LONG-TERM WATER QUALITY TRENDS IN A PARTLY FLOODED UNDERGROUND COAL MINE

Eric F. Perry and Henry W. Rauch

Abstract. Water quality trends for an 8 year period were analyzed for two acidic springs draining from a partially flooded underground coal mine, and the composite mine-pool outflow of 10 discharges. Time series analysis was used to separate long-term data trends from short-term noise. Short-term variation usually constituted less than 30 percent of the trend concentration. Exponential functions were fitted to the trend data, and time estimates (t50C) for concentration to decline 50% were generated for Total Acidity, Fe, Al, SO4, Co, Ni, and Zn concentrations. Iron decline is similar at two springs with an estimated t50C of 60 months. Sulfate t50C is about 60 to 70 months at one spring and for the aggregate mine-pool. Cobalt, Ni and Zn declines are more rapid, with estimated t50C of about 30 to 50 months. Aluminum decline is 2 to 3 times slower than rates for other parameters, and mine-waters are near apparent equilibrium for the mineral jurbanite, Al(SO4)OH*5H2O. Constituent fluxes are controlled mostly by flow, and decline with time. Estimated time (t50F) for flux to decline 50% for the composite mine-pool outflow is about 85 months for Fe, 80 months for SO4 and 105 months for acid flux. Fluxes are 1.5 to 3 times greater in spring than fall, and reflect seasonal distribution of precipitation and recharge to the mine. Most of the improvement in mine-pool discharge results from declining pollutant concentrations. These trends suggest a slow decline in pyrite oxidation, with significant water quality improvement occurring on the order of years to decades.

Additional Key Words: acidity, flux, jurbanite.

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**Introduction**

Underground coal mining in Appalachia sometimes results in post-mining water pollution. Oxidation of iron disulfide minerals like pyrite generates strong acidity, low pH, elevated concentrations of metals and sulfate, and dissolution of carbonate and silicate minerals (Nordstrom, 1982; Rose and Cravotta, 1998). The longevity of pollutional discharges from abandoned underground mine works is a function of hydrogeologic setting, and geochemistry of the residual coal and associated rocks. This paper addresses time-dependent decline behavior, and mineralogical solubility controls on water composition from a partially flooded, closed mine that is located above the local base level drainage (“above-drainage mine”). Concentrations of Al, Fe, SO$_4$, and trace elements Ni, Co, Zn are declining through time, and respond to variations in flow, seasonality and reclamation activities. The time-dependent decline of dissolved constituents may represent depletion of stored acid products including metal sulfate salts, decreased availability of sulfide minerals, in situ neutralization, or less efficient leaching. Concentrations of some elements, including Al and SO$_4$, may be controlled by precipitation/dissolution solubility reactions of specific minerals.

**Geologic Setting**

The Omega mine is located about 10 km south of Morgantown, West Virginia in the Upper Freeport coal bed. This coal is stratigraphically located at the top of the Allegheny Group (Hennen and Reger, 1913). Coal thickness is commonly about 1.2 m, with a shale parting. The Bolivar fireclay, a hard siliceous mudrock, immediately underlies the coal bed. At this mine, the Uffington shale overlies the coal bed and is commonly less than 0.6 m thick. The Mahoning and Buffalo sandstones comprise most of the overburden above the Uffington shale. These rocks may reach a combined thickness exceeding 30 m, and where exposed at the mine faceup, they display prominent vertical fractures. Maximum overburden thickness at the Omega mine is about 52 m.

The West Virginia Geological and Economic Survey (2002) reports an average total sulfur content of about 2.5% and average pyritic sulfur content of about 1.7% for the Upper Freeport coal bed. Two core samples of Upper Freeport coal retrieved from the Omega mine complex contained over 5 and 12% total sulfur, respectively (EPRI, 2001).
The Omega mine is contained within a broad ridgetop on the western flank of the Chestnut Ridge anticline, and strata dip about 11% to the northwest. After closure, the mine partially flooded, and the general ground water flow pattern within the mine works is inferred to be in the direction of dip.

Site History

Coal was extracted by room and pillar methods from the Upper Freeport coal bed in about 69.8 ha of mine works until mine closure in 1989. Recovery ranged from 50% in first mined areas, to over 70% in areas of second mining. Average mining height was about 1.3 m. In the early 1990’s, acid drainage began seeping from several locations along the coal cropline (Fig. 1).

Mine drainage was collected and treated after several lateral boreholes were drilled into the northern mine works to divert mine-water away from a section adjoining a stream with a public water supply. Treatment sludge was initially injected into the mine works for disposal. The West Virginia Department of Environmental Protection (WVDEP) assumed control of the site in the mid 1990’s and currently treats the drainage. WVDEP discontinued sludge injection and currently disposes of the material offsite. WVDEP also installed a series of pipelines and manholes to more easily and securely collect, sample, measure, and convey mine-water to the treatment facility. In some instances, several adjacent seeps were combined into a single monitoring point. In 1998, a cooperative state, federal and privately funded grouting project was initiated to reduce or abate acidic discharges in the “North Lobe” (Fig. 1) of the mine (Gray et al, 1998; EPRI, 2001). This area comprises about 10.5 Ha, or 15% of the mined area, but was estimated to be discharging about 55% of the acid load (EPRI, 2001). About 61,000 m$^3$ of grout mix containing fluidized-bed combustion ash, flyash and cement were injected in the North Lobe. Subsequent drilling and borehole camera observations confirmed that, in general, the grout mixture provided near complete filling of mine voids. Water quality remained poor after grouting; however, flow, and consequently acid load decreased (EPRI, 2001).
The US Department of Energy (USDOE) began monitoring water quality and flow from the principal mine discharges in 1993 on a monthly basis and continued until 1999. Data were collected for pH, Total Acidity, Fe(II), Fe(III), Al, Mn, SO\(_4\), Ca, Mg, Na, K, Cl, NH\(_3\), As, Ba, Be, Cd, Co, Cr, Cu, Ni, Pb, Sb, Se, Zn, and Br. The WVDEP also began sampling discharges in 1996 at monthly intervals, and in 1997, initiated daily flow and on site precipitation measurements. WVDEP monitoring includes pH, Total Acidity, Fe, Al, Mn, SO\(_4\), specific conductance, total dissolved solids (TDS), and Total Suspended Solids (TSS). These data sets were combined into a single chronological file providing more than 8 years of data. Water samples were collected under this study during low flow conditions in 2002 and 2003 for the same parameters as the USDOE data set, plus field measurements of pH, Eh, temperature and
specific conductance. WVDEP monitoring continues as part of that organization’s ongoing site management and reclamation work.

A charge balance calculation was performed on samples with all major cations and anions to assess data reliability. Total acidity was evaluated from the reported values, and acidity was also calculated based on metals concentration and pH using the following formula:

$$\text{Acidity Calc} = 50\times(3\times\text{Fe}/55.85 + 3\times\text{Al}/26.98 + 2\times\text{Mn}/54.94 + 1000\times10^{-\text{pH}}) \quad (1)$$

where metal concentrations are in mg/L, and calculated acidity is in mg/L CaCO₃ Equivalents (Eq.). The calculated acidity values were used in subsequent calculations and analyses.

All statistical analyses were performed using Statgraphics for Windows version 4.1. Mineral saturation indices were calculated using the geochemical code PHREEQC (Parkhurst and Appelo, 1999).

**Site Conditions**

The Omega mine is believed to contain 3 separate mine-pools based on limited water level data, examination of mine maps, structural considerations and field observations. The pools are located in the “North Lobe”, the central section of the mine, and the southwest portion of the mine (Fig. 1). The maximum extent of flooding is estimated to be about 23 ha for the 3 pools combined, or about 33% of the total mined area. Thus, at least two thirds of the mine works are not flooded, and are subjected to conditions favoring pyrite oxidation. Based on mine-pool discharge measurements and flooding extent, the equivalent of one to two mine-pool volumes per year are estimated to circulate through the mine works. It is believed that preferred flow paths exist in areas where voids remain open, and zones of minimal or slow ground water circulation may occur in collapsed areas. Leaching efficiency is likely to vary depending on localized conditions. Mine-pool discharges respond to precipitation events within a few days, suggesting rapid infiltration and flow through.

Water quality data from three monitoring points were selected for in-depth analysis. The Marshall and DEF discharges (Fig. 1) are two acid springs located at and near the down dip end of the mine complex in the North Lobe mine-pool. These discharges have a continuous flow.
history, and represent a significant portion of the flow and acid load leaving the mine. The Marshall discharge is believed to represent water quality conditions near the end of the flow path within the North Lobe mine-pool. It is a horizontal borehole drilled into the lower end of the mine-pool. The DEF discharge is at an intermediate location on the flow path. Water quality at different flow path locations could exhibit evolutionary changes in water chemistry, as mine-water flows from unflooded to flooded portions of the mine works. The Marshall monitoring point is located near the grout injection area, and could show effects of acidic mine-pool water interacting with the grout. The DEF discharge was thought to be located far enough upgradient to have no significant interaction with the grout. The third monitoring point, Treatment Inlet (Fig. 1), represents the combined pipe flow of all discharges, and is used to assess overall conditions.

**Results and Discussion**

Table 1 shows median water quality data for the years 1993 at the beginning of the monitoring record, 2001 after grouting was completed, and single sample events from August, 2002 and August, 2003 for the three monitoring points. Overall water quality was very poor, exhibiting classic characteristics of acid drainage. The Marshall discharge exhibited the highest concentrations of acidity, metals, sulfate and trace elements, while DEF and the Treatment Inlet have similar composition and concentrations. At each site, there was a decline in median pollutant concentrations between 1993 and 2001. During that 8 year period median acidity, Fe, Al and SO$_4$ declined to about half of their initial values. Trace element concentrations of Co, Ni and Zn exhibited some variation between 1993 and 2002/2003, but declined more rapidly. Sites DEF and the Treatment Inlet shows little change in pH, while a modest improvement occurs at the Marshall site. Calcium and Mg show behavior similar to Fe, Al and SO$_4$. Sodium concentration, however, increased from 1993 to 2002/2003. Exchange of Na for other adsorbed cations, or dissolution of Na bearing minerals such as albite (NaAlSi$_3$O$_8$) would increase solution Na. Albite is about 8 to 10 orders of magnitude undersaturated in these waters, and Dulong et al (2002) have shown that small amounts of albite can be present in these rocks.
Table 1 Summary Water Chemistry for Marshall, DEF and Treatment Inlet Monitoring Sites \(^{(1)}\)

<table>
<thead>
<tr>
<th>Site</th>
<th>Year (^{(2)})</th>
<th>Flow</th>
<th>pH</th>
<th>Acidity Calc.</th>
<th>TDS</th>
<th>Fe</th>
<th>Al</th>
<th>Mn</th>
<th>SO4</th>
<th>Ca</th>
<th>Mg</th>
<th>Na</th>
<th>Co</th>
<th>Ni</th>
<th>Zn</th>
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<tr>
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<td>63</td>
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<td>8398</td>
<td>8398</td>
<td>1613</td>
<td>275</td>
<td>6.5</td>
<td>5975</td>
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<td>2001</td>
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<td>4636</td>
<td>4536</td>
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<td>108</td>
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<td>4203</td>
<td>564</td>
<td>88.7</td>
<td>2.9</td>
<td>2462</td>
<td>298</td>
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<td>18</td>
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<td>0.98</td>
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<td>4.15</td>
<td>1976</td>
<td>3980</td>
<td>460</td>
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<td>2200</td>
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<td>NM(^{(3)})</td>
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<td>Treatment Inlet</td>
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<tr>
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<td>2.77</td>
<td>1377</td>
<td>3457</td>
<td>301</td>
<td>101</td>
<td>3.80</td>
<td>2004</td>
<td>247</td>
<td>77</td>
<td>15</td>
<td>0.66</td>
<td>1.45</td>
<td>4.54</td>
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<tr>
<td></td>
<td>2003</td>
<td>172</td>
<td>3.11</td>
<td>979</td>
<td>2357</td>
<td>191</td>
<td>83</td>
<td>2.5</td>
<td>1404</td>
<td>155</td>
<td>52</td>
<td>20</td>
<td>0.49</td>
<td>1.05</td>
<td>3.14</td>
</tr>
</tbody>
</table>

(1) Flow in L/min, pH in standard units, Acidity in mg/L CaCO3 Eq., all others in mg/L.


(3) NM = Not Measured
Since most of the mine is not flooded, conditions are favorable for the formation of sulfate and hydroxysulfate minerals that characteristically occur in acidic environments. Melanterite, copiapite, halotrichite, gypsum, schwertmannite, various jarosites, and others are commonly present in mine spoil and underground mine works (Nuhfer, 1967; Bigham and Nordstrom, 2000; Rose and Cravotta, 1998). The specific mineral assemblage depends on pH and Eh conditions, as well as activities of the constituent ions. Some minerals such as melanterite are moderately soluble, and could redissolve as the mine is recharged. Mine-water outflows likely represents a combination of leaching stored sulfate minerals, and continued weathering of pyrite.

**Time-Series Analysis**

Concentration versus time scatter plots showed month-to-month variation. However, an underlying long-term trend, and a shorter seasonal trend were also present. These trends were examined with time-series analyses, including moving average, and seasonal decomposition, which breaks the data into trend, seasonal and irregular components. Log or other data transforms and nonparametric tests (Helsel and Hirsch, 1992); locally weighted scatter plot smoothing (Cleveland and Devlin, 1988); and seasonal decomposition (Cleveland and Terpenning, 1982) are suggested methods for analyzing noisy time-series data for trends and seasonal features.

Examples of raw and trend data are shown in Fig. 2, 3 and 4 for Fe, Al and SO$_4$ concentration data at the Marshall monitoring point. The plots display similar behavior, and there was a period of declining concentration from 1993 to late 1998. Iron and SO$_4$ trends decrease more rapidly than Al. In 1999, there was a rapid concentration increase for all parameters, followed by resumption in decline. The spike in concentrations closely follows the grouting conducted in mid to late 1998 in the nearby “North Lobe” of the mine. Calcium and Mg concentrations, which had been decreasing, also increased after grouting. These data show a rapid and short-term flushing by grout injection that displaced acid weathering products already present in the mine works. This behavior suggests that leaching efficiency is low for most recharge conditions. Only extreme disturbance to the system, such as from grout injection, or very large recharge events displace major amounts of soluble weathering products. Increasing Ca and Mg likely were derived from dissolution of the ash and cement based grout.
Figure 2. Iron Concentration Trend, Marshall Monitoring Point.

Figure 3. Aluminum Concentration Trend, Marshall Monitoring Point.
Differences between the raw unadjusted concentration and trend data represent the irregular component of the data. It may result from short-term events such as rapid recharge events, and fluctuations in mine-pool elevation or flow path.

Fig. 5 is a plot of Co and Ni raw and trend data for the DEF discharge. Concentrations of both metals decreased until about 1998 (Fig. 5), when grout injection occurred; then concentrations began to increase. Based on the trend data, Ni was declining slightly faster than Co. It was initially believed that site DEF was located far enough upgradient from the mine grout zone, that its water chemistry would not be influenced by grout injection. However, behavior of these elements at site DEF suggests that its’ water chemistry was affected by grout injection.

Cobalt and Ni-to-SO$_4$ mole ratios (Fig. 6) had a slow decline until about 1997. Both Co (r=0.97) and Ni (r=0.95) are strongly correlated to SO$_4$ concentration. Cobalt and Ni are common trace inclusions in pyrite at concentrations of less than a few percent (Rimstidt and Vaughan, 2003). Under the strongly acidic conditions like those at site DEF (pH<3.0), adsorption studies generally indicate little attenuation of Ni and Co (Bruemmer et al, 1988, Larsen and Postma, 1997, Geihyeon et al, 2002). If in-situ adsorption attenuation is minimal, then declining Ni and Co to sulfate mole ratios probably reflect a decrease in pyrite oxidation. Increased scatter in the plots for 1997 and 1998 reflects disturbance from mine site modification and grouting.
Figure 5. Cobalt and Nickel Concentrations Trends for DEF Monitoring Point.

Figure 6. Cobalt and Nickel-to-Sulfate Molar Ratios, for DEF Monitoring Point.

**Estimating Rate of Concentration Decrease**

Exponential and other model functions were fitted to the pre-grouting trend data to estimate rates at which mine-water concentrations decline over time. Least squares regression was used to examine different models. Because mine grouting impacted water chemistry, no model fitting was done for data during and immediately after grouting. Examination of different models, and
their associated $R^2$ values and residual plots, showed that the following exponential function provided a reasonable estimation of concentration change with time:

$$C_t = C_0 \times \exp^{-kt} \quad (2)$$

or

$$\ln(C_t/C_0) = -kt \quad (3)$$

where $C_t$ is concentration at time $t$, $C_0$ is concentration at time zero, $k$ is a constant in time$^{-1}$ units and $t$ is elapsed time. The function is identical to that used to describe radioactive decay. The constant, $k$, is the slope of a plot of $\ln(C_t/C_0)$ versus $t$. Other regression models generally did not describe the trends as well as an exponential function. The period required for a 50% decline in concentration, designated $t_{50C}$ in this paper, was estimated from equation 3. Estimated $t_{50C}$ for pre-grouting data at the three monitoring points are summarized in Table 2. All Table 2 data are statistically significant at 0.05 alpha.

Time-to-half concentration ranges from about 5 to 8 years for Acidity, Fe, Ca (except at Marshall site), Mg, SO$_4$, and TDS. Cobalt, Ni and Zn declined more rapidly, with time to half concentration ranging from about 2.5 to 5 years. The time to half concentration estimates in Table 2 are in general agreement with direct comparisons between 1993 and 2001 summary data in Table 1.

<table>
<thead>
<tr>
<th>Monitoring Point</th>
<th>Acidity</th>
<th>Al</th>
<th>Ca</th>
<th>Co</th>
<th>Fe</th>
<th>Mg</th>
<th>Ni</th>
<th>SO$_4$</th>
<th>TDS</th>
<th>Zn</th>
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<tbody>
<tr>
<td>Marshall</td>
<td>79</td>
<td>212</td>
<td>117</td>
<td>49</td>
<td>61</td>
<td>60</td>
<td>54</td>
<td>96</td>
<td>93</td>
<td>45</td>
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<tr>
<td>DEF</td>
<td>78</td>
<td>134</td>
<td>69</td>
<td>34</td>
<td>62</td>
<td>54</td>
<td>32</td>
<td>57</td>
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<tr>
<td>Treatment Inlet</td>
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<td>51</td>
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<td>57</td>
<td>57</td>
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</tbody>
</table>

Demchak et al (in press) examined drainage quality from 44 above-drainage underground mines, including sites with the same stratigraphy as the Omega mine. Water quality from 1968 compared to drainage in 1999-2000 showed that acidity had decreased an average of 56% in mine drainage from the Upper Freeport coal bed. Overall, iron concentrations declined about 80
%, and sulfate declined about 50 to 75 %. Average data (Demchak et al, in press) seem to indicate a slower rate of concentration decline than data presented here for the Omega mine. However, their data show some variation among individual mines, and the rate of chemical change seems to be influenced by site specific factors.

Drainage from flooded underground coal mines in Great Britain shows about a 50 % reduction in Fe concentration for each mine-pool volume discharged (Glover, 1983), implying an exponential decay. Younger (1997) further characterized British mine-waters as consisting of two acidity sources; recently generated from ongoing sulfide oxidation, and stored acidity. Younger estimates that stored acidity is removed in the first flush of the mine-pool, usually within 40 years, while continued oxidation is projected to last for hundreds of years. Most of the long-term discharge records described by Younger (1997) exhibit an exponential decay for Fe and become asymptotic after 10 to 20 years. Long-term Fe concentrations range from 1 to 30 mg/L.

Pollutant concentration behavior in Omega mine drainage is similar to the general decay model described for British mines. Omega mine drainage has not progressed far enough through its life cycle to determine whether concentrations become asymptotic in the long term.

Mineralogical Controls

Aluminum has the longest estimated $t_{50C}$ of the parameters in Table 2, ranging from about 12 to 18 years. The slow decline for Al is a function of mine-pool pH, which is usually between 2.6 and 3.5. Dissolution of clay minerals, such as kaolinite, and Al hydroxide minerals is favored under these conditions as reaction 4 shows:

$$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 + 6 \text{H}^+ \rightarrow 2\text{Al}^{3+} + 2\text{H}_4\text{SiO}_4 + \text{H}_2\text{O}$$

(4)

So long as mine-pool pH remains below about 4.0, dissolution of clay minerals and Al hydroxides could occur; thus there is a large source for soluble Al; hence concentrations may to decline more slowly than other constituents.

Saturation indices for jurbanite, an Al-hydroxysulfate, are plotted in Fig. 7 for the Marshall and DEF sites. Both waters show apparent near equilibrium conditions, where DEF (intermediate flow path location) is slightly undersaturated, and Marshall (end of flow path) is
slightly oversaturated. Waters in the DEF discharge approach, but do not exceed, the equilibrium saturation index of 0, suggesting that jurbanite poses an upper limit to Al concentration at site DEF.

Jurbanite is stable in acidic waters (Nordstrom, 1982b) and can persist in the pH range of zero up to 3 to 5 in sulfate rich waters. Jurbanite could form from kaolinite alteration as reaction 5 shows:

\[
\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 + 2 \text{SO}_4^{2-} + 6 \text{H}_2\text{O} + 4 \text{H}^+ \rightarrow 2 \text{Al(SO}_4\text{(OH)} *5 \text{H}_2\text{O} + 2 \text{H}_4\text{SiO}_4 \quad (5)
\]

Waters at the Marshall discharge are slightly oversaturated for jurbanite. Slight over saturation suggests that within the mine either a slightly more soluble poorly crystalline phase of jurbanite is forming, the jurbanite reaction rate is slow, the “dissolved” fraction on which the saturation index calculations were based, contains colloidal Al, or the jurbanite is not actually forming. Our current knowledge of the mine precludes identification of which scenario is allowing slight jurbanite super saturation at the Marshall discharge. The mine works are not accessible for sediment sampling for mineralogical analysis to confirm or deny the presence of

![Figure 7. Jurbanite Saturation Indices at Marshall and DEF Sites.](image)
jurbanite. However, its characteristic occurrence is in acid soils and mine-waters (Nordstrom, 1982b).

Superimposed on the overall trend in Fig. 7 is a cyclic, seasonal variation in saturation index. Indices are largest in periods corresponding to low flow conditions, and smallest during high-flow periods. The inverse relation between saturation index and flow suggests mine-waters are diluted during seasonal recharge and more concentrated for drier periods of the year. Mineral saturation and precipitation should be favored during dry periods.

Goethite (FeOOH) saturation indices for the Marshall and DEF sites, computed from measured Eh in 2002 and 2003, show the mine-waters are slightly oversaturated (indices about +0.05 to +0.5). Iron could be attenuated within the mine-pool by precipitation as an oxyhydroxide, either amorphous, or crystalline form such as goethite. The metastable hydroxysulfates, schwertmannite and jarosite, if present initially may also transform to goethite with time (Bigham and Nordstrom, 2000).

In acid oxidizing sulfate waters, formation of the Fe bearing minerals Fe(OH)$_3$(am); schwertmannite, Fe$_3$O$_6$(OH)$_6$SO$_4$$^*$nH$_2$O; H-jarosite HFe$_3$(SO$_4$)$_2$(OH)$_6$; Na-jarosite NaFe$_3$(SO$_4$)$_2$(OH)$_6$; and K-jarosite, KFe$_3$(SO$_4$)$_2$(OH)$_6$ is feasible. Mine-waters are 1 to 4 orders of magnitude undersaturated for Fe(OH)$_3$(am), and 2 or more orders of magnitude oversaturated for schwertmannite. These minerals are likely not present in the Omega mine. K-jaorosite is commonly 1-2 orders of magnitude oversaturated while H-jarosite and Na-jaorosite are slightly undersaturated. K-jaorosite is reported to sometimes be super saturated without actually forming, and Na-jaorosite is relatively rare (Bigham and Nordstrom, 2000). Indices decline with time suggesting that the system is not at equilibrium with them and they are likely not present.

The cycling of iron in the Omega mine is not clearly associated with any one mineral, with the possible exception of goethite.

Fig. 8 shows gypsum saturation indices for the Marshall and DEF sites. Both sites are slightly undersaturated for gypsum and are becoming more so with time. Calcium and SO$_4$ solubility are not currently controlled by gypsum. However, in 1993-1994 at the beginning of monitoring, the Marshall discharge was near equilibrium for gypsum. No data are available prior to 1993 to estimate whether gypsum saturation was actually achieved shortly after mine closure. The gypsum plot (Fig. 8) shows a similar seasonal dilution/concentration effect as that for the jurbanite plot (Fig. 7).
Flux (Loading)
Trends for flux data (chemical concentration x flow) versus time were poorly described by exponential or other simple mathematical functions that did not account for variable flow rates. Fig. 9 is a scatter plot of sulfate flux (load) and flow rate from the Treatment Inlet for the period 1993-2002. There is a pronounced seasonal effect in flow and flux, with both constituents reaching maximums during the spring of the year and minimums in the fall. Sulfate flux is strongly correlated to flow ($r=0.78$), as are Acidity, Fe, Al, and TDS loadings ($r=0.77$ to 0.82).
An extensive study of surface mine discharges also found flow to be the dominant component of flux (Hawkins, 1994).

Within the 9 year record there is an observable trend of long-term decline in sulfate flux. Fig. 9 also includes the trace of the best fit regression line from a linear model. The regression slope indicates the long term decline in flux, but clearly does not account for the seasonal cycles. Simple models cannot estimate short term flux because of variable flow rates. In turn, discharge quantity is driven by precipitation and recharge events, and changes in mine hydrology.

Table 3 summarizes estimates of time to half flux generated from best fit regression models for the Treatment Inlet. These values represent the long-term decline, and do not model the seasonal cyclical features seen in Fig. 9. Comparing the Treatment Inlet time to half flux in Table 3, to time to half concentration (Table 2), shows that flux is declining more slowly than concentration. Thus, most of the improvement in mine-pool chemical discharge is attributable to decreasing concentrations instead of changes in flow.

Table 3. Time to Half Flux Estimates, \( t_{50F} \), Regression Models, Treatment Inlet. \(^{(1)}\)

<table>
<thead>
<tr>
<th>Method</th>
<th>Acid Flux</th>
<th>Al Flux</th>
<th>Fe Flux</th>
<th>SO4 Flux</th>
<th>Co Flux</th>
<th>Ni Flux</th>
</tr>
</thead>
<tbody>
<tr>
<td>Regression</td>
<td>106</td>
<td>169</td>
<td>85</td>
<td>77</td>
<td>64</td>
<td>56</td>
</tr>
</tbody>
</table>

(1)Time in months. “Best fit” flux models are square root of time functions, except Co and Ni which show linear functions with time.

**Seasonality**

Chemical concentration and flux both exhibit seasonal variation. Median values for each month were divided into two seasons, corresponding to periods of minimum and maximum trend values. The “spring season” for high flux data is February to July, and the “Fall Season” is August to January. Selected data from the Treatment Inlet site are shown in Fig. 10, and Tables 4 and 5. Median flux and flow for the spring season is about 2 to 3 times greater than that for the fall, and peak fluxes occur around March to April (Fig. 10). About 75% of the total yearly flux is discharged during the spring season. Flux is at a minimum in October to December. All median flux values and flow values for spring and fall seasons are significantly different at alpha probability =0.01, using the nonparametric Mann-Whitney test.
There is a weak inverse relationship, or slight dilution effect, between flow and concentration by season (Table 5). Median concentrations are greater in the low-flow fall season, while lower concentrations occur in the spring season. The differences are not statistically significant for Fe and Al, however.

Table 5. Median Seasonal Concentrations for Treatment Inlet^{(1)}

<table>
<thead>
<tr>
<th>Season</th>
<th>Acidity</th>
<th>Al</th>
<th>Fe</th>
<th>SO(_4)</th>
<th>Co</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spring</td>
<td>1875</td>
<td>105</td>
<td>465</td>
<td>2454</td>
<td>0.78</td>
<td>1.64</td>
</tr>
<tr>
<td>Fall</td>
<td>2042</td>
<td>114</td>
<td>501</td>
<td>2870</td>
<td>0.95</td>
<td>2.04</td>
</tr>
<tr>
<td>Significant Difference</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
</tr>
</tbody>
</table>

(1) Concentrations in mg/L. Significant differences at p=0.01.

Summary and Conclusions

The Omega mine has been discharging acidic drainage containing elevated amounts of acidity, Fe, Al, SO\(_4\) and trace elements for about 14 years. Pollutant concentrations declined over an 8 year period, but there was little change in pH. The continuing concentration decline
likely reflects a combination of depletion of oxidizable pyrite, continued leaching of stored acidity, in-situ neutralization, and inactivation of some pyrite surfaces by sedimentation, precipitation or other means. An exponential function described the long term concentration trends, but there are both seasonal (cyclic) and short-term irregular departures. Short-term variation represents response to transient features such as rapid recharge events. Concentrations of Fe, SO₄, and acidity were estimated to decline by half over about 5 to 8 years for individual mine drainage springs and the composite mine-pool.

Aluminum concentrations declined 2 to 3 times slower, and mine-waters are near apparent equilibrium for the Al-hydroxysulfate mineral jurbanite. The very acid conditions which remain in the mine-pool (pH ~2.5 to 3.5) favor the dissolution of aluminosilicates and Al hydroxides. As long as pH remains below about 4.0, the reservoir of potentially mobilofe Al is large.

Metals and sulfate concentration declines estimated from exponential functions compared reasonably well to actual data. Concentrations estimates were usually within 15 % of actual values and most were within 30%.

Concentrations of trace elements Co, Ni, and Zn were estimated to decline by half in about 3 to 5 years. These elements occur as trace inclusions in pyrite and may be a surrogate for recently generated acidity.

Iron cycling in the Omega mine is complex. No Fe bearing hydroxysulfate mineral was identified as controlling soluble Fe. Apparent equilibrium is indicated for goethite, based on a few measurements, and this oxyhydroxide may control soluble Fe in the long term. The presence of specific minerals cannot be confirmed because the mine works are not accessible for sediment sampling.

An apparent long-term trend for near equilibrium for jurbanite, and possibly goethite, suggests that the mine-pool chemistry is partially controlled by local equilibrium conditions. The mine-pool is however, periodically stressed by seasonal and single event recharge pulses that usually result in dilution.

Soluble acid weathering products are not uniformly leached from the mine works, due to preferential flow paths and zones of limited or slow ground water circulation. Zones with little flushing accumulate acid products, which may only be mobilized when the system is subjected to large stress. Grout injection completely filled one section of the mine works, displaced stored acidity, and caused a short-lived increase in acidity and metals concentrations. Leachate
mobilization from the mine works is ultimately transport controlled. Aggressive reclamation strategies such as grout injection can increase pollutant discharge in the short term.

Flux or load is controlled mostly by flow, and there is a distinct seasonality to the mine-pool discharge. About 75% of the total yearly flux is discharged in the spring season. The most rapid abatement method for pollutant flux for the Omega mine-pool would be to reduce mine recharge, and grouting a portion of the mine did ultimately reduce flux from that section. However, grouting an entire underground mine complex post-closure can be technologically difficult or cost prohibitive.

It is uncertain if the Omega mine-pool will continue to follow the decline shown in its’ first 10 years of activity, or if the trend will become asymptotic in the future. Most of the mine-water chemistry improvement results from declining concentrations. Current behavior shows that mine-pool drainage quality improvement occurs on the order of years to decades.

Acknowledgements

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