Geochemistry of coal mine drainage

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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 N2-5	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	359	6.1	64	120	2,200	320	242	30.00	58.00
WMS N3-1	19.2	1,270	.20	378	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 S1-5	1.5	3,400	--	--	6.9	0	580	2,100	660	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	3.10
LMS S2-5	1.5	4,370	--	--	7.3	0	750	2,300	560	210	.04	6.60
LMS S2-15	4.6	3,890	--	--	6.9	0	730	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)												
WMS A1	10.0	2,120	--	--	2.5	688	0	913	83	74	174.00	25.50
WMS A2	10.2	2,980	--	--	2.4	1,080	0	1,350	97	102	182.00	38.70
WMS B1	10.5	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	388	62	50	140.00	23.70
WMS C1	8.4	5,270	--	--	2.3	2,380	0	2,844	131	136	566.00	47.60
WMS C2	7.1	5,110	--	--	4.3	3,060	0	4,034	206	198	1,560.00	84.40
OMS Dm	0	4,700	--	--	2.2	2,160	0	3,444	93	105	433.00	39.10
Mine 3. Clarion County, C & K Mine #69 (lat 41°09'15" N, long 79°29'30" W)												
WMS 14B	33.4	2,870	.16	234	5.7	50	81	2,185	384	250	48.10	24.50
WUB 14A	33.2	2,960	.20	289	5.4	122	54	2,251	325	229	62.80	24.10
WUB 14	33.3	3,030	.20	294	5.2	136	33	2,049	306	215	63.40	26.60
WMS 15B	16.3	5,030	2.70	598	2.6	1,660	0	3,457	331	287	375.00	36.10
WMS 15A	24.8	6,040	1.90	577	2.5	2,680	0	4,404	279	234	683.00	41.10
WMS 15	36.4	4,840	1.55	558	3.4	1,604	0	3,675	353	270	477.00	45.30
OMS 15	0	3,260	.63	370	5.2	22	56	2,252	311	288	15.80	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	64	32	24	6	.80	.80
WUB 1C	25.4	188	1.30	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	24.9	2,340	.82	485	3.8	460	0	2,100	250	230	130.00	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	650	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	.66	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	460	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	650	0	4,600	650	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	.95	510	4.0	130	0	1,400	260	240	12.00	70.00
WMB 7C	31.5	2,150	1.20	290	5.5	390	26	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°35'45" N, long 78°23'30" W)												
OUB 413	0	34	9.50	--	5.6	10	9	17	5	3	<.01	.03
WUB W3A	30.3	241	.96	--	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 PA09	--	24	--	--	4.1	4	0	1.6	.3	<.1	.03	<.01
SOM PA04	--	38	--	--	4.0	5	0	3.8	.8	<.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 measured	CO_2 measured	CO_2 computed	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	--	--	--	14.6	5.8	3.5	-0.1	-2.2	-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	-1.2	-1.4	1.9	-0.7
1.10	<.01	.23	.22	--	--	--	--	--	14.4	-2.3	-2.3	1.2	-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 1951-75; sampled September 1990)													
68.90	.08	1.56	2.25	--	-0.9	9.5	--	--	--			-2.4	-1.0
91.50	.20	1.89	3.59	--	1.3	11.4	--	--	--			-2.4	-0.9
190.00	.08	3.47	3.96	-10.6	-1.4	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	3.88	4.49	--	-0.2	10.2	--	--	--			-6.0	-0.8
39.50	.36	8.35	8.31	--	.1	10.5	--	--	--			-0.3	-0.3
141.00	.24	2.81	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
.33	.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	2.03	1.95	-10.3	-3.6	6.7	--	--	--			-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	6.3	--	--	--			-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	.03	--	.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	--	--	--	20.8	.05	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	.08	--	--	--	--	--	.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	--	--	--			2.6	.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	.02	.20	.32	--	--	--	--	--	.2	-2.9	-4.0	-2.5	-1.5
77.00	.22	10.00	15.00	--	-4.6	6.2	--	--	--			-0.8	.1
.53	.03	1.20	.65	-11.5	-2.6	8.4	--	--	--			.6	-0.1
13.00	.08	1.90	1.80	-10.9	-4.2	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	--	--	.02	--	--	--	--	--	2.4	-4.2	-3.3	-2.7	-3.2
<.13	--	--	.05	--	--	--	--	--	1.1	-0.8	-3.5	-3.9	-2.8
<.13	--	--	.01	--	--	--	--	--	.7	-0.5	-1.2	-1.4	-2.5
--	--	--	--	--	--	--	--	--	--	--	--	--	--
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 -- Lescinsky et al. (1993), Cravotta et al. (1994a,b), Site 2---Brady et al. (1996, site9), Dugas et al. (1993), Williams et al. (in press), Site 3---Dugas et al. (1993), Cravotta (1994); Site 4---Loper et al. (1991), Durlin and Schaffstall (1992, 1993), Guo et al. (1994), Cravotta (1998) 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 P_{O_2} or ratio of Fe^{3+}/Fe^{2+}.

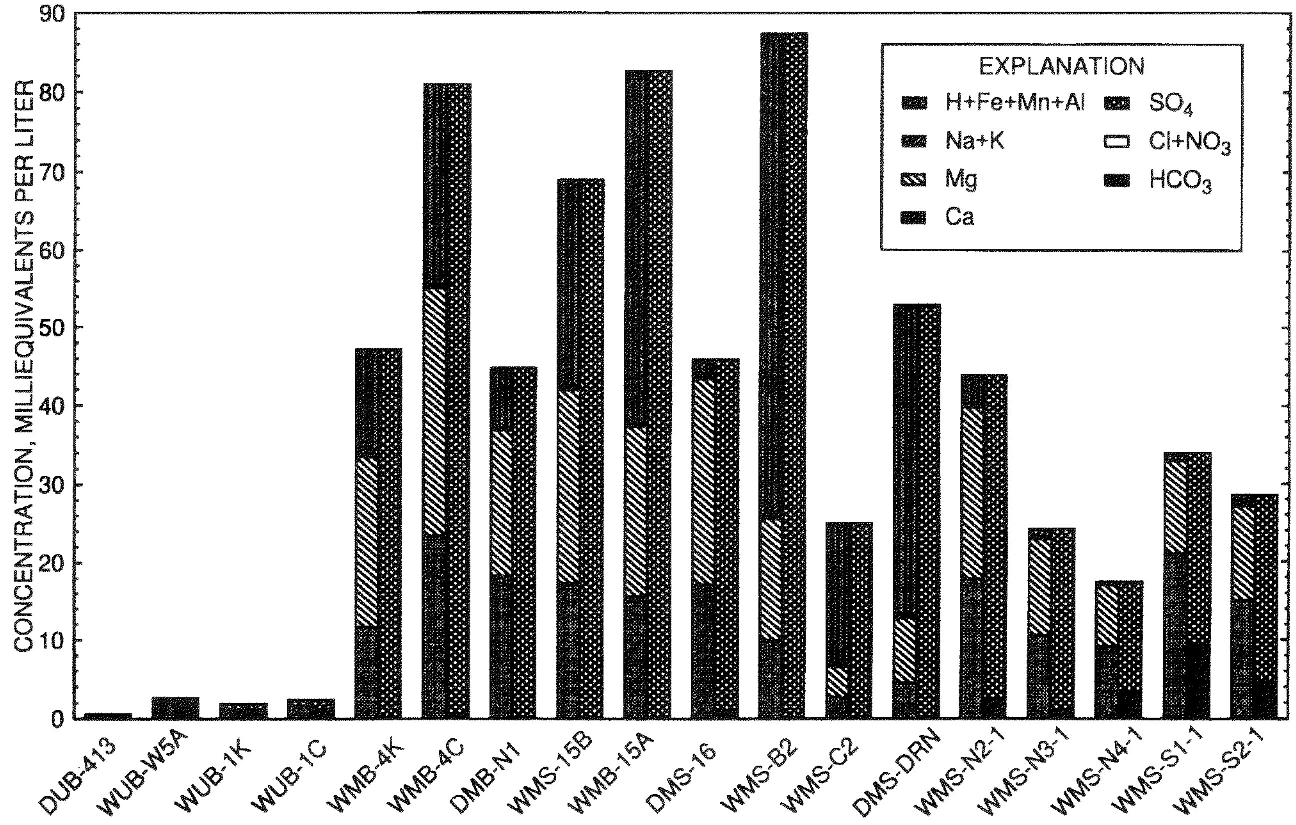


Figure 1.1 Major ions in water samples from surface-coal mines in western Pennsylvania (selected data from table 1.1). The first four samples on the left are characteristic of conditions unaffected by mining; the other samples are characteristic of conditions affected by mining, which include elevated 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.

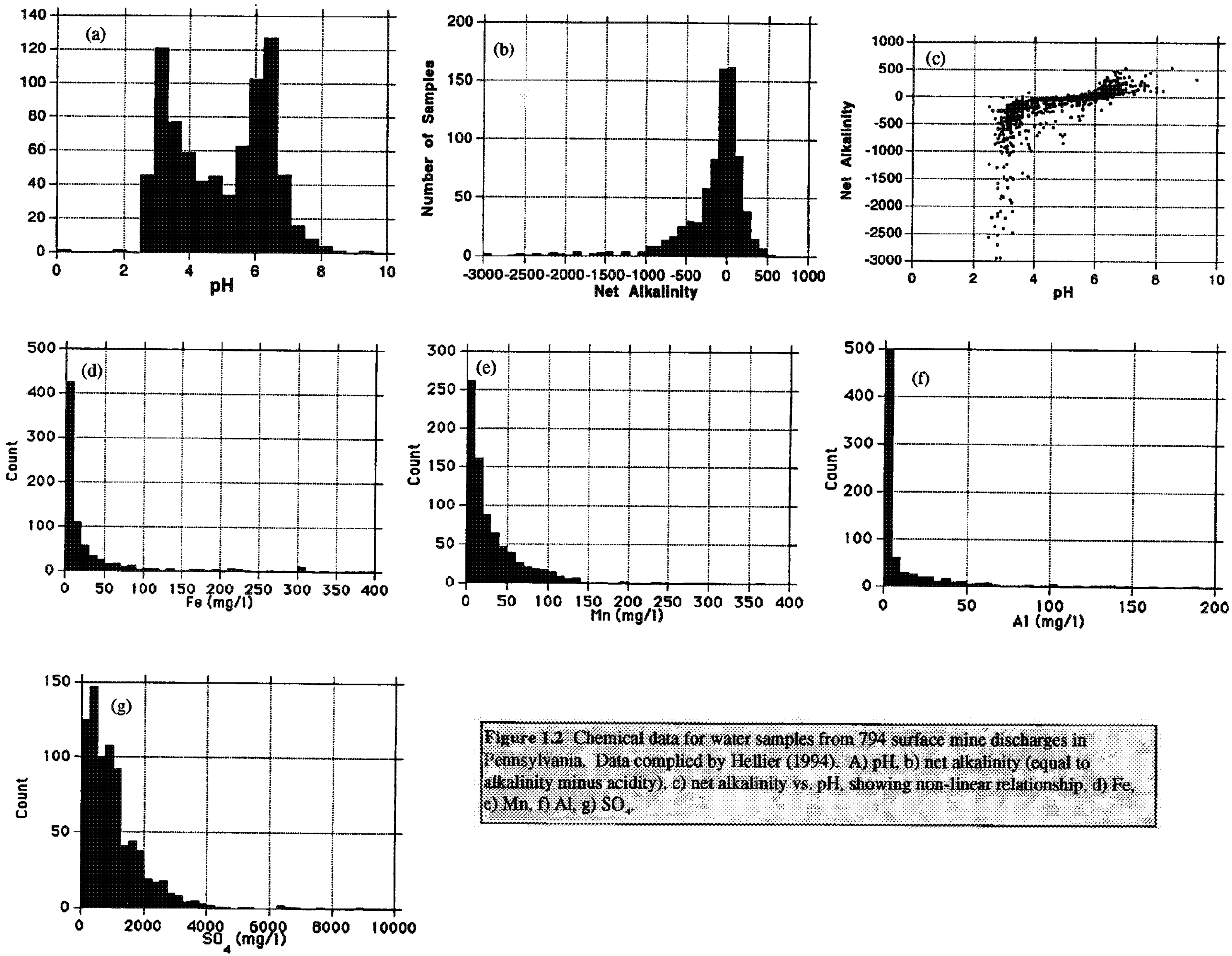


Figure 1.2 Chemical data for water samples from 794 surface mine discharges in Pennsylvania. Data complied by Hellier (1994). A) pH, b) net alkalinity (equal to alkalinity minus acidity), c) net alkalinity vs. pH, showing non-linear relationship, d) Fe, e) Mn, f) Al, g) SO_4.

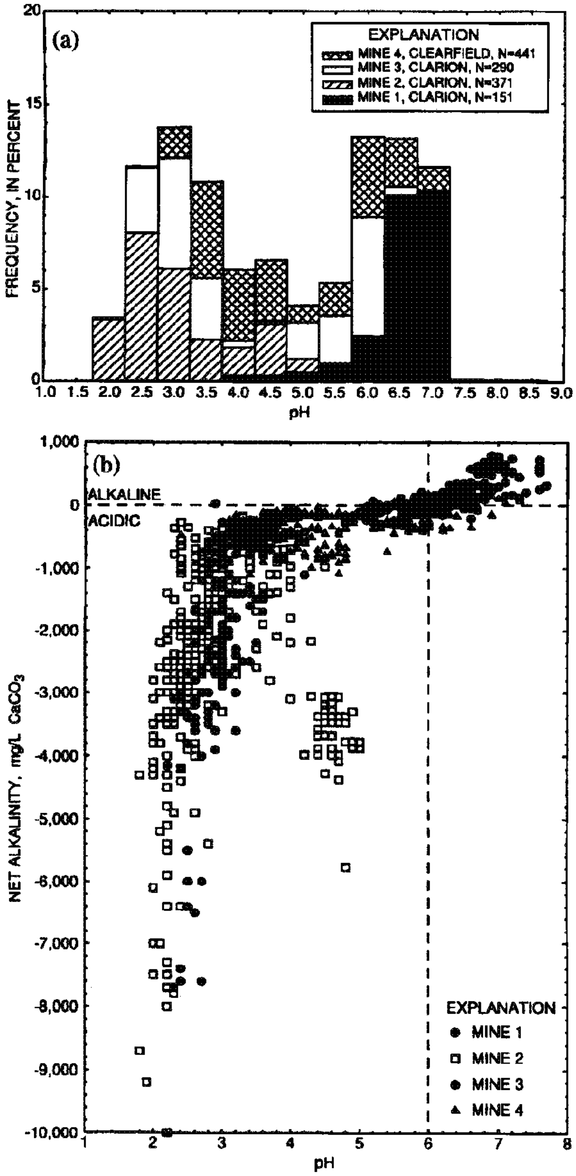


Figure 1.3 (a) Frequency distribution of pH, showing bimodal pattern similar to Figure 1.2a. Acidity, alkalinity, and pH data for 1253 water samples from the four coal mines contributing data to Table 1.1, weighted to 25% from each mine. (b) Net alkalinity (alkalinity - acidity) relative to pH of the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

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

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

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

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

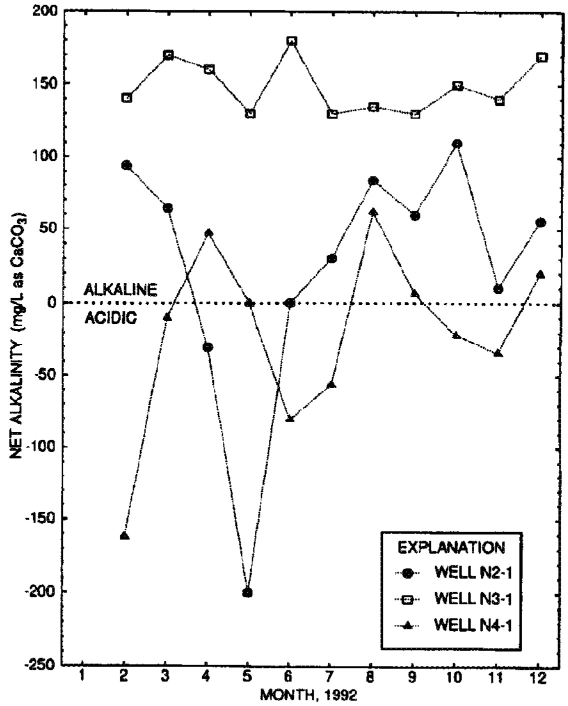
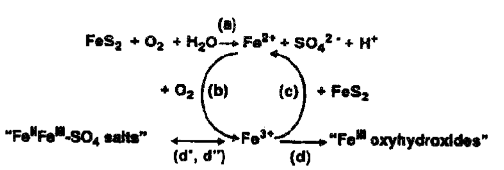


Figure 1.4 Temporal variations in net-alkalinity data for groundwater samples from three sites at a reclaimed surface coal mine in western Pennsylvania (mine 1 in table 1.1; data from Lescinsky et al., 1993, and Cravotta et al., 1994 a, b).

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

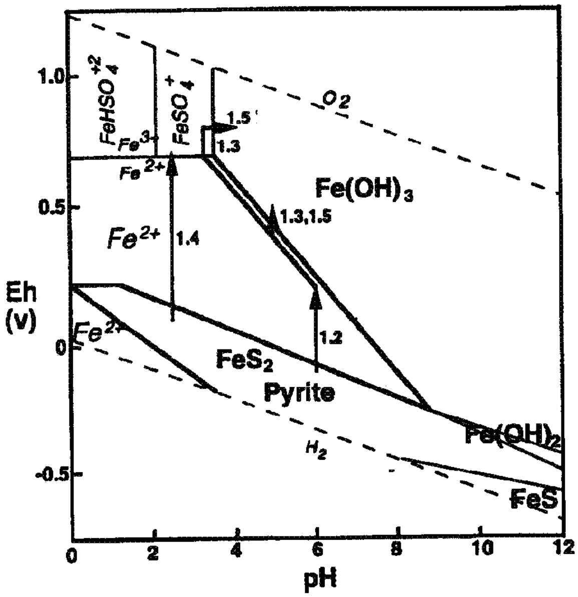


Figure 1.6 Eh-pH diagram showing theoretical stability fields for system Fe-O-H-S. Boundaries for stability fields of solid phases (vertical letters) and dissolved species (slanted letters) calculated for activities of Fe=$2x10^{-5}$ (~1 mg/L) and S = 3 x 10^{-3} (~300 mg/L as SO_4), and with pK=37.5 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.

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).

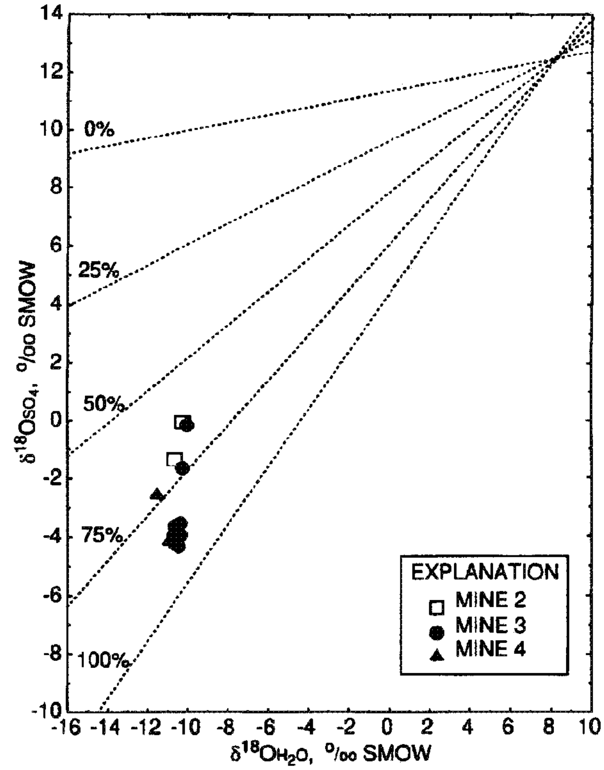


Figure 1.7 Isotopic composition of oxygen in dissolved sulfate ($\delta^{18}O_{SO4}$) of water samples from surface coal mines in western Pennsylvania (data from table 1.1) vs. isotopic composition of oxygen in associated groundwater ($\delta^{18}O_{H2O}$) originating from local precipitation, relative 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

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.

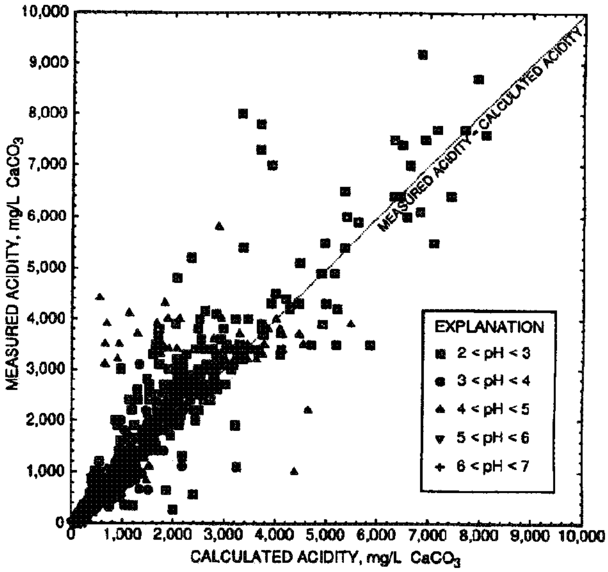


Figure 1.8 Comparison of measured acidity and calculated acidity. Acidity is calculated using equation 1.9 in text and data from sites in table 1.1. Causes for deviations from the line include hydroxyl complexing and HSO_4.

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.

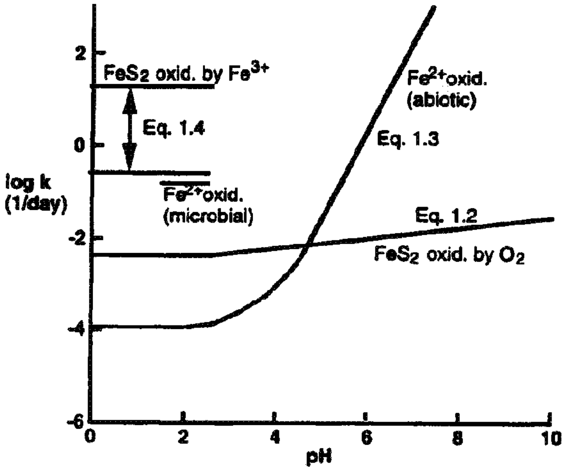


Figure 1.9 Comparison of rate constants as a function of pH for: I. The oxidation of pyrite by oxygen (reaction 1.2); II. The oxidation of ferrous iron by oxygen (reaction 1.3); and III. The oxidation of pyrite by ferric iron (reaction 1.4). Modified from Nordstrom (1982); bacterial oxidation of Fe based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

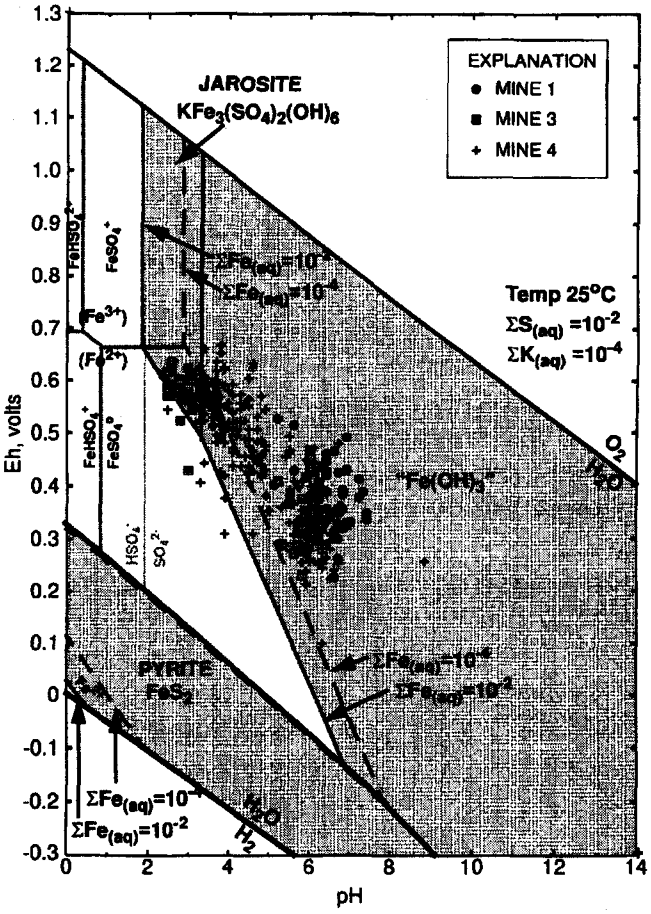


Figure 1.10 Eh-pH diagram for the system Fe-O-H-S-K and data points for measured Eh and pH of water samples from selected coal mines (Table 1.1). Boundaries for stability fields of solid phases (shaded pattern) and dissolved species calculated for activities of Fe = 10^{-2} (~560 mg/l) and 10^{-4} (~5.6 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

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

or coquimbite

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

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:

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

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

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

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

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

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):

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

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:

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

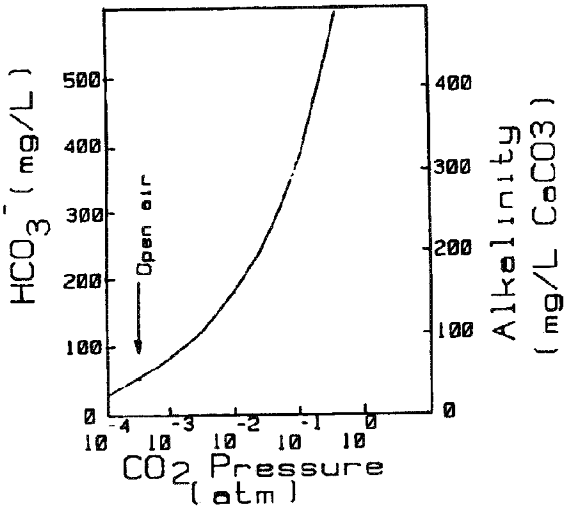


Figure 1.11 Equilibrium concentration of HCO_3^- (alkalinity) from dissolution of calcite ($CaCO_3$) by pure water at various partial pressures of carbon dioxide (P_{CO2}) at 25°C. Calculated after Garrels and Christ (1965).

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:

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

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

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

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 ($CaSO_4 \bullet 2H_2O$) 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

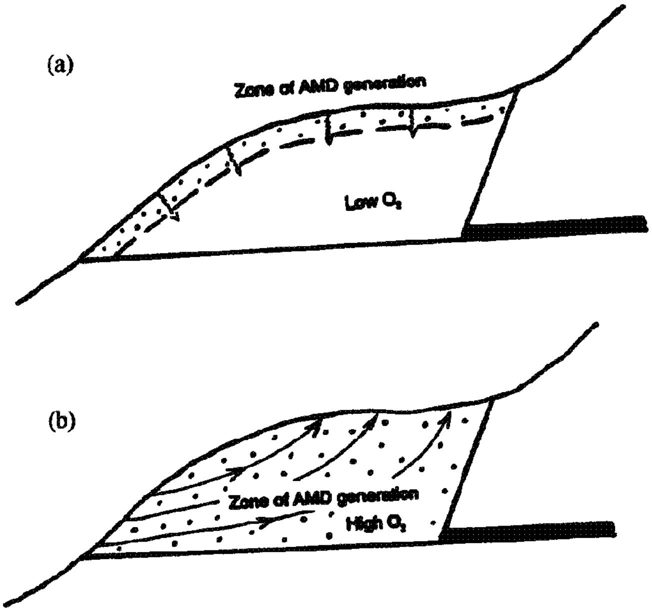


Figure 1.12 Conceptual models of O_2 transport in mine spoil profiles: a) Diffusive transport of O_2, dominant where air permeability of spoil is low, such as compacted, shaley spoil; b) advective transport of O_2, dominant where air permeability of spoil is high, such as blocky, sandstone spoil. Modified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

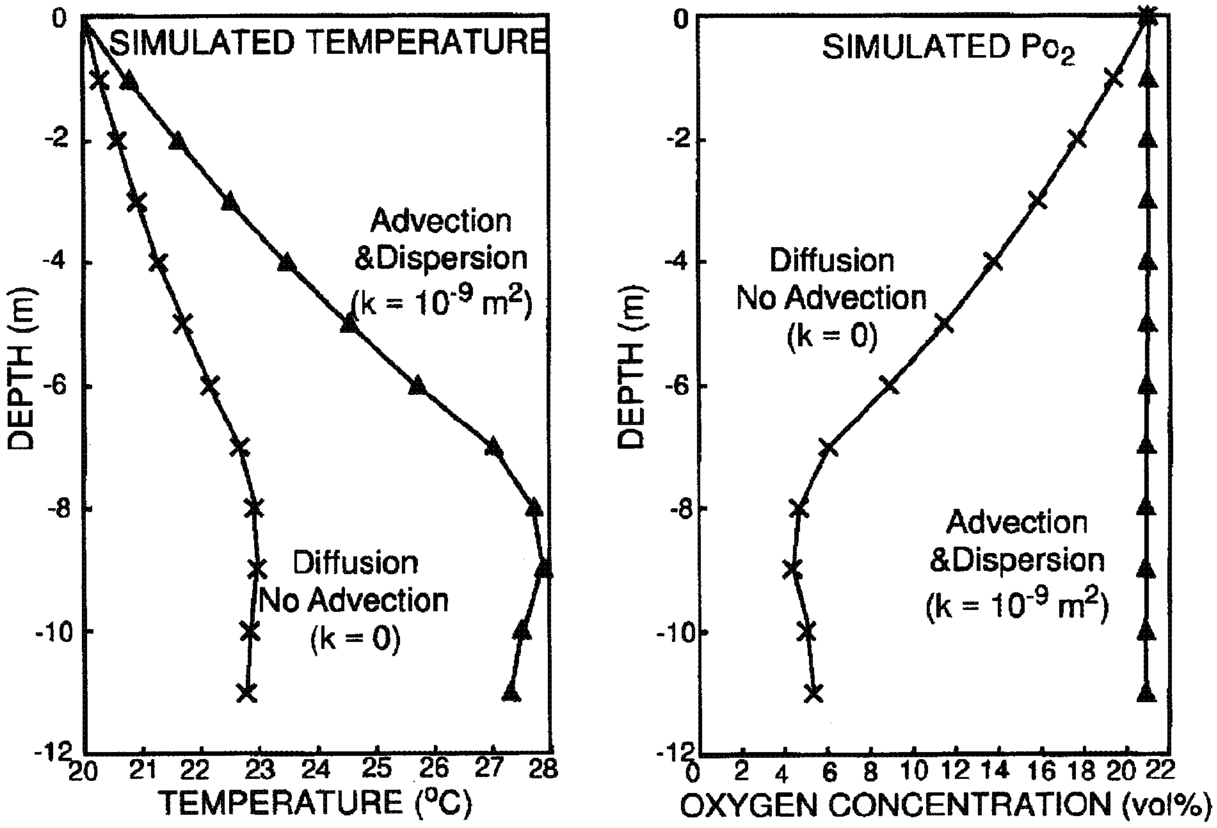


Figure 1.13 Simulated profiles of temperature and O_2 in spoil with different air permeabilities (k), which result in advective ($k>10^{-9}$ m^2) or diffusive ($k<10^{-18}$ m^2) dominated transport. Modified from Guo (1993).

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. Surface 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-

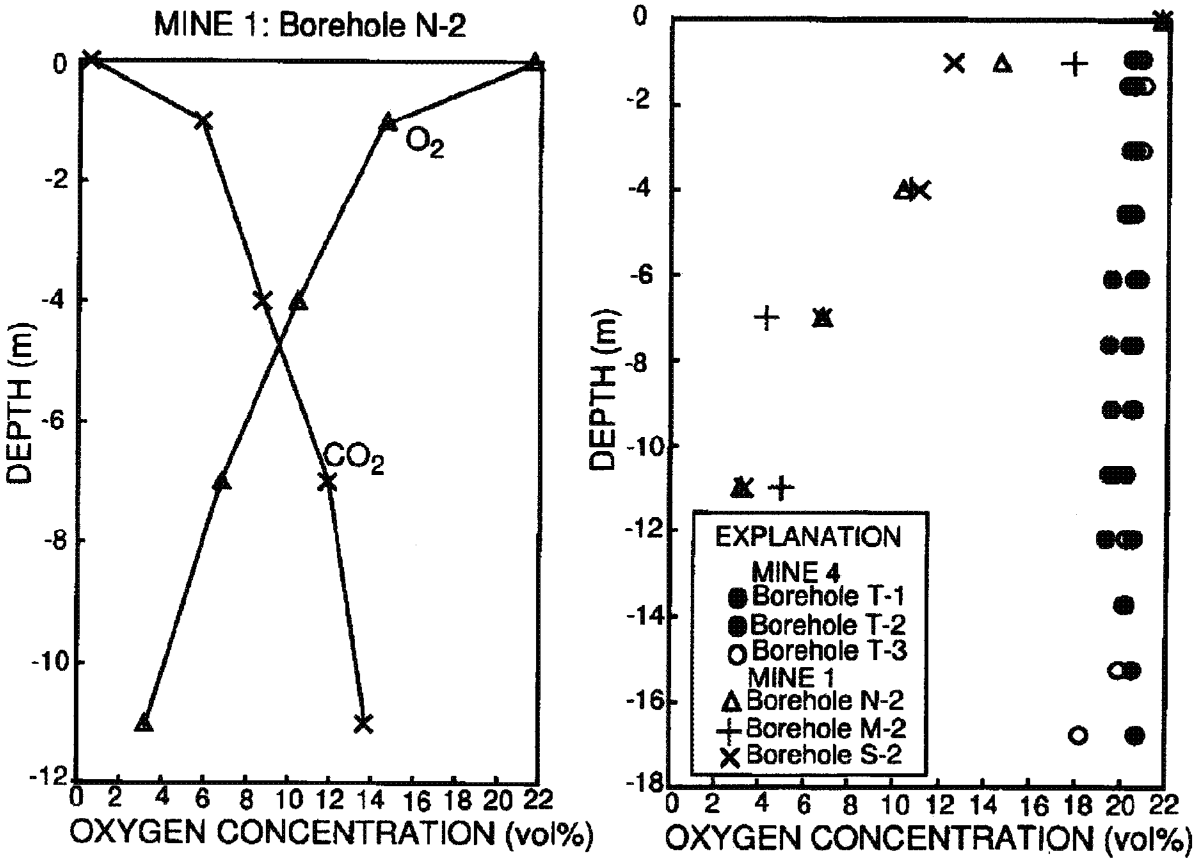


Figure 1.14 Measured profiles of oxygen and CO_2 in unsaturated spoil, after Guo et al (1994) and Guo and Cravotta (1996). At Mine 1, gas transport is by diffusion, and at Mine 4 it is by convection.

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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