Estimating Water Quality Trends in Abandoned Coal Mine-pools

Eric F. Perry[1] and Henry Rauch[2]
[1]USDI Office of Surface Mining, Pittsburgh, PA 15220 USA
[2]Dept. of Geology and Geography, West Virginia University, Morgantown, WV 26506 USA

Abstract: Temporal changes in chemical composition of five coal mine-pools in Appalachia, USA, were fitted to a first order decay function for total acidity; dissolved Fe, Al, sulphate; and total dissolved solids. The period of record ranged from 14 to 35 years, and included flooded and mostly unflooded mines, with acidic and circumneutral pH.

Median computed decay constants describing the rate of chemical change ranged from -1.3×10^{-4}/day for total dissolved solids and Al, to -3×10^{-4}/day for Fe. Total acidity, sulphate, and total dissolved solids concentrations decreased more rapidly in flooded than in unflooded mines. Chemical concentration decay was 1.5 to 3 times faster during initial flushing of the mine-pools, compared to long term flushing. Chemical ratios were useful for identifying the transition from initial to long term flushing.

Simple box model flushing calculations were performed to determine if mine-pool flushing rate or diffusion were likely controls on the rate of chemical concentration change. Observed temporal sulphate concentrations could be explained by a model of slow mine-pool flushing.

Decay constants are useful for estimating chemical concentration trends if hydrogeologic and geochemical conditions are consistent. In aged mine-pools however, chemical concentrations may be controlled by mineral solubility.

Key Words: chemical evolution, initial flushing, long term leaching

Introduction

Drainage from closed underground coal mines are a significant source of water pollution in northern Appalachia, USA and elsewhere (Kleinmann et al., 2000; Younger, 1997). The longevity or duration of polluting discharges, and chemical characteristics over time is of interest to governmental agencies, the mining industry, and the public. In this paper, we report on fitting a first order decay function to long term water quality discharge data from five closed underground coal mines in Appalachia, USA. We also examine some physical and chemical factors that may influence discharge chemistry and time dependent behaviour.

Glover (1983) observed that drainage from flooded underground coal mines in Great Britain showed about a 50% reduction in iron concentration for each pool volume discharged, implying an exponential decay. Younger (2000) found that Fe concentrations became asymptotic at values of about 1 to 40 mg/L in drainage from British coal mines after flushing for a period of a few years to several decades. Younger (1997) also characterized British mine waters as having juvenile and vestigial acidity. Vestigial acidity is associated with acidic chemicals pre-existing the closed mine's initial flooding, and is removed within the initial flushing of the mine-pool, usually within 40 years. Juvenile acidity results from ongoing pyrite oxidation and is projected to last for hundreds of years. Wood et al. (1999) concluded that pollution from closed underground coal mines in Scotland was most severe in the first few decades, and that iron (Fe) concentrations would decline to 30 mg/L or less within 40 years.

Younger and Thorn (2006) estimated that initial flooding of a recently closed coal mine in the U.K. would produce acidic water, based on observations of flowpath, and analyses of water encountered during mining. They correctly predicted the acidic nature of the discharge, but the actual Fe concentration was more than three times greater than predicted. They suggested that better understanding of flowpaths in mine-pools could improve water quality prediction.

Demchak et al. (2004) reported that iron concentration had decreased an average of about 80% in 44 free-draining underground mine discharges in West Virginia over a 30 year period. This study included mines in the same coalbeds, Upper Freeport and Pittsburgh seams, as in this work. Demchak et al. compared water quality from a 1968 survey with drainage in 1999-2000 and found that acidity had decreased an average of 56% in Upper Freeport mines. Overall, iron concentrations declined about 80%, and sulphate declined about 50 to 75%. The average data included substantial variation among individual mines. Thus, while most mines showed improvement in water quality, the rate and degree of chemical change seems to have been influenced by site specific factors. More recently, Skousen et al. (2006) supplemented the 2004 study with some additional data They concluded that seasonal variation should be examined further to quantify the effect of flow on underground mine chemistry. Skousen et al.’s study included a large number of mines, but with a limited number of sample events through time. Short term features are therefore difficult to identify and evaluate. All of the mines in Skousen’s study were abandoned at closure.

Donovan et al. (2003) describe the flooding history and chemical evolution of a mostly flooded underground mine in the Pittsburgh coal bed in southwestern Pennsylvania. They describe three phases of water chemistry including an initial flooding phase of peak concentrations of Fe and other pollutants over a two year period. Second was a transition phase lasting two to four years with decline in iron and other parameter concentrations; then there was a third phase, where Fe declined to less than 10% of initial concentration, and net alkaline conditions developed.

Perry et al. (2005) found that after 14 years and pumping approximately 21 pool volumes, Fe and sulphate concentrations in a mostly flooded mine-pool had declined to about 20 % of their initial values. In 1986, leakage from an overlying mine complex further diluted the mine-pool. Since that time, Fe and sulphate concentrations have continued to decrease at the rate of 1 to 2 mg/L/yr for Fe and about 10 to 15 mg/L/yr for sulphate. The long term concentration trends can be described with exponential models, which project that objectionable Fe levels may persist for decades.

Koryak et al. (2004) summarized more than 30 years of stream monitoring data in several major tributaries of the Allegheny River in northern Appalachia. This area has been degraded by acid drainage from abandoned coal mines. They found over three decades a steady decreasing trend in acidity concentration, and associated increases in pH and alkalinity. Since the 1970s, acidity had declined by an average of 63%. They attributed the water quality improvements to “exhaustion” of pyritic materials. The stream data are an indirect gage of the acid loading in the watershed. The observed time frames and relative improvements are consistent with the behavior described for mine-pools.

Younger (2000) described a simplified generic model for estimating iron behavior in flooded mines in the U.K. Younger examined 81 discharge records from closed, mostly to fully flooded mines, and concluded that flushing could be described using decay type functions.

Methodology

Five mine-pools, two in West Virginia and three in Pennsylvania, USA with reasonably complete long term (i.e. greater than 10 years) water quality monitoring were evaluated. Two are partly flooded, and discharge acidic, metal rich drainage, whereas the other three are mostly flooded and have circumneutral water. The flooded mine-pools however, still discharge waters with objectionable concentrations of Fe and sulphate. All five mine-pools are developed in closed underground coal mines in Upper Pennsylvanian age rocks. General characteristics of the five mine-pools are summarized in Table 1.

Table 1
General Characteristics of Long Term Discharge Data Sets

Mine	Coalbed	Location	Period of Record	Water Quality	Flow/Pump Data
T&T #2	Upper Freeport	WV	1994-2007	Strongly acidic, high Fe, Al, SO_4	Average Flow 1850 L/min
Omega	Upper Freeport	WV	1993-2007	Strongly acidic, high Fe, Al, SO_4	Average flow 240 L/min
Hahn	Pittsburgh	PA	1980-1999	Alkaline, Fe, high Na	Average pump rate 13250 L/min
Arden	Pittsburgh	PA	1986-1999	Alkaline, Fe, high Na	Average pump rate 6800 L/min
Barnes & Tucker	Lower Kittanning	PA	1969- 2005	Marginally alkaline, Fe	Average pump rate 22700-26500 L/min

Time series plots of chemical concentrations in the five mine-pools often exhibited curvilinear behavior. A semi-log plot of these concentrations vs. time is similar to idealized plots of 1st or 2nd order rate laws. Figure 1, showing a semi-log plot of iron concentration versus time in a mostly flooded mine, exemplifies this trend. This suggests the long-term chemical trends can be represented by an exponential expression that describes the rate of change as a function of time.

Chemical data were fitted to the general decay equation of the form:

$$\mathbf{C_t = C_o \times e^{-kt}} \qquad \mathbf{(1)}$$

where:
C_t = concentration at time t
C_o = concentration at time zero
e = base e, approximate value of 2.718
k = decay constant, rate of concentration change per unit time
t = time

The decay constant, k, was estimated by rearranging equation (1) and solving, with k in dimensions of t^{-1}.

Gzyl and Banks (2007) use the term "decay" to describe the rate of change in pH and sulphate concentration in flooding Polish coal mines. The term decay is used for convenience in this paper in the context of describing rate of change in mine-pool chemical concentration. Decay constants (k) were estimated for chemical parameters Fe, Al, sulphate, total dissolved solids (TDS), total acidity, and hydrogen ion activity (pH) for the five mine-pools where data were available. Aluminum decay constants were computed for the Omega and T&T mine-pools because only these two sites had appreciable concentration data for Al.

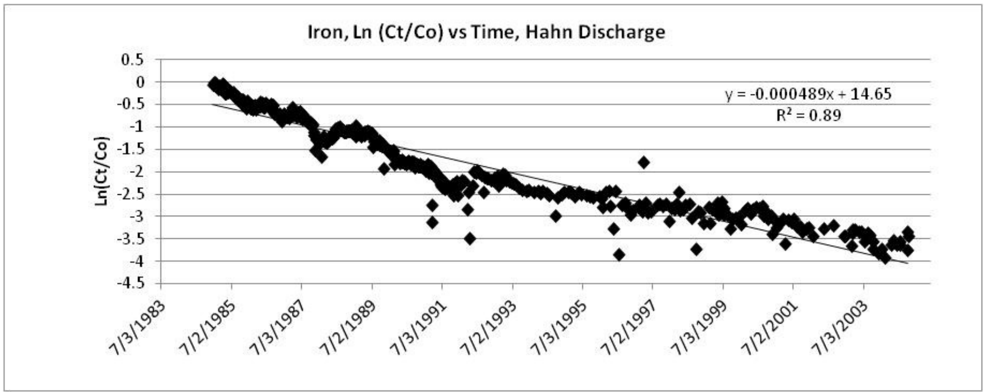

Figure 1. Plot of Ln (C_t/C_0) for Fe versus time in a Flooded Mine, With Fitted Regression and R^2 =0.89. Slope of the fitted regression equals the decay constant k, -4.89 $\times 10^{-4}$ d^{-1}.

Four of the five mine-pools had distinct changes in chemical composition that were related to flooding phase or in-situ treatment. The monitoring record was analyzed for decay behavior in several ways including:

- A single decay function for the entire period of record, assuming flooding phase or in-situ treatment had no effect on decay.
- Dividing the record into pre and post in-situ treatment and computing separate decay values for each period.
- Computing decay on data smoothed with a 5 point moving average.
- Dividing the record based on flooding phases, and computing separate decay values for each period.
- Examining semi-log scale plots of concentration against time for rate changes, manifested by change in slope.

Decay constants based on concentration data for Total Acidity; dissolved Fe, Al, sulphate; and TDS for the five mine-pools were compiled if they were statistically significant at P=0.05. Constants were derived using least squares regression methods. The constant k is the slope of the fitted regression, as shown in figure 1. Sample size, n, for the five mines ranged from 230 sampling events for the Omega site, to about 1,300 sampling events for the Barnes and Tucker site.

Results

The significant decay constants span about one order of magnitude, around -10^{-4}/day, regardless of the degree of flooding, or stage of flooding (initial flush or long term). The only exceptions were several long term scenarios where the decay constant is statistically insignificant, and Al and TDS decay for parts of the record in the unflooded Omega and T&T mine-pools. The relatively narrow range of decay constants suggests that k is not greatly influenced by chemical conditions, but may be in part, a function of physical conditions of the mine-pool and leaching efficiency. All five mines are in the northern Appalachian plateau with similar hydrogeologic and climatic controls.

The decay constants are summarized in Table 2 by parameter, degree of flooding, all combined data, initial flushing, and long term flushing stage. For every parameter, the greatest rate of concentration decline occurred in the initial flushing stage. Overall, Fe had the most rapid decay rate of the five parameters, followed by total acidity and sulphate. Aluminum change was compiled only for the two acidic mostly unflooded mines, and had a slower decay rate. TDS decay rates, available for four mines, had the slowest overall rate of concentration decline. Standard deviations for flooded mines data were equivalent to about five percent of the value of the derived constants. Unflooded mines with more scattered data and periodic flushing and drying events had standard deviations equivalent to about 20 to 30 percent of the value of the derived constant.

Mack and Skousen (2008) reported a survey of acidity decay in about 40 mines located above base level drainage in West Virginia. Their surveyed mines included the T&T complex described in this study, and other older mines in the Upper Freeport and Pittsburgh coalbeds. Most of the mines had been closed for 50 to 70 years. They plotted acidity decay curves with k of 2, 5 and 10% per year and compared them to time series plots of acidity concentration They concluded that most mines fit best a 5%/year decay curve, or about -1.4 x 10^{-4}/day. The T&T mine-pool mean annual acidity most closely approximated a 10% decay, or about -2.7 x 10^{-4}/day. This study estimated a similar value for acidity decay at -1.62 x 10^{-4}/day, using the regression techniques described previously. The 2 and 5 %/year decay curves that Mack and Skousen used are well within the range of decay constants computed in this study. Mack and Skousen's data, and this study's results suggest it is possible to define chemical concentration decay estimates within about one order of magnitude for mines in similar hydrogeologic and geochemical settings.

Table 2
Summary of Computed Decay Constants

Site	Flooding state	Total Acidity k($\mathbf{d}^{-1}$)	Iron k($\mathbf{d}^{-1}$)	Aluminum k($\mathbf{d}^{-1}$)	Sulphate k($\mathbf{d}^{-1}$)	TDS k($\mathbf{d}^{-1}$)
Omega all data	Unflooded	-2.35 x 10^{-4}	-2.59 x 10^{-4}	-1.09 x10^{-4}	-1.31 x10^{-4}	-1.05 x10^{-4}
Omega, Initial	Unflooded	-2.92 x 10^{-4}	-3.86 x 10^{-4}	-1.97 x 10^{-4}	-4.46 x10^{-4}	-3.5 x10^{-4}
Omega, long term	Unflooded	-1.58 x 10^{-4}	-2.57 x 10^{-4}	-1.46 x 10^{-4}	-1.43 x10^{-4}	-1.23 x10^{-4}
T&T, all data	Unflooded	-1.62 x 10^{-4}	-3.86 x 10^{-4}	-1.01 x 10^{-4}	-1.05 x10^{-4}	N.S.
T&T, Initial	Unflooded	-1.85 x 10^{-4}	-3.96 x 10^{-4}	N.S. (1)	-4.37 x10^{-4}	-5.67 x10^{-4}
T&T, long term	Unflooded	N.S.	-4.29 x 10^{-4}	N.S.	N.S	-6.4 x10^{-5}
Hahn all data	Flooded	-4.88 x 10^{-4}	-4.89 x 10^{-4}	-(2)	-4.18 x 10^{-4}	-4.14 x 10^{-4}
Hahn, initial flush	Flooded	-8.28 x 10^{-4}	-8.16 x 10^{-4}	-	-4.76 x 10^{-4}	-4.33 x 10^{-4}
Hahn, long term	Flooded	-2.89 x 10^{-4}	-2.99 x 10^{-4}	-	-2.72 x 10^{-4}	-4.63 x 10^{-4}
Arden, all data	Flooded	-2.50 x 10^{-4}	-2.48 x 10^{-4}	-	-1.64 x 10^{-4}	-1.29 x 10^{-4}
Arden, Initial	Flooded	-3.55 x 10^{-4}	-3.55 x 10^{-4}	-	-1.78 x 10^{-4}	-1.84 x 10^{-4}
Arden, long term	Flooded	N.S.	N.S.	-	-1.08 x 10^{-4}	N.S.
B&T, all data	Flooded	-2.20 x 10^{-4}	-2.23 x 10^{-4}	-	-1.31 x 10^{-4}	-
B&T, initial	Flooded	-2.52 x 10^{-4}	-2.52 x 10^{-4}	-	-1.75 x 10^{-4}	-
B&T, long term	Flooded	-1.12 x 10^{-4}	-1.12 x 10^{-4}	-	-1.05 x 10^{-4}	-

(1) N.S. = Not statistically significant at P=0.05
(2) "-" indicates no data for this parameter

Figure 2 compares median decay constants for mostly flooded to mostly unflooded, and early flushing to late leaching conditions for the five mine-pools. The mostly flooded mines decay faster for total acidity, sulphate and dissolved solids in comparison to the mostly unflooded mines. Iron, however, is exceptional, with a slower decay rate in flooded mines. The implication is that flooding reduces weathering rates, in particular oxidation reactions, hence the decline in concentration is more rapid. The slower iron decay in flooded conditions suggests that soluble Fe may be generated from sources other than pyrite, such as the reductive dissolution of Fe oxyhydroxide minerals at circumneutral pH. No redox measurements of the Hahn and Arden mine-pools are available, and the tendency for these mine-pools to dissolve Fe oxyhydroxides can only be approximated from indirect means. Six Eh measurements were made by the first author over an 18 month period of the main discharge from the mostly flooded Barnes&Tucker mine-pool. Eh ranged from +160 to +290 mV. The calculated saturation indices for Fe oxyhydroxides indicated under-saturation for poorly crystalline forms and approximate equilibrium with goethite. These lines of evidence are indirect, but show that it is possible that Fe in mostly flooded, reduced mine-pools could be generated from reductive dissolution of Fe oxyhydroxide minerals.

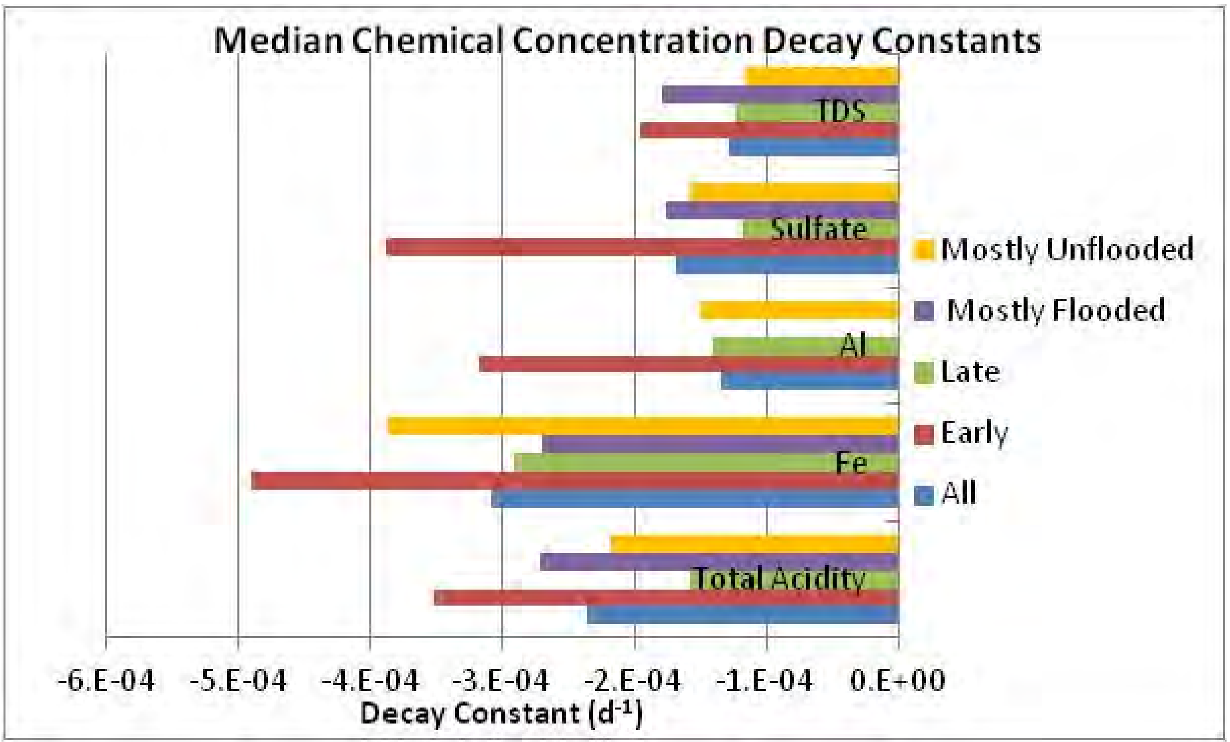

Figure 2 Chemical Concentration Decay Constants in $d^{-1}$by Parameter,
Degree of Flooding and Flushing Stage. Median Values for Five Mine-pools.

Figure 2 also shows a comparison of decay constants for early flushing versus late or long term conditions. Early decay ranges from about 1.5 to 3 times faster than late decay for the five parameters, with the largest disparity reported for sulphate. In all parameters, the difference is likely attributed to the initial flush of accumulated and highly soluble minerals, followed by continued weathering and slower leaching of soluble minerals. Younger (1997, 2000), and Wood et al.(1999) have made similar observations to explain the discharge quality of coal mines in the U.K.

Data in table 2 and figure 2 suggest that modeling chemical concentration decay in mines should be based on separate decay values for early flushing and long term leaching. Chemical molar ratios, such as Fe:SO_4 approach constant values in these mine-pools as they age and transition from early flushing to long term leaching. Figures 3a and 3b show time series plots of Fe:SO4 molar ratio for the flooded Hahn mine-pool and the unflooded Omega site, respectively. These plots show the largest ratios present during initial flushing, then declining to a near constant value, with time series slope approaching zero in the flooded mine. The approach of a near constant ratio approximately coincides with the demarcations made from semi-log plots. A constant ratio also suggests that the initial transient flushing condition has passed and the mine-pool is in a long term leaching mode.

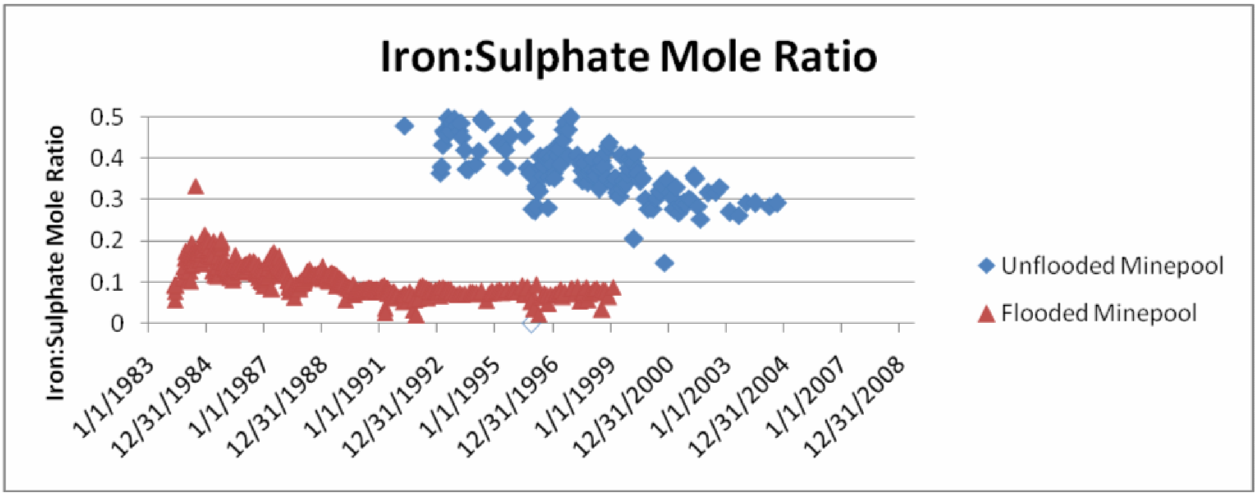

Figure 3 Chemical Molar Ratio Time Series for a Flooded and an Unflooded Mine.

The chemical ratio approached near constant value in late 1989 in the flooded Hahn mine-pool, about 5 years after flooding was complete. It is equivalent to the exchange of about 1.25 pool volumes. Changes in the Omega mine-pool were more subtle, but occurred around 1996, or about 6 years after mine closure and exchange of about 10 pool volumes. Prior to 1996, chemical ratios exhibit short term fluctuations as the mine-pool is subjected to repeated transient flushing cycles. After 1996, chemical ratios show less short term fluctuation, and the slope of the plotted data starts to decrease. For two of the three mostly flooded mines, Fe to sulphate ratio approached a constant value after the mine-pool flushed slightly more than one pool volume. The two acidic mostly unflooded mines had less distinct slope changes, and exchanged an estimated 8 to10 pool volumes before stabilizing. The contrast between flooded and mostly unflooded mines could be attributed to the active ongoing chemical weathering in the aerated mine-pools, and less aggressive weathering in the mostly flooded mines. Element ratios can be a useful tool for separating initial flushing and long term leaching.

Figures 4a and 4b are time series plots of raw data, decay estimated from a single k value, and decay estimated in two phases; initial flushing and long term leaching as identified from chemical ratio data, for a flooded and an unflooded mine. The single decay value was derived from a least squares regression on the entire data set. The initial and long term decay values were also derived with least squares regression, but with separate analysis of the two data subsets. The fit of the decay lines was assessed by tabulating residuals (difference of raw data minus decay estimate). Residuals, expressed as a percentage of the raw data for total acidity declined from a median 39% to 14 % when data were modeled in two decay steps for the flooded Hahn mine-pool, when compared to using a single decay value. A modest improvement from a median 12 to 10 % residual occurred when total acidity was modeled in two steps compared to a single decay value in the Omega mine-pool.

Data presented in figure 4 show that in general, agreement between raw and calculated decay data can be improved using a two phase decay model. The poorest fit usually occurred in the middle of a curve, at the expense of closer agreement at the beginning and end of the decay line. This systematic error suggests that the decay function does not completely describe the physical and chemical processes at work. Neither does the decay equation accommodate short term and seasonal variations in chemical composition. The decay function is useful however as a trend estimator.

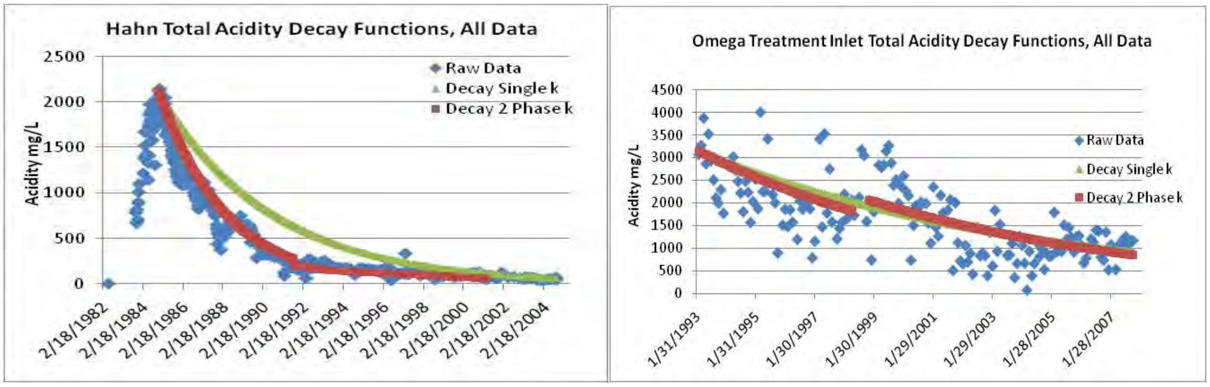

Figure 4. Total Acidity Decay Estimated as One and Two Phase Functions for Flooded and Unflooded Mine-pools.

The application of decay constants to mine-pool chemical concentrations has two significant implicit assumptions:

- Hydrogeologic conditions will remain constant through time, and
- Geochemical conditions will remain constant through time.

The hydrogeology of closed mines can be affected by pumping, and flooding or dewatering of hydrologically connected mines and aquifers. Effects from adjacent mines will be site-specific. A second issue is the alteration in aquifer properties of the mine-pool by continued physical weathering, pillar crushing and collapse of roof rock. The significance of continued weathering of aquifer rocks in underground mines is not developed here. However, Hawkins (2004) reported that hydraulic conductivity of surface mine-spoil more than 2.5 years old was less than that for newly reclaimed rocks. He attributed this, in part, to continued physical weathering. Rehm et al. (1980) also reported that hydraulic conductivity decreased with age on surface mine spoil in North Dakota. A plausible effect of decreasing hydraulic conductivity would be to reduce ground water flow velocity, and hence decay rates. The assumption of constant hydrogeologic conditions over a prolonged period may not be completely valid.

The second assumption, that geochemical conditions remain constant through time may also be suspect. As the mine-pool solution becomes increasingly dilute, concentrations of Fe and other elements could be controlled by mineral solubility, and perhaps influenced by changes in redox conditions. pH dependent kinetics may also change as mine-pools age. The Hahn and Barnes and Tucker mine-pools were initially acidic (pH less than 4), but gradually evolved to circumneutral (pH about 6.5) conditions after flooding and initial flushing.

The decay equation (1) was solved for time t, to reach specific target chemical concentrations for sulphate total acidity, Fe, TDS, and Al using the derived values for “k” and initial mine-pool concentrations. Target concentrations of 10, 3.5 and 1 mg/L were selected for Fe. One mg/L Fe is a suggested water quality standard for aquatic life (US EPA, 1986), whereas the 3.5 mg/L is a 30 day US EPA average National Pollutant Discharge Elimination System (NPDES) discharge standard for US coal mines. A target concentration of 1 mg/L was selected for Al, which is similar to the recommended standard of 0.75 mg/L for aquatic life (US EPA, 1986b). Target values of 500 mg/L total dissolved solids, and 250 mg/L for sulphate were selected based on US national secondary drinking water standards. A target value of

300 mg/L acidity was selected as a condition where passive treatment systems that add alkalinity might be feasible.

The estimated times to attain target concentration values are shown for sulphate in figure 5 for the five mine-pools. Sulphate decay to 250 mg/L is estimated to require between 15 and 58 years for the five mine-pools, as a function of both initial concentration and the value of “k”. The estimated time for Fe concentration to attain 1 mg/L ranged from 39 to 105 years. A change of aluminum concentration to less than 1 mg/L is estimated to require 69 to more than 100 years in the acidic mostly unflooded mines. Several decay scenarios have statistically insignificant rates and no estimates were calculated.

This set of estimated decay times also implies near steady conditions in physical and chemical properties through time. Aluminum, with its strong pH-solubility dependence, exemplifies a parameter whose decay behavior could change significantly if mine-pool conditions are altered. Nevertheless, the target concentration estimates show that mine-pool waters of these starting chemical compositions are likely to require decades to achieve acceptable chemistry. Excluding total acidity, most parameter decay estimates are between 20 and 70 years to achieve target concentrations.

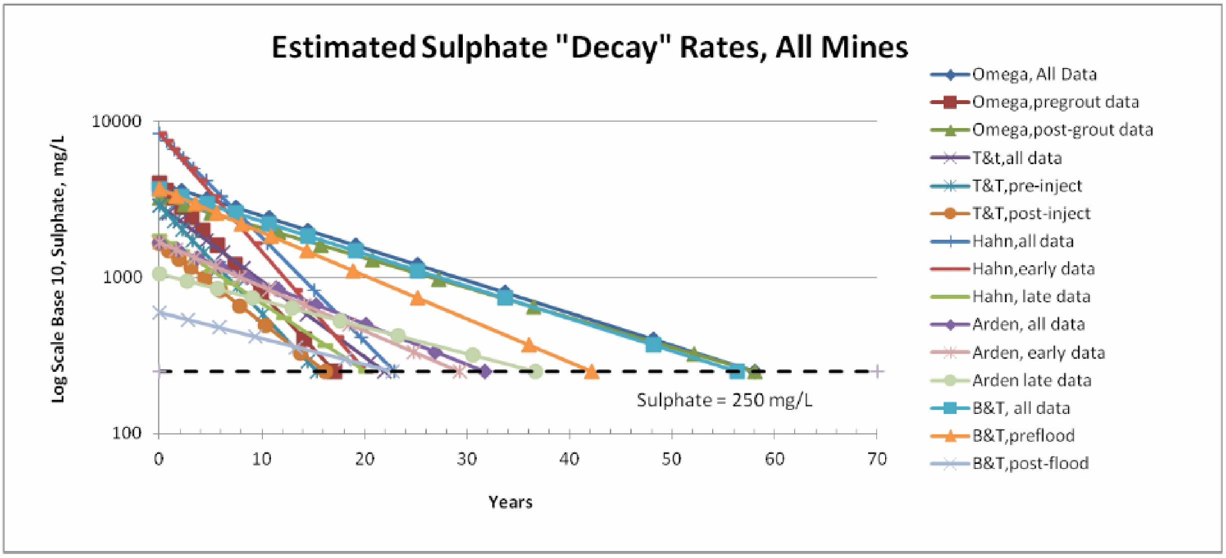

Figure 5 Estimated Time for Sulphate to Attain 250 mg/L Concentration in Five Mine-pools.

Box Model Flushing Analysis

The decay constant values generally ranged over about one order of magnitude, suggesting that there might be underlying controls on the magnitude of ”k”. The decay function itself gives little indication of the underlying geochmical and hydrogeologic variables that control it’s magnitude. Therfore a simple set of box model calculations were performed, with the goal of identifying what process or combination of processes controls the magnitude of “k”.

Dissolution rates for moderately soluble minerals are rapid relative to diffusion of reactants and products within mineral grains and bulk solution. Therefore, diffusion was considered a potential control on decay rate. Surface controlled reactions for these moderately soluble minerals are also often rapid relative to the flushing provided by ground water flow. An initial analysis of macroscale variables included mine recharge rate, percent flooded, mine area, average residence time, maximum flow-path length and initial chemical concentration. These parameters were compared with decay constant values for all monitoring data, early or initial flushing phase, and late or long term leaching. Most decay constants showed little correlation with the macroscale parameters. The lack of a strong relationship to macroscale features implies that transport control may be at the microscale. This initial analysis prompted a closer examination of the effects of diffusion and flushing rate on mine water decay functions.

Berner (1978) described a simple box model calculation to illustrate the effects of flushing and diffusion on mineral dissolution rates. Berner's equations are based on conservation of mass principles. The rate of concentration change affected by flushing is expressed as:

$$\frac{dc}{dt} = R - \frac{F}{V} c \qquad (2)$$

where:

$\frac{dc}{dt}$ = rate of concentration change

F = Flushing rate
V = Unit Fluid Volume
R = Dissolution Rate

At high flushing rates (high ground water flow velocities); a maximum dissolution rate is reached, controlled by the surface reaction rate on the mineral grain. At the other extreme, where flushing rate is small (low ground water flow velocity) compared to mineral reaction rate, chemical concentration (c) approaches saturation, and flushing or flow rate (F) controls dissolution rate (R). In the case of small ground water flow rates and slow flushing, Berner (1978) notes that $c \approx C_{eq}$, or equilibrium concentration for a specified mineral phase. Under these conditions, the dissolution rate is approximated as the product of flushing frequency and equilibrium concentration. If flushing frequency and equilibrium concentration values are known, then dissolution rate (R) can be estimated. In the case of rapid flushing of the mine-pool, Berner notes that $R \approx k\, C_{eq,}$ where k is approximated as the product of the dissolution rate constant for a specified mineral and equilibrium concentration. A consistent set of values for R could explain the observed magnitude of decay constants.

Slow flushing rate conditions were used to estimate R for sulphate concentration for the five mine-pools. Sulphate flushing calculations were successively performed assuming solution control by gypsum, pyrite, and for the two acidic mine-pools, jurbanite to represent aluminum sulfate minerals. The equilibrium concentration C_{eq}, was estimated using the geochemical code PHREEQC (Parkhurst and Appelo, 1999) and equilibrating the mine water to a saturation index of zero for gypsum, pyrite or jurbanite. This concentration was used to represent concentration (c) in equation 2. Average flushing rate (F) was estimated from time required to discharge a pool volume and the unit volume was set to one liter. Solving equation 2 for slow flushing rate, i.e small ground water flow velocities, gave apparent dissolution rates, R, on the order of 10^{-9} to 10^{-11} mol/L-s, regardless of which mineral is specified as controlling sulphate concentration. The dissolution rate is most influenced by assigned flushing rate, not the choice of controlling mineral. Mineral mass and surface areas per unit volume of the mine-pools are not known. However, the estimated dissolution rates could support continued weathering and chemical concentrations actually observed in mine water, with relatively small amounts of accessible minerals. Thus, a slow flushing model relative to mineral dissolution reaction rates, provides indirect evidence that the decay constant is at least partly a transport function.

A set of calculations using Berner's box model approach, but assuming rapid flushing relative to dissolution, was also compiled for the five mine-pools. For the rapid flushing model, R can be estimated from equilibrium concentration $C_{eq,}$ and a dissolution rate constant, k. Rate constants for gypsum and pyrite dissolution were taken from Palandri and Kharaka (2004), and equilibrium concentrations estimated with PHREEQC. For a rapid flushing model, dissolution estimates are strongly influenced by the choice of controlling mineral. Dissolution estimates of sulphate based on pyrite control produced apparent dissolution rates (R values) ranging over nine orders of magnitude from 10 to 10^4 moles/L-sec, to 10^{-5} moles/L-sec for gypsum controlled dissolution. These rates are unreasonably largefor the geochemical system being considered. Even the values derived for gypsum control indicate a rapid rate of weathering that would deplete the source mineral within a short time and produce chemical concentrations in the mine water that far exceed those actually produced. These results indicate that rapid flushing relative to dissolution is not an appropriate model for these mine-pools.

Summary and Conclusions

Chemical concentration data from five closed underground coal mines were fitted to a first order decay function to describe rate of change as function of time. The parameters included total acidity, Fe, Al, SO_4 and TDS. Three mines were flooded and pumped at constant discharge rates, while two unflooded mines flow in response to recharge events and mine-pool storage changes. The principal conclusions are:

- The general form of the decay equation was useful for estimating the long term trends for total acidity, Fe, Al, sulphate and TDS. Computed decay constants are with few exceptions, are on the order of -10^{-4}/d.
- Chemical decay can be divided into early and late phases. The early phase includes the flushing of accumulated salts and acid weathering products including “vestigial” acidity. Concentrations decline most rapidly during the early flushing phase. The late phase includes the continued weathering of pyrite and other minerals and removal of “juvenile acidity”. Element ratios of Fe to sulphate may be a useful method to separate early and late phase decay.
- Time frames to reach specified water quality concentrations were on the order of decades. In general, most decay predictions ranged from about 30 to 70 years duration. They are controlled by the initial or starting concentration, target concentration and the magnitude of the decay constant. Aluminum was predicted to have the longest decay period, in some instances exceeding 100 years, due to slow rates of change and a small target concentration of 1 mg/L. The range of statistical uncertainty can span one to two decades for these long term estimates to reach prescribed water quality conditions. Long term water quality estimates should include consideration of the model’s uncertainty.
- Decay rates are useful for long term trend estimates. They are less useful for estimating concentration at specific points in time. The mathematical formulation of the decay function does not explicitly account for seasonal variation, or other short term transient stresses, such as a large recharge and flushing event.
- The decay constant is a lumped variable that includes both chemical reaction and transport elements. A box model analysis based on slow flushing or rapid flushing of a mine-pool produced apparent dissolution rates suggesting that the decay constant values are dependent on transport properties of the mine-pool. Decay in these mine-pools can be described as a slow flushing process.

The derived decay constants illustrate two observations of practical significance: chemical concentrations exhibit a relatively rapid initial decline on the order of a few years to 10 to 20 years after mine closure, where water treatment needs are at a maximum; and a long term leaching phase occurs with a slow rate of change, during which water treatment demands are reduced, but needed over a longer period.

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Literature Cited

Berner, R., 1978. Rate Control of Mineral Dissolution Under Earth Surface Conditions, American Journal of Science, Vol. 278, p 1235-1252.

Demchak, J., Skousen, J. and L. McDonald, 2004. Longevity of Acid Discharges From Underground Mines Located Above the Regional Water Table, Journal Environmental Quality Vol 33, p 656-668.

Donovan, J., Leavitt, B., and E. Werner, 2003. Long-Term Changes in Water Chemistry As a Result of Mine Flooding in Closed Mines of the Pittsburgh Coal Basin, USA, In Proceedings 6th International Conference on Acid Rock Drainage, p 869-875.

Glover, H., 1983. Mine Water Pollution- An Overview of Problems and Control Strategies in the United Kingdom, Water Science Technology, Vol. 15, p 59-70.

Gzyl, G. and D. Banks, 2007. Verification of the First Flush Phenomenon in Mine Water from Coal Mines in the Upper Silesian Coal Basin, Poland, Journal of Contaminant Hydrology, Vol. 92 p 66-86.

Hawkins, J. 2004. Predictability of Surface Mine Spoil Hydrologic Properties in the Appalachian Plateau. Ground Water, Vol. 42, No.1, p 119-125.

Kleinmann, R., Hornberger, R., Leavitt, B., and D. Hyman, 2000. Introduction and Recommendation, The Nature of the Problem, In Prediction of Water Quality at Surface Coal Mines, Acid Drainage Technology Initiative, Prediction Workgroup, National Mined Land Reclamation Center, West Virginia University, Morgantown, WV, 254 pps.

Koryak, M., Stafford, L., and R. Reilly, 2004. Declining Intensity of Acid Mine Drainage in The Northern Appalachian Bituminous Coal Fields: Major Allegheny River Tributaries. Journal American Water Resources Association, Vol. 40, No. 3, p 677-689.

Mack, B., and J. Skousen, 2008. Acidity Decay Curves of 40 Above Drainage Mines in West Virginia, In R. I. Barnhisel (ed) Proc. American Society of Mining and Reclamation National Meeting, p 612-627.

Palandri, J., and Y. Kharaka, 2004. A Compilation of Rate Parameters of Water Mineral Interaction Kinetics, US Geological Survey Open File Report 2004-1068.

Parkhurst, D., and C. Appelo., 1999. User's Guide to PHREEQC (Version 2)- A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations, US Geological Survey Water Resources Investigation Report 99-4259.

Perry, E., J. Hawkins, M. Dunn, R. Evans and J. Felbinger, 2005. Water Quality Trends in a Flooded 35 Year Old Mine-pool. In R. I. Barnhisel (ed) Proc. American Society Mining and Reclamation 22st Annual National Conference, p 904-920.

Rhem, B., Groenwald, G,. and K. Morin, 1980. Hydraulic Properties of Coal and Related Materials, Northern Great Plains, Ground Water, Vol. 20, p 217-236**.**

Skousen, J., McDonald, L., Mack, B., and J. Demchak, 2006. Water Quality From Above Drainage Mines Over A 35 Year Period. In Proceedings 7th International Conference on Acid Rock Drainage, American Society of Mining and Reclamation, p 2044-2054.

US Environmental Protection Agency, 1986. Quality Criteria For Water 1986. Office of Water Regulation and Standards EPA 440/5-86-001.

US Environmental Protection Agency. 1986b. Aluminum. Office of Water Regulation and Standards EPA 440/5-86-008.

Wood, S., Younger, P. and N. Robins, 1999. Long-term changes in the Quality of Polluted Minewater Discharges from Abandoned Underground Coal Workings in Scotland, Quarterly Journal of Engineering Geology, Vol. 32, p 69-79.

Younger, P., 1997. The Longevity of Minewater Pollution: A Basis for Decision Making, The Science of the Total Environment, Vol. 194&195, p 457-466.

Younger, P., 2000. Predicting Temporal Changes in Total Iron Concentrations in Waters Flowing From Abandoned Deep Mines: A First Approximation, Journal of Contaminant Hydrology, Vol. 44, p 47-69.

Younger, P., and P. Thorn, 2006. Predictions and Reality: Generation of Strongly Net-Acidic Mine waters Through Flooding of Underground Coal Mine Workings With Limestone Roof Strata, Blenkinsopp Colliery (Northumberland, UK), In Proceedings 7th International Conference on Acid Rock Drainage, American Society of Mining and Reclamation, p 2542-2557.