“Estimating Water Quality Trends in Abandoned Coal Mine-pools”

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

Median decay constants describing the rate of chemical change ranged from \(-1.3 \times 10^{-4}/\text{day}\) for total dissolved solids and Al, to \(-3 \times 10^{-4}/\text{day}\) for Fe. Total acidity, sulfate, 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.

Slightly larger decay constants on the order of 6 to 8 \(\times 10^{-4}/\text{day}\) were fitted to chemical load data for one mine with variable discharge. The loading decay behavior suggests that mine-pool flushing is influenced by ground flow rate and leaching efficiency. 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 and elsewhere (Kleinmann et al., 2000; Younger, 1997). The longevity or duration of pollutional 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 northern Appalachia. We also examine some physical and chemical factors that may influence discharge chemistry and time dependent behavior.

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 reached near constant conditions 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. 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. The Demchak et al. 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 sulfate declined about 50 to 75%. The average data showed variation among individual mines. Thus, while most mines showed improved water quality, and behaved in a similar manner, the rate and degree of chemical change seems to be somewhat site specific. 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 et al.’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 sulfate 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 sulfate concentrations have continued to decrease and are now, after 35 years, about seven and four percent, respectively, of their initial concentrations at mine closure and initial flooding.

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, with reasonably complete long term (i.e. greater than 10 years) water quality monitoring were evaluated. Two are mostly unflooded, 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 sulfate. 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

<table>
<thead>
<tr>
<th>Flooding</th>
<th>Coalbed</th>
<th>Location</th>
<th>Period of Record</th>
<th>Water Quality</th>
<th>Average Flow/Pump Data</th>
</tr>
</thead>
<tbody>
<tr>
<td>mostly unflooded</td>
<td>Upper Freeport</td>
<td>WV</td>
<td>1994-2007</td>
<td>Strongly acidic, high Fe, Al, SO₄</td>
<td>488 gpm (Variable Flow)</td>
</tr>
<tr>
<td>mostly unflooded</td>
<td>Upper Freeport</td>
<td>WV</td>
<td>1993-2007</td>
<td>Strongly acidic, high Fe, Al, SO₄</td>
<td>63 gpm (Variable Flow)</td>
</tr>
<tr>
<td>flooded</td>
<td>Pittsburgh</td>
<td>PA</td>
<td>1980-1999</td>
<td>Alkaline, Fe, high Na</td>
<td>3500 gpm (pump)</td>
</tr>
<tr>
<td>flooded</td>
<td>Pittsburgh</td>
<td>PA</td>
<td>1986-1999</td>
<td>Alkaline, Fe, high Na</td>
<td>1800 gpm (pump)</td>
</tr>
<tr>
<td>flooded</td>
<td>Lower Kittanning</td>
<td>PA</td>
<td>1969-2005</td>
<td>Marginally alkaline, Fe</td>
<td>6000-7000 (pump)</td>
</tr>
</tbody>
</table>

Time series plots of chemical concentrations in the five mine-pools often exhibited curvilinear behavior. This suggests that 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:

\[ C_t = C_0 e^{kt} \]  
(1)

where:  
- \( C_t \) = concentration at time \( t \)  
- \( C_0 \) = 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 \( t^{-1} \). Figure 1 is an example semi-log plot of iron concentration data. The slope of the line represents the rate of change in chemical concentration, i.e., the decay constant which in this case is \( -4.89 \times 10^{-4} \ \text{d}^{-1} \). The decay constant is expressed as negative to emphasize that concentration is decreasing with time.

Gzyl and Banks (2007) use the term “decay” to describe the rate of change in pH and sulfate 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, sulfate, total dissolved solids (TDS), and total acidity for the five mine-pools where data were available. Aluminum decay constants were computed only for the two acidic mine-pools because only these two sites had appreciable soluble Al concentration. Chemical loading or flux data were also compiled for one site with variable discharge rate, and decay constants were derived.
The five mine-pools had distinct changes in chemical composition that were related to flooding state or in-situ treatment. The monitoring record was analyzed for changes in chemical concentration or “decay” behavior in several ways including:

- Deriving a single decay function for the entire period of record, assuming flooding phase or in-situ treatment had no effect.
- Dividing the record based on two flooding phases of initial flushing, and long term leaching; then computing separate decay values for each period.
- Dividing the record into pre and post in-situ treatment and computing separate decay values for each period.

Constants were derived using regression methods with results displayed as in Figure 1. Decay constants for Total Acidity, dissolved Fe, Al, sulfate; and TDS for the five mine-pools were compiled if they showed a statistically significant trend with time. Sample size, n, for the five mines ranged from 230 to about 1,300 sampling events.

**Results**

The decay constants span about one order of magnitude, around \(-10^{-4}/\text{day}\), regardless of the degree of flooding, or stage of flooding (initial flush or long term). A few exceptions were several long term flushing scenarios where the chemical concentration change rate was small and statistically insignificant. This occurred for Al and TDS in mostly unflooded or free draining mines. The relatively narrow range of decay constants suggests that \(k\) is not greatly influenced by chemical conditions, but may depend more on physical conditions of the mine-pool and how efficiently the pool is leached or flushed. All five mines are in the northern Appalachian plateau with similar climate and hydrogeologic controls.

The decay constants are summarized in Table 2 by parameter, degree of flooding, for all combined data, 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 sulfate. 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.
In general, total acidity, sulfate, and total dissolved solids chemical concentrations decrease more rapidly in flooded mines, in comparison to the mostly unflooded mines. Sulfate and total dissolved solids represent, in general terms, conservative chemical parameters derived partly or mostly from the chemical weathering of pyrite and other minerals. Since flooding halts or inhibits pyrite weathering, the decrease in sulfate and TDS should represent mostly flushing of materials already present at mine closure, with little new weathered material added after flooding. The unflooded mines however can continue to generate “new” sulfate and dissolved solids after closure from the continued chemical weathering of pyrite.

Iron concentrations, however, tended to decrease more rapidly in the mostly unflooded mines. The reactive characteristics of ferric iron (Fe III) and tendency to form solid minerals in unflooded mines may account for the more rapid reduction of iron concentrations in these mine discharges.

Long term flushing rates are, in general, less than single decay rates computed for the overall data sets in both flooded and unflooded mines. The difference is likely attributed to the initial flush of accumulated and highly soluble minerals, followed by continued weathering and slower leaching of less soluble minerals during long-term leaching. Younger (1997, 2000), and Wood et al. (1999) have made similar observations to explain the discharge quality of coal mines in the U.K.

<table>
<thead>
<tr>
<th>Site</th>
<th>Flooding state</th>
<th>Total Acidity k(d⁻¹)</th>
<th>Iron k(d⁻¹)</th>
<th>Aluminum k(d⁻¹)</th>
<th>Sulfate k(d⁻¹)</th>
<th>TDS k(d⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mine 1, all data</td>
<td>Unflooded</td>
<td>-1.62 x 10⁻⁴</td>
<td>-3.86 x 10⁻⁴</td>
<td>-1.01 x 10⁻⁴</td>
<td>-1.05 x 10⁻⁴</td>
<td>-1.05 x 10⁻⁵</td>
</tr>
<tr>
<td>Mine 1, long term</td>
<td>Unflooded</td>
<td>-1.31 x 10⁻⁵</td>
<td>N.S.</td>
<td>-4.29 x 10⁻⁴</td>
<td>-9.4 x 10⁻⁷</td>
<td>-5.8 x 10⁻⁵</td>
</tr>
<tr>
<td>Mine 2, all data</td>
<td>Unflooded</td>
<td>-2.35 x 10⁻⁴</td>
<td>-2.59 x 10⁻⁴</td>
<td>-1.09 x 10⁻⁴</td>
<td>-1.31 x 10⁻⁴</td>
<td>-1.05 x 10⁻⁴</td>
</tr>
<tr>
<td>Mine 2, long term</td>
<td>Unflooded</td>
<td>-1.58 x 10⁻⁴</td>
<td>-2.57 x 10⁻⁴</td>
<td>-1.46 x 10⁻⁴</td>
<td>-1.43 x 10⁻⁴</td>
<td>-1.23 x 10⁻⁴</td>
</tr>
<tr>
<td>Mine 3, all data</td>
<td>Flooded</td>
<td>-4.88 x 10⁻⁴</td>
<td>-4.89 x 10⁻⁴</td>
<td>N.S.</td>
<td>-4.18 x 10⁻⁴</td>
<td>-4.14 x 10⁻⁴</td>
</tr>
<tr>
<td>Mine 3, long term</td>
<td>Flooded</td>
<td>-2.89 x 10⁻⁴</td>
<td>-2.99 x 10⁻⁴</td>
<td>-</td>
<td>-2.72 x 10⁻⁴</td>
<td>-4.63 x 10⁻⁴</td>
</tr>
<tr>
<td>Mine 4, all data</td>
<td>Flooded</td>
<td>-2.50 x 10⁻⁴</td>
<td>-2.48 x 10⁻⁴</td>
<td>-</td>
<td>-1.64 x 10⁻⁴</td>
<td>-1.29 x 10⁻⁴</td>
</tr>
<tr>
<td>Mine 4, long term</td>
<td>Flooded</td>
<td>-5.6 x 10⁻⁵</td>
<td>N.S.</td>
<td>-4.5 x 10⁻⁵</td>
<td>-1.08 x 10⁻⁴</td>
<td>-1.6 x 10⁻³</td>
</tr>
<tr>
<td>Mine 5 all data</td>
<td>Flooded</td>
<td>-2.20 x 10⁻⁴</td>
<td>-2.23 x 10⁻⁴</td>
<td>-</td>
<td>-1.31 x 10⁻⁴</td>
<td>-</td>
</tr>
<tr>
<td>Mine 5, long term</td>
<td>Flooded</td>
<td>-1.12 x 10⁻⁴</td>
<td>-1.12 x 10⁻⁴</td>
<td>-</td>
<td>-1.05 x 10⁻⁴</td>
<td>-</td>
</tr>
</tbody>
</table>

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

The results of this study were evaluated against data from similar work. 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 also included 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 best fit a

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5%/year decay curve, equivalent to about \(-1.4 \times 10^{-4}/\text{day}\). Mine 2 in this paper was also included in Mack and Skousen’s study. This study estimated a similar value for acidity decay at \(-1.62 \times 10^{-4}/\text{day}\), or about 5.9% using the regression techniques described previously. The 5 and 10%/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 or less for mines in similar hydrogeologic and geochemical settings.

Figure 2 illustrates the expected behavior of chemical concentration data that follows a typical decay constant of \(2.52 \times 10^{-4}/\text{d}\). The y-axis shows the fraction of the original concentration remaining as a function of time. The time to reach 0.5, 0.1 and 0.05 of original concentration are 7.5, 25 and 32.6 years respectively, assuming the mine discharge continues to follow a decay pattern. The constants can be useful as part of a collection of tools and techniques to estimate expected impacts and treatment needs. Because none of the discharges and chemical parameters fit the generalized curve exactly, the decay constants have some associated statistical uncertainty. Any derived concentration estimates have a corresponding plus/minus envelope of estimated values.

**Figure 2.** Generalized decay curve showing fraction remaining as a function of time. The value of \(-2.52 \times 10^{-4}/\text{d}\) is a typical value for this study.

Figures 3a and 3b 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, for a flooded mine and an unflooded mine. The single decay value was derived from the entire data set. The initial and long term decay values were derived with separate analysis of the two data subsets. The fit of the decay lines was assessed by tabulating residuals (difference of actual raw data minus decay estimate). In both the flooded and unflooded mines, the predictive accuracy improved if the mine-pool is evaluated in two steps; first undergoing a rapid initial flush, followed by long term leaching.

Data in figure 3 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 consider short term and seasonal variations in chemical composition. The decay function is useful however as a long term trend estimator.

Decay constants were also estimated for chemical flux or load for two mostly unflooded mine-pools with variable discharge rates. Figure 4 shows estimated yearly loading for the parameters of TDS, sulfate, and total acidity in one mostly unflooded mine. The decreasing yearly load values can also be fitted to a decay function. Based on the estimated yearly load summaries, the rate of change for TDS, sulfate and acidity were estimated as $6.43 \times 10^{-4}$, $6.98 \times 10^{-4}$ and $8.08 \times 10^{-4}$, respectively for the years 1995-2002. The load decay values are slightly greater than the chemical concentration constants.

Figure 4 also shows one of the shortcomings of using decay constants or other long term trend estimators. In early 2003, the internal flowpaths of this mine-pool were apparently obstructed. Outflow decreased significantly and hydraulic head, measured in several wells, rapidly increased. The head pressure eventually disrupted or broke the internal obstructions. A rapid major flushing event followed with large outflows of poor quality drainage. Once this unanticipated event had passed, annual loading again began

Figure 3 Total Acidity Decay Estimated as One and Two Phase Functions for Flooded and Unflooded Mine-pools.

Figure 4. Annual Chemical Flux From a Mostly Unflooded Mine-pool.
to decline following an exponential decay.

The decay constant itself is simply a lumped or “black box” variable that does not indicate whether chemical or physical processes control the flushing of mine-pools. An analysis of simple geochemical and flushing models by Perry (2009) indicates that a slow flushing sequence best describes the removal of chemical constituents from mine-pools. Ground water flow rate and flushing efficiency seem to be the major controls on the magnitude of the decay constant. The fit of the loading data to a decay function in Figure 4 are consistent with the concept of flow rate control on mine-pool flushing.

The application of decay constants to mine-pool chemical concentrations has two major 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. Physical weathering effects on aquifer properties after underground mine closure is not well documented. Data on surface mine spoil from Hawkins (2004) shows that hydraulic conductivity of surface mine-spoil more than 2.5 years old was less than that for newly reclaimed sites. Hawkins 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 flushing rate, and hence reduce chemical concentration decay rates. The assumption of constant hydrogeologic conditions over a prolonged period may not be completely valid.

Table 3 shows median water quality conditions at mine 5 under two different pumping rates. Alkalinity decreased about 23% from 230 to 170 mg/L under higher pumping rates, and concentrations of iron, manganese and sulfate also increased about 50 and 68% respectively. Pumping rate effects on water quality show that if stress on this mine-pool is increased, water is delivered from storage areas with more chemical weathering products, and/or areas that have undergone less flushing and leaching. These may be zones with slow or limited ground water circulation within the mine-pool. Aljoe and Hawkins (1991) have suggested that “short circuiting” and preferential flow-paths probably exist in mine-pools.

### Table 3

<table>
<thead>
<tr>
<th>Discharge (gpm)</th>
<th>pH</th>
<th>Alkalinity</th>
<th>Iron</th>
<th>Sulfate</th>
<th>Manganese</th>
<th>Aluminum</th>
</tr>
</thead>
<tbody>
<tr>
<td>3250</td>
<td>6.7</td>
<td>230</td>
<td>32.6</td>
<td>298.6</td>
<td>0.60</td>
<td>0.5</td>
</tr>
<tr>
<td>6500</td>
<td>6.5</td>
<td>169.3</td>
<td>47.7</td>
<td>401.5</td>
<td>1.00</td>
<td>6.5</td>
</tr>
</tbody>
</table>

(1) pH in standard units, Alkalinity in mg/L CaCO₃ Eq, all others in mg/L. Values are median data.
(2) 17 samples collected during 3250 gpm discharge rate, 24 samples during 6500 gpm discharge rate.

The second assumption, of constant geochemical conditions may not hold over long time frames or in different flooding phases in mine-pools. As the mine-pool becomes increasingly dilute, concentrations of Fe and other elements could be controlled by mineral solubility, chemical kinetics (rates of reaction) and perhaps influenced by changes in redox conditions. Pools in Mines 3 and 5 were initially acidic (pH less than 4), but gradually evolved to circumneutral (pH about 6.5) conditions after flooding and initial
flushing. In mine 3, dissolved aluminum was present in concentrations of 20 to 30 mg/L for several years of initial flooding and low pH conditions. As pH increased above 6.0, dissolved aluminum concentration rapidly declined to less than 1 mg/L. The change is attributable to pH control of aluminum solubility.

The decay equation (1) was solved for time t, to reach specific target chemical concentrations for sulfate 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 sulfate 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. Excluding total acidity, most parameter decay estimates are between 20 and 70 years to achieve target concentrations and are discussed further by Perry (2009).

This set of estimated decay times 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 several decades to achieve acceptable chemistry.

Estimated and actual long term water quality data are summarized for mines one and five; an acidic mostly unflooded and a net alkaline flooded mine, respectively. At mine one, drainage from an adjacent abandoned underground mine in the same coalbed and closed for about fifty years, provided similar geologic and hydrologic conditions for comparison. Samples of the mine five discharge were collected representing conditions about 35 years after closure. The estimated and actual concentrations are shown in table 5. The decay constants provided reasonable estimates of chemical conditions that might be expected as these mine-pools undergo continued flushing. Sulfate concentration was over-estimated compared to measured values for both mines. Soluble iron persists in the acid mine-pool even though the decay trend suggests it should have largely disappeared. The decay constant has no explicit provision for including continued chemical weathering effects at low metals concentrations. It is therefore uncertain if chemical concentrations continue to slowly decrease in aged mine-pools or whether they will maintain low concentrations indefinitely.

<table>
<thead>
<tr>
<th>Mine</th>
<th>Acidity Estimated mg/L</th>
<th>Acidity Actual mg/L</th>
<th>Iron Estimated mg/L</th>
<th>Iron Actual mg/L</th>
<th>Sulfate Estimated mg/L</th>
<th>Sulfate Actual mg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mine 1 (acid, unflooded)</td>
<td>25 (50 years)</td>
<td>31 (50 years)</td>
<td>&lt;0.1 (50 years)</td>
<td>6.6 (50 years)</td>
<td>399 (50 years)</td>
<td>235 (50 years)</td>
</tr>
<tr>
<td>Mine 5 (net alkaline, flooded)</td>
<td>112 (35 years)</td>
<td>69 (35 years)</td>
<td>53 (35 years)</td>
<td>43 (35 years)</td>
<td>693 (35 years)</td>
<td>266 (35 years)</td>
</tr>
</tbody>
</table>

The uncertainties of decay behavior at long time frames and limited ability to estimate initial water quality before mine closure need to be considered when using trend estimators like the decay constant.

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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 a function of time. The parameters included total acidity, Fe, Al, sulfate 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, sulfate and TDS. Computed decay constants are with few exceptions, are on the order of \(10^{-4}/d\).

- Chemical decay can be divided into initial flushing and long term leaching. The early phase includes the flushing of accumulated salts and acid weathering products including stored acidity. Concentrations decline most rapidly during the early flushing phase. The long term phase includes the continued weathering and flushing of pyrite and other minerals.

- 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 seems to have the longest decay period in acid mines. The range of statistical uncertainty can span one to two decades for these long term estimates to reach target water quality conditions.

- 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. Analysis based on slow flushing or rapid flushing of a mine-pool suggests 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.

- A constraint on estimating mine water composition with decay functions is the ability to predict starting composition of the mine water at closure, or Co. The overall ability to estimate concentrations of specific parameters of Acidity, Fe, Al, sulfate and TDS in mine-pools before they flood is not well developed. We often rely on experience of analogues of nearby mines believed to have similar conditions.

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.
**Literature Cited**


