager and general manager. In 1993 he became vice president of Amerikohl. Prior to working for Amerikohl he worked for Walter E. Fike, P.L.S. preparing surface mining permit applications. Dave has an associate degree in petroleum engineering from the University of Pittsburgh and a wealth of practical mining experience.

Eric F. Perry - is a hydrologist with the US Office of Surface Mining, Appalachian regional office in Pittsburgh (OSM). He has thirteen years experience with OSM in technical investigations, training, and applied studies. Prior to OSM, he worked for five years as a consultant in waste management and mine permitting projects. He holds B.S. and M.S. degrees in soil science from West Virginia University, and is currently engaged in Ph.D. studies in hydrogeology. His professional interests include geochemistry and mine water quality, and quantitative hydrology of underground mines.

Arthur W. Rose - received a B.S. in geology from Antioch College and a Ph.D. in geology and geochemistry from the California Institute of Technology. From 1957 to 1964 he was an exploration and research geologist for Kennecott Copper Co., and from 1964 to 1967 he mapped geology for the Alaska Division of Mines and Minerals. In 1967 he joined the Department of Geochemistry at Penn State University, where he taught exploration and environmental geochemistry, and economic geology. He conducted research on geology and geochemistry of ore deposits, exploration geochemistry, acid mine drainage and geochemistry of radon and uranium decay products in soils. In 1996 he retired as Professor of Geochemistry, but continues investigations of alkaline addition and passive treatment of acid mine drainage. Art has authored numerous publications on a wide range of geochemical topics.

Joseph H. Schueck has a B.S. in geology from Indiana University of Pennsylvania. He worked for the Pennsylvania Department of Transportation as a soils engineer from 1970 to 1978. Joe is a registered professional engineer in geotechnical engineering, and a registered professional geologist. Since 1978 he has been employed by PA DEP's Bureau of Mining and Reclamation. His professional interests are the application of geophysical methods to characterize mine sites and the abatement and remediation of AMD. In 1994 was honored as the Conservation Professional of the Year by the Pennsylvania Federation of Sportsmen and Conservationist of the Year by the National Association of State Land Reclamationists.

Dennis J. Shaffer - is owner of Fike Associates Inc., a consulting firm in Clarion, PA. From 1987 to 1997 he was employed by Walter E. Fike, P.L.S., predecessor of the company he now owns. Previous employment includes 3 years as a geologic field director for Vendel Enviro-Industrial Consultants in Pittsburgh, PA. Denny holds B.S. degrees in geology and geography, both from Clarion University. He is a member of professional associations and societies in geology, hydrogeology, surveying and mapping, and is a member of the Pennsylvania Mining Professionals and the Pennsylvania Coal Association.

Michael W. Smith - is District Mining Manager at PA DEP's Hawk Run District Mining Office. He is a registered professional geologist and has worked for PA DEP as a hydrogeologist for over 16 years in the mining, waste management, geologic survey, and water quality programs. He earned a B.A. in geology and environmental sciences from Susquehanna University and a M.S. in geology (emphasis in hydrogeology) from the Pennsylvania State University. He has published articles on remining and alkaline addition, serves as an instructor for OSM's applied hydrology and surface and groundwater courses, and worked on the development of Pennsylvania's remining program.

G. Nevin Strock - is Chief, Surface Mining Section, Division of Permits, Bureau of Mining and Reclamation, PA DEP. He has been employed since 1970 in Pennsylvania's mining regulatory program, including 9 years of field work involving reclamation and revegetation of coal surface mines. He has a B.S. in forest technology from Pennsylvania State University. Nevin has been a member of the Society of American Foresters (SAF) since 1966 and has served as Chairman of the Pinchot Chapter of SAF. He has also served as Chairman of the Pennsylvania Council for Surface Mining Reclamation Research.

Joseph M. Tarantino - is a hydrogeologist with PA DEP. He has worked at the Knox District Mining office since 1980. Prior to that he worked two years as a physical lab technician with IU Conversion Systems specializing in the stabilization of Coal Ash, SO_2 scrubber sludge and other industrial waste products. Joe is an instructor for the Office of Surface Mining's Acid-Forming Materials: Fundamentals and Applications course and their Surface and Groundwater Hydrology course. He is also a member of the Acid Drainage Technology Initiative's Prediction Work Group. Joe has a B.S. in geological sciences from Pennsylvania State University; and is a registered professional geologist in Pennsylvania.

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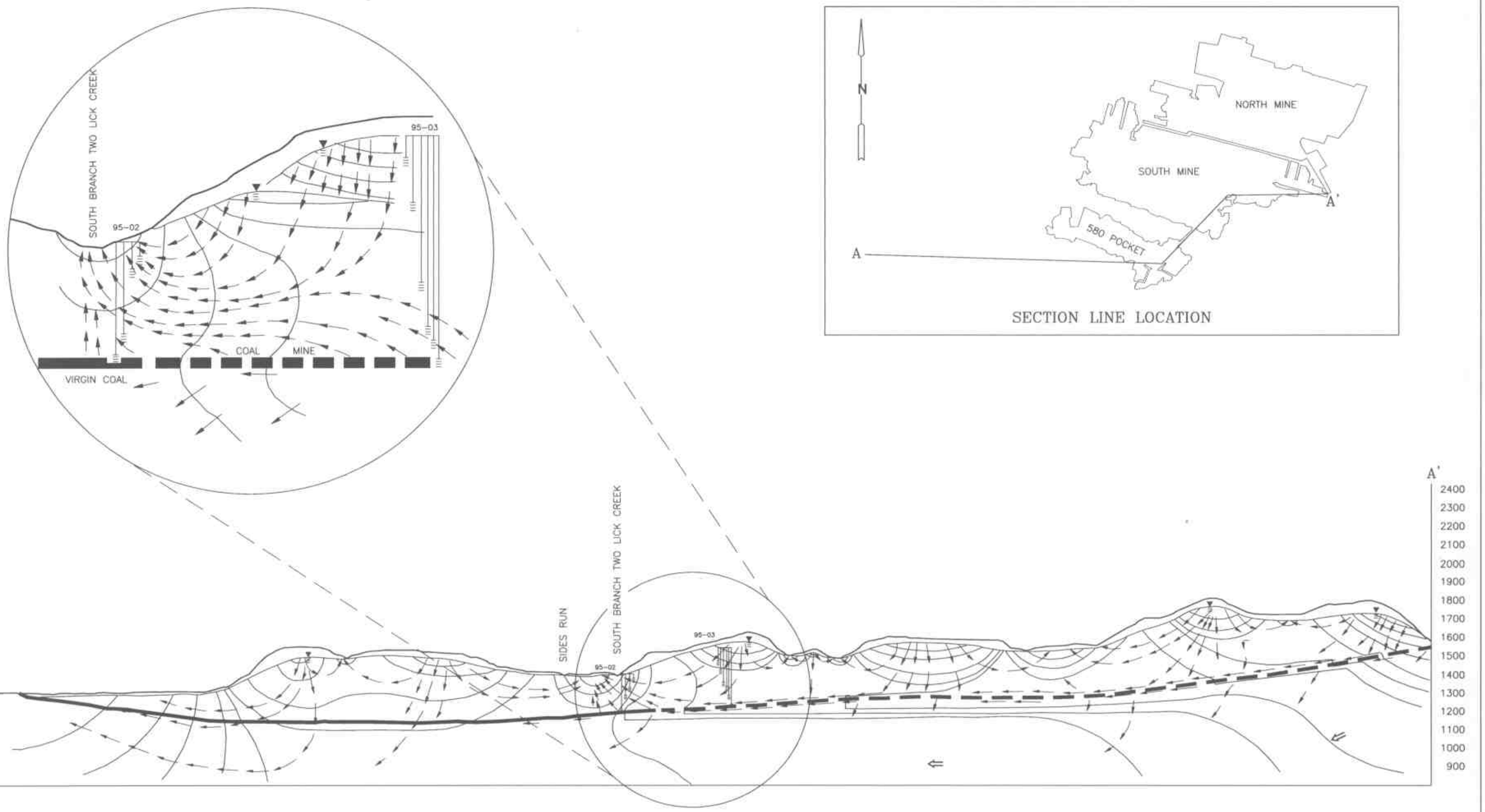
FIGURE 2.20 Qualitative Flow Net (South Mine and 580 Pocket)



SECTION LINE A – A'

(HOR. : VER. = 5:1)

Coal Mine Drainage Prediction
and
Pollution Prevention in Pennsylvania
Figure 8.2

Figure 8.2. Generalized stratigraphic section of the bituminus coal field of western Pennsylvania, showing positions of principle coals, marine zones, and major freshwater limestones. Also shown are distributions of rock types and carbonates that can influence mine drainage quality. Histograms should be considered semi-quantitative. Formation thicknesses are to approximate scale of 1 in. = 100 ft. (2.5 cm =30.5 m). Coal and limestone thicknesses are not to scale, but are located in their approximate stratigraphic position. Coal seams and limestones are generally not continuous or present in all areas. ▽▽▽ Marine Fossils × × × Brackish Fossils

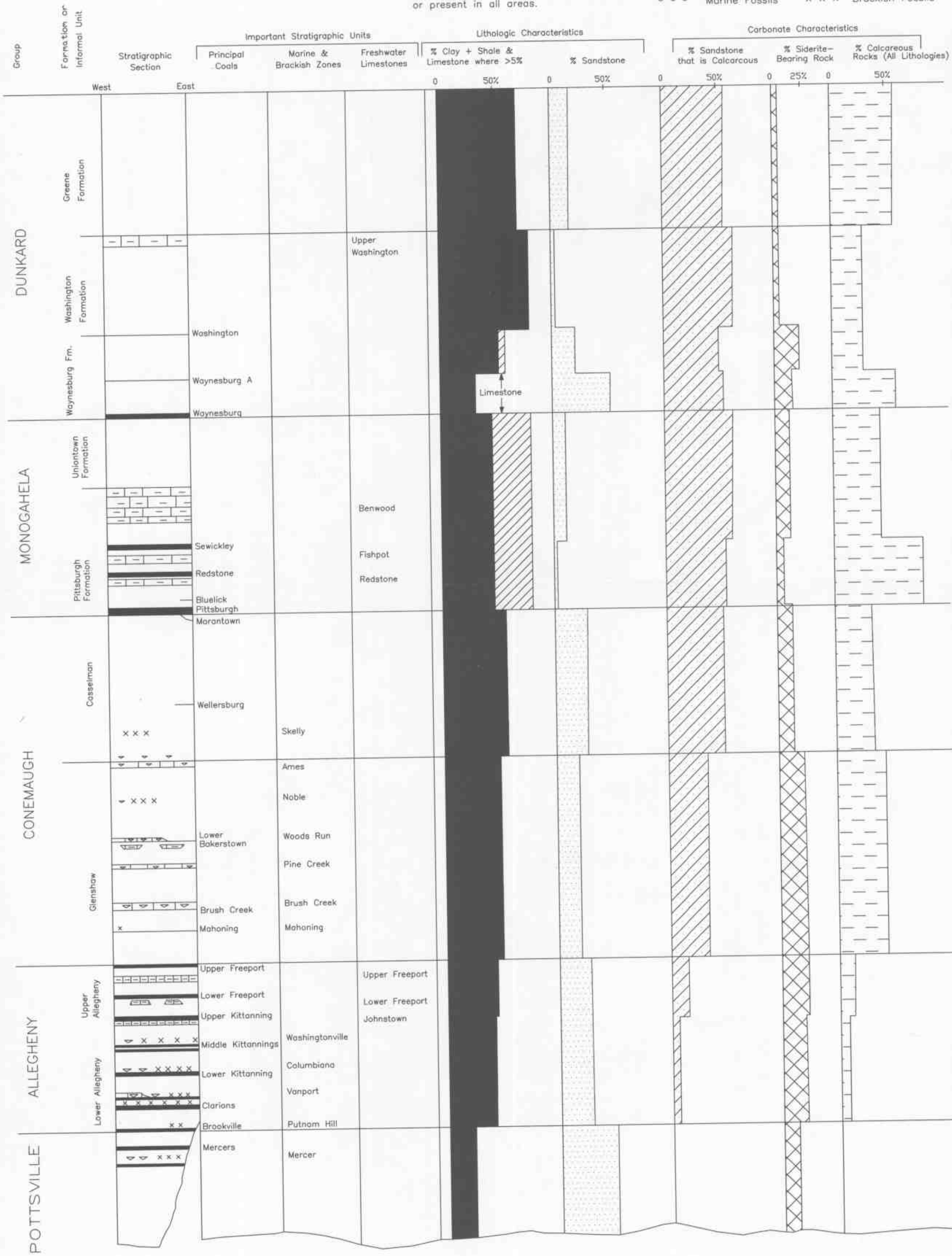
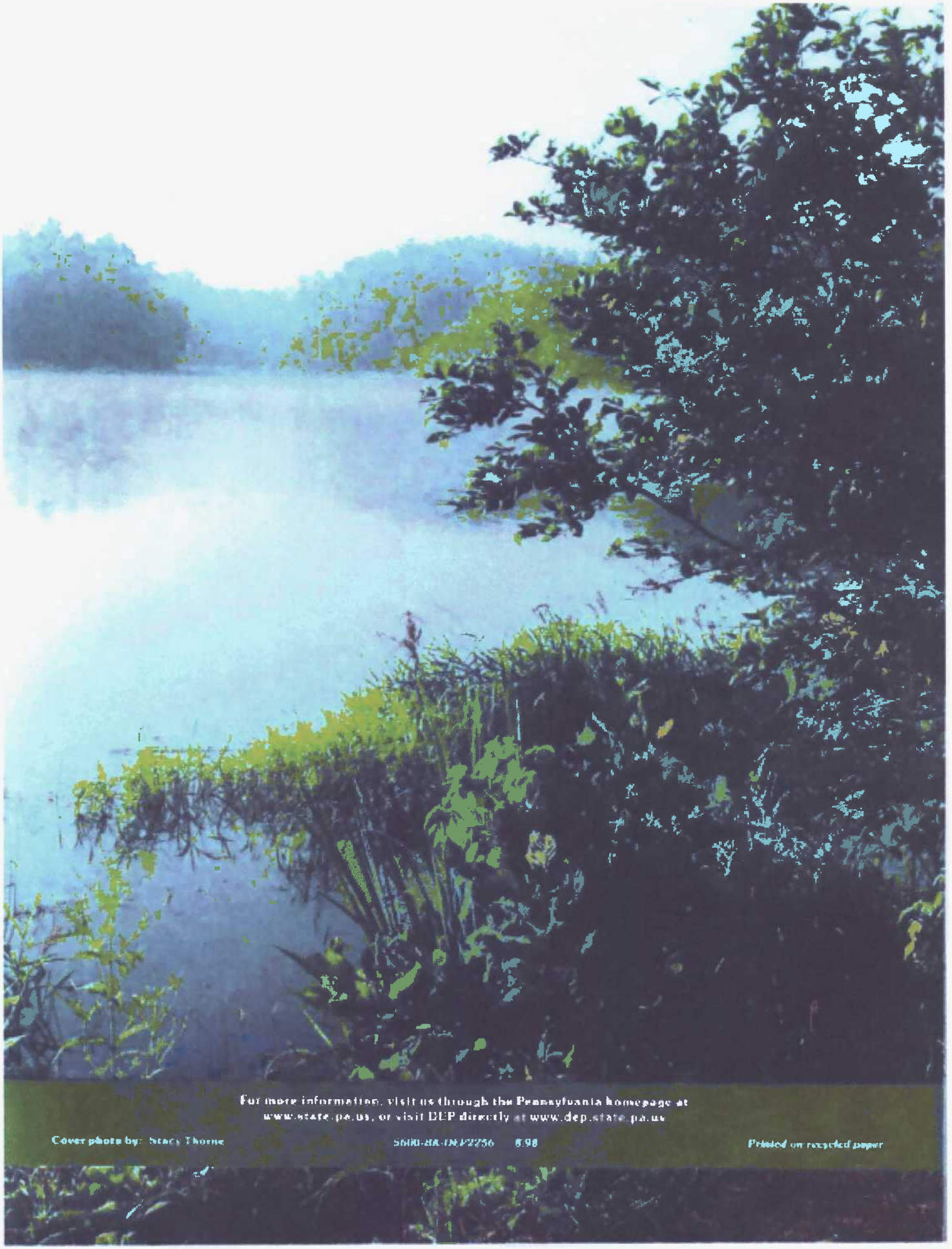


Table 8.2 Postmining water quality of Pennsylvania Bituminous Coal Region by stratigraphic interval.

	SMP #	Site Name	Township	County	Stratigraphic Interval	Date Sampled	pH	Alkalinity mg/L *	Acidity mg/L *	Fe mg/L	Mn mg/L	Al mg/L	SO_4 mg/L	TSS mg/L	Type of Sample	Comments
Dunkard Group	30813011	Willow Tree	Greene	Greene	Waynesburg	11/5/80	7.8	379.0	0.0	0.12	0.04	no data	165.0	17.0	Seep	at deep mine DM-2, pre-mining, 1 gpm
	30813009	Susan Ann	Greene	Greene	Waynesburg	5/29/81	4.3	340.0	0.0	3.04	0.02	no data	180.0	27.0	Seep	at deep mine DM-2, pre-mining, <1 gpm
	30813009	Susan Ann	Greene	Greene	Waynesburg	6/14/85	3.3	0.0	1500.0	324.40	89.70	92.40	2616.0	12.0	Seep	near DM-2 sealed entry, during mining, <1 gpm
	30813009	Susan Ann	Greene	Greene	Waynesburg	6/14/85	3.4	0.0	306.0	101.30	34.70	19.40	1122.0	8.0	Seep	near DM-2 sealed entry, during mining, <1 gpm
	30813009	Susan Ann	Greene	Greene	Waynesburg	6/13/91	6.8	142.0	0.0	< 0.30	6.20	< 0.50	624.0	10.0	Seep	near deep mine DM-1, post-mining, 5 gpm
	30813009	Susan Ann	Greene	Greene	Waynesburg	6/13/91	7.7	244.0	0.0	7.34	20.20	< 0.50	1380.0	27.0	Spoil Discharge	discharge F, 8 gpm
	30813009	Susan Ann	Greene	Greene	Waynesburg	10/24/91	7.9	288.0	0.0	2.61	17.60	< 0.50	1392.0	15.0	Spoil Discharge	discharge F, <1 gpm
	30813009	Susan Ann	Greene	Greene	Waynesburg	11/5/80	8.0	292.0	0.0	0.24	0.09	no data	170.0	7.0	Spring	combined flow of springs pre-mining, 1.5 gpm
	30813009	Susan Ann	Greene	Greene	Waynesburg	8/7/81	7.9	296.0	0.0	0.49	0.09	< 0.10	124.0	no data	Stream	headwaters tributary pre-mining
	30813009	Susan Ann	Greene	Greene	Waynesburg	8/29/81	7.7	288.0	0.0	0.11	0.04	no data	180.0	< 10.0	Stream	tributary A above site post mining, <1 gpm
	30813009	Susan Ann	Greene	Greene	Waynesburg	8/11/83	8.0	213.0	0.0	0.22	0.13	no data	133.0	2.0	Stream	tributary C below haulroad pre-mining, 33 gpm
	30813009	Susan Ann	Greene	Greene	Waynesburg	8/10/88	7.1	238.0	0.0	0.37	0.17	0.08	140.0	25.0	Stream	tributary C below haulroad during mining, 20 gpm
	30813009	Susan Ann	Greene	Greene	Waynesburg	10/24/91	7.9	238.0	0.0	< 0.30	< 0.05	< 0.50	312.0	< 2.0	Stream	tributary C below haulroad post-mining, 8 gpm
	30850103	Viable	Greene	Greene	Waynesburg	7/25/85	5.8	18.0	4.0	< 0.30	0.10	< 0.50	62.0	6.0	Deep Mine Disch.	MP-MD1, punch mine discharge, <0.5 gpm
	30850103	Viable	Greene	Greene	Waynesburg	7/25/85	6.3	60.0	0.0	< 0.30	0.12	< 0.50	88.0	4.0	Deep Mine Disch.	MP-MD2, punch mine discharge, 2-3 gpm
Monongahela Group	26870107	Bertovich	Nicholson	Fayette	Sewickley	11/4/87	3.1	0.0	378.0	74.80	9.14	30.50	1098.0	18.0	Deep Mine Disch.	MP-1, 2 gpm
	26910106	Nobel	Georges	Fayette	Sewickley	4/1/76	4.2	0.0	22.0	4.32	9.97	2.92	964.0	23.0	Seep	MP-N7, flow to ponds near final highwall, <1 gpm
	26910106	Nobel	Georges	Fayette	Sewickley	5/21/91	3.1	0.0	120.0	10.10	7.67	9.40	812.0	20.0	Seep	MP-N9, flow near southern limit of mine, <1 gpm
	65900107	Smith	Mt. Pleasant	Westmoreland	Redstone	7/16/92	7.7	246.0	0.0	1.47	0.27	1.22	122.0	57.0	Pit Water	at lowwall sump on Redstone seam
	65900107	Smith	Mt. Pleasant	Westmoreland	Redstone	3/12/92	7.1	216.0	0.0	3.23	3.22	< 0.50	285.0	no data	Seep	MP-18, pre-existing spoil discharge, <2 gpm
	65900103	Tarrs	E Huntingdon	Westmoreland	Redstone	2/23/90	7.3	86.0	0.0	0.75	0.07	0.65	115.0	10.0	Pond	MP-BS2, impoundment phase 1A
	65900103	Tarrs	E Huntingdon	Westmoreland	Redstone	2/19/91	8.3	298.0	0.0	3.03	0.09	3.39	217.0	58.0	Spring	MP-1, 5 gpm
	65930104	Smith	E Huntingdon	Westmoreland	Redstone	3/15/94	7.2	254.0	0.0	2.24	0.05	< 0.50	72.0	34.0	Well	Kimmel water supply near mine site
	65930104	Smith	E Huntingdon	Westmoreland	Redstone	10/18/94	8.1	338.0	0.0	0.66	0.33	0.52	181.0	< 3.0	Spring	Kimmel spring near cropline of Redstone coal
	26910115	Brown	Upper Tyrone	Fayette	Redstone	6/11/93	6.9	238.0	0.0	< 0.30	< 0.05	< 0.50	456.0	12.0	Spring	Brown spring near cropline of Redstone coal
	26910115	Brown	Upper Tyrone	Fayette	Redstone	8/17/93	7.4	626.0	0.0	1.65	1.05	< 0.50	1440.0	12.0	Spring	Brown spring near cropline of Redstone coal
	26910115	Brown	Upper Tyrone	Fayette	Redstone	3/9/94	6.8	196.0	0.0	< 0.30	< 0.05	< 0.50	329.0	< 3.0	Spring	Brown spring near cropline of Redstone coal
	26910115	Brown	Upper Tyrone	Fayette	Redstone	7/25/94	6.5	210.0	0.0	15.70	0.39	2.48	367.0	8.0	Well	Shaw water supply near mine site
	56880109	Blue Lick #3	Brothersvalley	Somerset	Redstone to Morantown	5/10/95	6.8	166.0	0.0	2.86	0.52	< 0.50	220.0	24.0	Pit Water	sump in Blue Lick seam pit
	56880109	Blue Lick #3	Brothersvalley	Somerset	Redstone to Morantown	4/22/96	7.0	156.0	0.0	0.91	0.73	< 0.50	376.0	< 3.0	Pit Water	sump in Blue Lick seam pit
	56880109	Blue Lick #3	Brothersvalley	Somerset	Redstone to Morantown	7/24/96	6.7	156.0	0.0	0.79	1.11	< 0.50	615.5	4.0	Pit Water	sump in Blue Lick seam pit
	56880109	Blue Lick #3	Brothersvalley	Somerset	Redstone to Morantown	3/28/96	2.9	0.0	2594.0	> 300.00	35.70	180.00	2701.0	5.0	Seep	pre-existing seep from adjacent area
	56880109	Blue Lick #3	Brothersvalley	Somerset	Redstone to Morantown	4/22/96	6.8	216.0	0.0	3.68	1.52	< 0.50	439.0	10.0	Seep	on west side of township road T-568
	56880109	Blue Lick #3	Brothersvalley	Somerset	Redstone to Morantown	9/7/95	7.6	220.0	0.0	2.84	0.43	0.67	710.0	10.0	Seep	MP-SP37
	56880109	Blue Lick #3	Brothersvalley	Somerset	Redstone to Morantown	4/22/96	5.2	11.8	64.0	7.49	5.15	1.71	913.0	18.0	Mine Discharge	MP-SP39
	56880109	Blue Lick #3	Brothersvalley	Somerset	Redstone to Morantown	3/28/96	6.5	112.0	0.0	< 0.30	< 0.05	< 0.50	214.0	< 3.0	Deep Mine Disch.	MP-SP33
	56880109	Blue Lick #3	Brothersvalley	Somerset	Redstone to Morantown	10/29/96	4.9	24.0	90.0	8.18	10.00	11.00	643.3	< 3.0	Spoil Discharge	flowing from SW corner of Phase II, 1-3 gpm
	56880109	Blue Lick #3	Brothersvalley	Somerset	Redstone to Morantown	12/29/94	6.7	78.0	0.0	12.30	0.49	< 0.50	590.0	36.0	Spring	MP-SP27
	56880109	Blue Lick #3	Brothersvalley	Somerset	Redstone to Morantown	12/29/94	6.8	180.0	0.0	17.20	1.69	< 0.50	253.0	32.0	Spring	MP-SP32
	56880109	Blue Lick #3	Brothersvalley	Somerset	Redstone to Morantown	12/29/94	7.9	276.0	0.0	< 0.30	< 0.05	< 0.5	436.0	< 3.0	Spring	MP-SP15
	56880109	Blue Lick #3	Brothersvalley	Somerset	Redstone to Morantown	9/7/95	6.4	114.0	0.0	3.24	0.37	1.12	454.0	48.0	Stream	MP-SP15, unnamed tributary to Blue Lick Creek
	56880109	Blue Lick #3	Brothersvalley	Somerset	Redstone to Morantown	12/29/94	6.5	38.0	0.0	< 0.30	< 0.05	< 0.50	21.0	10.0	Stream	MP-SP48, Blue Lick Creek upstream of site
	56880109	Blue Lick #3	Brothersvalley	Somerset	Redstone to Morantown	9/17/96	7.1	98.0	0.0	1.37	1.14	2.11	506.8	16.0	Pond Disch.	untreated flow pumped from Blue Lick seam pit
	56940101	Krause	Brothersvalley	Somerset	Sewickley to Morantown	5/22/95	6.9	84.0	0.0	0.31	0.05	< 0.50	211.0	< 8.0	Mine Discharge	MP-13, pre-mining
	56940101	Krause	Brothersvalley	Somerset	Sewickley to Morantown	9/18/95	8.1	172.0	0.0	< 0.30	< 0.05	< 0.50	342.0	< 3.0	Mine Discharge	MP-13, pre-mining
	56940101	Krause	Brothersvalley	Somerset	Sewickley to Morantown	5/9/96	5.9	11.0	4.4	0.48	0.11	< 0.50	39.0	< 3.0	Spring	MP-SW22
	56940101	Krause	Brothersvalley	Somerset	Sewickley to Morantown	9/18/95	7.2	90.0	0.0	0.45	< 0.05	< 0.50	27.0	6.0	Stream	MP-SW20, unnamed tributary to Buffalo Creek
	02920103	Plum #1	Plum Borough	Allegheny	Pittsburgh	3/3/89	3.2	0.0	464.0	24.50	2.35	33.30	510.0	22.0	Mine Discharge	MP-1 pre-mining, 20 gpm
	02920103	Plum #1	Plum Borough	Allegheny	Pittsburgh	7/16/94	2.9	0.0	105.0	15.40	3.57	68.30	775.0	< 1.0	Mine Discharge	MP-1, 19 gpm
	02920103	Plum #1	Plum Borough	Allegheny	Pittsburgh	2/10/90	3.1	0.0	360.0	6.37	3.24	34.80	570.0	6.0	Mine Discharge	MP-BS12, pumped discharge on Plum Creek, 321 gpm
	65880112	Trees Mills	Salem	Westmoreland	Pittsburgh	10/6/88	2.4	0.0	2086.0	371.00	20.04	159.90	2409.3	26.0	Deep Mine Disch.	MP-1 pre-mining, 8 gpm
	65880112	Trees Mills	Salem	Westmoreland	Pittsburgh	11/29/90	2.5	0.0	3616.0	190.40	13.50	73.14	1497.8	10.0	Deep Mine Disch.	MP-1, 13 gpm
	65880112	Trees Mills	Salem	Westmoreland	Pittsburgh	11/29/90	2.6	0.0	2720.0	79.90	11.34	50.88	1271.5	6.0	Seep	MP-5, 13 gpm
Conemaugh Group	56850112	Emerick	Southampton	Somerset	Wellersburg		6.9	80.6	0.0	15.40	1.49	no data	397.0	no data	Mine Discharge	related to adjacent permit-coal correlation confirmed
	56920105	State Line	Southampton	Somerset	U. & L. Bakerstown	4/29/96	6.4	24.0	12.0	1.90	0.06	3.37	< 20.0	< 3.0	Pit Water	water in Lower Bakerstown seam pit
	56920105	State Line	Southampton	Somerset	U. & L. Bakerstown	4/29/96	7.2	72.0	0.0	< 0.30	< 0.05	< 0.50	29.0	< 3.0	Pit Water	water in Upper Bakerstown seam pit
	56920105	State Line	Southampton	Somerset	U. & L. Bakerstown	9/26/96	6.0	10.8	4.4	0.65	0.27	0.79	29.8	4.0	Pit Water	water in Lower Bakerstown seam pit
	56920105	State Line	Southampton	Somerset	U. & L. Bakerstown	12/18/96	5.5	9.8	8.6	< 0.30	0.28	< 0.50	35.3	< 3.0	Pit Water	sump in Lower Bakerstown seam pit
	56920105	State Line	Southampton	Somerset	U. & L. Bakerstown	12/18/96	6.1	14.4	3.6	< 0.30	0.21	< 0.50	28.1	< 3.0	Pit Water	sump in Upper Bakerstown seam pit
	56920105	State Line	Southampton	Somerset	U. & L. Bakerstown	1/17/95	7.3	118.0	0.0	2.63	5.87	1.24	566.0	6.0	Pit Water	pool in L. Bakerstown pit from highwall seeps
	56920105	State Line	Southampton	Somerset	U. & L. Bakerstown	4/29/96	5.8	210.0	0.0	< 0.30	1.37	< 0.50	416.0	< 3.0	Spoil Discharge	post-mining seep from eastern portion of Phase I
	56920105	State Line	Southampton	Somerset	U. & L. Bakerstown	1/17/95	6.3	16.0	1.6	1.48	0.09	0.96	22.0	28.0	Deep Mine Disch.	MP-SP22
	56920105	State Line	Southampton	Somerset	U. & L. Bakerstown	1/17/95	6.0	14.8	7.0	< 0.30	< 0.05	< 0.50	< 20.0	< 3.0	Spring	MP-SP4, Lee spring
	56920105	State Line	Southampton	Somerset	U. & L. Bakerstown	4/29/96	6.6	24.0	0.0	4.15	0.14	2.91	< 20.0	115.0	Spring	MP-SP7, unnamed tributary downstream from site
	56920105	State Line	Southampton	Somerset	U. & L. Bakerstown	9/28/94	8.2	180.0	0.0	0.97	0.08	0.66	53.0	12.0	Stream	MP-SP7, unnamed tributary downstream from site
	56920105	State Line	Southampton	Somerset	U. & L. Bakerstown	12/18/96	6.8	52.0	0.0	0.37	< 0.05	< 0.50	124.2	8.0	Stream	MP-SP40
	56920105	State Line	Southampton	Somerset	U. & L. Bakerstown	1/17/95	5.9	9.4	7.0	< 0.30	0.10	< 0.50	20.0	< 3.0	Stream	MP-SP10, pre-existing, below mine site, 14 gpm
	56900103	Cover Hill	Brothersvalley	Somerset	Lower Bakerstown	2/6/90	4.0	0.0	50.9	0.10	8.80	9.32	343.0	14.0	Spoil Discharge	MP-SP11, from abandoned pit below site, 1.8 gpm
	56900103	Cover Hill	Brothersvalley	Somerset	Lower Bakerstown	8/29/89	3.6	0.0	168.1	0.83	14.80	31.70	787.0	2.0	Mine Discharge	MP-SP11, from abandoned pit below site, 1.8 gpm
	56900103	Cover Hill	Brothersvalley	Somerset	Lower Bakerstown	2/6/90	4.0	0.0	130.0	0.23	12.20	24.80	881.0	27.0	Spoil Discharge	MP-SP12, pre-existing seep below site, 1.3 gpm
	56900103	Cover Hill	Brothersvalley	Somerset	Lower Bakerstown	11/29/89	4.1	0.0	101.2	0.21	10.90	19.50	861.0	2.0	Seep	MP-SP18, pre-existing discharge, <1 gpm
	26920107	Hager	Wharton	Fayette	Brush Creek	7/12/95	7.0	95.5	no data	0.10	0.13	0.12	201.0	1.0	Spring	MP-28, Hager springhouse, <1 gpm
	26920107	Hager	Wharton	Fayette	Brush Creek	7/12/95	6.9	189.4	no data	0.21	0.40	0.07	68.2	1.0	Spring	MP-35, Logan spring, 4 gpm
	26920107	Hager	Wharton	Fayette	Brush Creek	7/12/95	8.0	84.9	no data	0.26	0.05	0.24	60.6	7.0	Spring	MP-63, headwaters tributary, <1 gpm
	26910113	Ryan	Wharton	Fayette	Brush Creek	7/14/93	7.1	109.8	no data	0.53	0.15	no data	18.0	4.0	Well	MP-5, C. Ryan well
	26910113	Ryan	Wharton	Fayette	Brush Creek	3/23/94	6.5	4.0	[3] 3.0	0.16	0.05	no data	14.1	no data	Stream	MP-7, unnamed trib. to Big Sandy Creek, 31 gpm
Upper Allegheny Group	17910103	Fruithill	Jordon & Knox	Clearfield	Upper & Lower Freeport	1/30/95	7.5	132.0	0.0	0.01	0.13	0.01	400.0	2.7	Deep Mine Disch.	MP-510, on L. Freept seam post U. Freept mining
	17910103	Fruithill	Jordon & Knox	Clearfield	Upper & Lower Freeport	5/10/94	7.8	238.0	0.0	0.01	0.01	no data	458.0	0.3	Deep Mine Disch.	MP-511, from L. Freept seam, 60 gpm
	17910103	Fruithill	Jordon & Knox	Clearfield	Upper & Lower Freeport	11/1/95	8.0	152.0	0.0	0.01	0.01	no data	453.0	3.7	Deep Mine Disch.	MP-511, from L. Freept seam, 25 gpm
	17910103	Fruithill	Jordon & Knox	Clearfield	Upper & Lower Freeport	8/1/94	7.1	68.0	0.0	3.51	0.47	no data	105.0	34.7	Seeps	MP-513, U. Freept post-mining discharges, <1 gpm
	17910103	Fruithill	Jordon & Knox	Clearfield	Upper & Lower Freeport	7/10/95	7.2	58.0	0.0	7.98	0.54	no data	76.0	5.3	Seeps	MP-513, U. Freept post-mining discharges, <1 gpm
	17910101	Witherow	Knox	Clearfield	Upper Freeport	6/30/90	7.6	98.0	0.0	0.01	0.01	0.05	478.0	0.3	Seeps	MP-6, spoil spring, 5 gpm
	17910101	Witherow	Knox	Clearfield	Upper Freeport	6/30/90	7.4	166.0	0.0	0.01	0.15	0.09	367.0	0.3	Seeps	MP-7, spoil seep, post-mining, 17 gpm
	17930115	Beaver #1	Chest	Clearfield	Lower Freeport	3/4/95	7.0	40.0	0.0	0.09	0.26	0.09	143.0	0.7	Stream	MP-8, unnamed tributary to Wilson Creek, 738 gpm
	17930115	Beaver #1	Chest	Clearfield	Lower Freeport	7/12/96	7.1	86.0	0.0	0.04	0.64	0.04	378.0	0.3	Stream	MP-8, unnamed tributary to Wilson Creek, 50 gpm
	17930115	Beaver #1	Chest	Clearfield	Lower Freeport	3/4/95	6.9	38.0	0.0	0.01	0.01	0.03	128.0	0.7	Stream	MP-19, unnamed tributary to Wilson Creek, 75 gpm
	17930115	Beaver #1	Chest	Clearfield	Lower Freeport	8/22/95	7.6	114.0	0.0	0.06	0.61	0.01	366.0	1.7	Stream	MP-19, unnamed tributary to Wilson Creek, 1 gpm
	17930115	Beaver #1	Chest	Clearfield	Lower Freeport	2/1/96	6.2	18.0	0.0	0.01	0.20	0.03	163.0	0.3	Stream	MP-19, unnamed tributary to Wilson Creek, 100 gpm
	17930115	Beaver #1	Chest	Clearfield	Lower Freeport	8/22/95	7.1	38.0	0.0	0.38	0.37	0.01	53.0	3.7	Mine Discharge	MP-13, L. Freept strip mine discharge, 30 gpm
	17930115	Beaver #1	Chest	Clearfield	Lower Freeport	3/4/95	6.9	32.0	0.0	0.02	0.01	0.08	39.0	15.0	Mine Discharge	MP-13, L. Freept strip mine discharge, 2 gpm
	17890105	Fink/Mays	Ferguson/Pike	Clearfield	U. Freept. to U. Kittng.	8/23/93	8.1	182.0	2.0	0.20	0.06	0.94	401.0	4.0	Mine Discharge	MP-424, surface mine discharge, 2 gpm
	17890105	Fink/Mays	Ferguson/Pike	Clearfield	U. Freept. to U. Kittng.	9/23/92	7.1	106.0	5.0	0.33	0.69	1.12	114.0	94.0	Mine Discharge	MP-426, surface mine discharge, <1 gpm
	17890105	Fink/Mays	Ferguson/Pike	Clearfield	U. Freept. to U. Kittng.	8/4/94	7.8	145.0	6.0	0.21	0.25	< 0.10	184.0	6.0	Mine Discharge	MP-429, surface mine discharge, 3 gpm
	11840111	Shero Strip	West Carroll	Cambria	L. Freept. to U. Kittng.	8/8/94	6.8	376.0	0.0	3.72	6.06	1.00	760.0	8.0	Seep	post-mine discharge downgradient of spoil
	11840111	Shero Strip	West Carroll	Cambria	L. Freept. to U. Kittng.	9/12/95	6.9	380.0	0.0	2.88	6.33	< 0.50	761.0	4.0	Seep	post-mine discharge downgradient of spoil
	11960106	Laurel Hill #2	Jackson	Cambria	L. Freept. to U. Kittng.	7/7/97	7.3	208.0	0.0	< 0.30	< 0.05	< 0.50	33.0	< 3.0	Well	MP-184, Dougherty well
	11940103	Laurel Hill #1	Jackson	Cambria	U. Freept. to U. Kittng.	9/3/97	7.9	264.0	0.0	< 0.30	< 0.05	0.75	396.1	8.0	Stream	MP-60, headwaters tributary below spoil
	11940103	Laurel Hill #1	Jackson	Cambria	U. Freept. to U. Kittng.	5/14/96	7.7	176.0	0.0	< 0.30	< 0.05	< 0.50	178.0	< 3.0	Seep	MP-SP002, pre-existing
	11940103	Laurel Hill #1	Jackson	Cambria	U. Freept. to U. Kittng.	1/6/97	8.1	484.0	0.0	0.97	1.98	1.04	590.0	34.0	Seep	toe of slope seep near SP 302
	11940103	Laurel Hill #1	Jackson	Cambria	U. Freept. to U. Kittng.	4/20/94	6.0	18.4	14.8	< 0.30	< 0.05	< 0.50	< 20.0	4.0	Stream	MP-30, unnamed tributary at logging trail
	11940103	Laurel Hill #1	Jackson	Cambria	U. Freept. to U. Kittng.	5/23/95	7.3	68.0	0.0	< 0.30	< 0.05	< 0.50	25.0	14.0	Stream	MP-30, unnamed tributary at logging trail, 3 gpm
	11940103	Laurel Hill #1	Jackson	Cambria	U. Freept. to U. Kittng.	1/6/97	7.9	162.0	0.0	< 0.30	< 0.05	< 0.50	242.2	10.0	Stream	MP-30, unnamed tributary at logging trail
	11940103	Laurel Hill #1	Jackson	Cambria	U. Freept. to U. Kittng.	5/23/95	7.8	126.0	0.0	< 0.30	< 0.05	< 0.50	< 20.0	16.0	Spring	MP-76 background sample, 1 gpm
	32850115	Nashville	Grant	Indiana	L. Freept. to L. Kittng.	4/14/92	6.7	52.0	0.0	0.53	2.73	< 0.50	65.0	< 2.0	Seep	seep from backfill above sed. pond ditch
	32850115	Nashville	Grant	Indiana	L. Freept. to L. Kittng.	4/14/92	8.4	158.0	0.0	< 0.30	4.63	< 0.50	334.0	< 2.0	Seep	MP-17, seep along LR 32162
	32850115	Nashville	Grant	Indiana	L. Freept. to L. Kittng.	4/14/92	7.7	194.0	0.0	< 0.30	0.09	< 0.50	218.0	10.0	Seep	MP-22, mine drainage
	32850115	Nashville	Grant	Indiana	L. Freept. to L. Kittng.	4/14/92	6.8	198.0	0.0	< 0.30	0.12	< 0.50	224.0	2.0	Seep	MP-17, mine drainage
	26950102	Schmunk	Wharton	Fayette	L. Freept. & U. Kittng.	8/15/95	6.5	18.4	no data	0.28	0.03	0.42	12.0	6.0	Spring	MP-3, near U. Kittanning cropline, 1 gpm
	26950102	Schmunk	Wharton	Fayette	L. Freept. & U. Kittng.	10/11/95	6.6	66.4	no data	3.94	1.03	0.20	105.0	11.0	Stream	MP-5, headwaters tributary to Stony Fork, 1 gpm
	26950102	Schmunk	Wharton	Fayette	L. Freept. & U. Kittng.	8/15/95	7.2	74.8	no data	0.32	0.08	0.22	20.5	5.0	Spring	MP-10, headwaters tributary to Stony Fork, 2 gpm
	26950102	Schmunk	Wharton	Fayette	L. Freept. & U. Kittng.	1/23/96	5.2	15.9	24.3	3.43	2.74	1.37	17.8	16.0	Spring	MP-17, seep below U. Kittanning outcrop 1.5 gpm
	26950102	Schmunk	Wharton	Fayette	L. Freept. & U. Kittng.	12/22/94	6.3	4.1	3.2	0.18	0.07	0.04	11.0	1.0	Stream	MP-24, downstream Stony Fork trib. #2
	26950102	Schmunk	Wharton	Fayette	L. Freept. & U. Kittng.	6/14/95	7.9	134.6	no data	0.32	0.02	< 0.02	18.2	4.0	Well	MP-30A, Waggoner water supply
	26950102	Schmunk	Wharton	Fayette	L. Freept. & U. Kittng.	9/19/95	7.1	113.8	no data	0.05	< 0.02	0.05	19.4	3.0	Spring	MP-30B, Waggoner spring
	26950102	Schmunk	Wharton	Fayette	L. Freept. & U. Kittng.	9/19/95	7.6	212.7	no data	6.92	1.74	0.16	61.9	4.0	Drainage	MP-8, 10 gpm
	3374SM6	Chanin	Springfield	Fayette	U. Freept. to U. Kittng.	8/13/81	6.0	30.0	24.0	72.80	6.40	0.17	204.0	no data	Spoil	little iron discharge, 1 gpm
	3374SM6	Chanin	Springfield	Fayette	U. Freept. to U. Kittng.	1/4/89	4.3	7.0	186.0	0.30	28.40	24.60	1152.0	8.0	Spoil	MP-71-25a, near Lower Freeport outcrop
	26840109	Morrison	Wharton	Fayette	Upper Kittanning	6/22/89	7.0	308.0	0.0	0.63	3.49	< 0.50	327.0	5.0	Seep	Seep C, near collection ditch, <1 gpm
	3378BC19	Stuart	Wharton	Fayette	Upper Kittanning	6/25/93	2.8	0.0	1290.0	56.70	49.20	164.00	1467.0	7.0	Seep	seepage area, post-mining
	26890109	Rennie	Wharton	Fayette	Upper Kittanning	8/11/93	7.8	114.8	no data	0.60	0.23	0.18	17.4	11.0	Spring	MP-18, 1 gpm
Lower Allegheny Group	24930101	Johnson Run	Horton	Elk	Middle Kittanning	4/8/97	6.8	63.0	0.0	< 0.30	< 0.05	< 0.50	31.9	< 3.0	Pit Water	accumulation at southeast corner of Pond A
	33880108	Reiter	Winslow	Jefferson	Middle Kittanning	1/11/89	5.8	11.0	24.0	2.33	3.91	2.29	152.0	no data	Pit Water	
	33773120	Lewis	Winslow	Jefferson	Middle Kittanning	6/22/89	6.7	40.0	0.0	2.53	0.93	1.79	35.0	no data	Pit Water	
	33870113	Anderson	Winslow	Jefferson	Middle Kittanning	9/30/91	6.4	34.0	0.0	3.25	3.36	< 0.50	35.0	9.0	Pit Water	
	33870113	Anderson	Winslow	Jefferson	Middle Kittanning	6/15/94	7.4	86.0	0.0	0.68	0.31	0.73	30.0	no data	Pit Water	
	33930113	Clinger	Pine Creek	Jefferson	Middle Kittanning	9/19/95	6.8	190.0	0.0	< 0.30	1.28	< 0.50	184.0	< 3.0	Pit Water	
	33920103	Zimmerman	Pine Creek	Jefferson	Middle Kittanning	5/24/95	6.6	98.0	0.0	< 0.30	0.92	< 0.50	64.0	no data	Pit Water	
	3375SM54	Shaffer	Saltlick	Fayette	Middle Kittanning	5/9/83	6.2	158.0	0.0	15.56	10.10	0.03	570.0	20.0	Surface Disch.	flow from southeast corner of reclaimed mine site
	3375SM54	Shaffer	Saltlick	Fayette	Middle Kittanning	4/13/95	6.3	92.0	0.0	18.40	3.77	< 0.50	267.0	6.0	Surface Disch.	flow from southeast corner of reclaimed mine site
	4278BC10	Swiscambria	Reade	Cambria	Lower Kittanning	10/25/90	3.7	0.0	62.0	0.14	12.00	7.94	370.0	8.0	Seep	270 ft north of MP-SBG2, freshwater LK paleoenvt.
	4278BC10	Swiscambria	Reade	Cambria	Lower Kittanning	10/25/90	4.2	5.0	88.0	0.09	24.20	10.00	1070.0	36.0	Seep	280 ft south of MP-SBG2, freshwater LK paleoenvt.
	3267BSM42	Betty #1	Boggs	Clearfield	Lower Kittanning	9/18/90	3.5	0.0	326.0	52.00	54.00	25.00	2300.0	no data	Seep	USGS/MP-N1, brackish LK paleoenvironment
	3267BSM42	Betty #1	Boggs	Clearfield	Lower Kittanning	3/12/90	3.2	0.0	372.0	1.80	82.00	52.00	1900.0	no data	Seep	USGS/MP-S1, brackish LK paleoenvironment
	17813091	Albert #1	Graham	Clearfield	Lower Kittanning	1/30/89	3.1	0.0	1335.0	186.00	111.00	no data	3288.0	0.0	Spoil Discharge	MP-7, black shale, brackish paleoenvt., 55 gpm
	17813091	Albert #1	Graham	Clearfield	Lower Kittanning	2/6/90	3.1	0.0	670.0	144.00	81.20	no data	2520.0	10.0	Spoil Discharge



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