

WATER QUALITY EVOLUTION IN FLOODED AND UNFLOODED COAL MINE-POOLS¹

Eric F. Perry² and Henry W. Rauch

Abstract: Water quality and flow data from a pumped, mostly flooded, and a free draining, mostly unflooded coal mine-pools were analyzed for temporal trends. Both mine-pools began discharging acidic drainage, with pH < 3, iron (Fe) concentrations of 200 to > 900 mg/L, and sulfate (SO₄⁻²) values of about 2,500 to 4,000 mg/L, less than one year after closure. Each site had an initial flushing period, lasting about 2 years in the unflooded mine, and 8 years in the flooded mine. The flushing included a rapid decline in concentrations, and large variations in water chemistry. Chemical concentrations declined more rapidly in the flooded mine-pool, to about 20 to 30% of the initial values for Fe and SO₄⁻². In contrast, after initial flushing, water from the unflooded mine had Fe, SO₄⁻², and aluminum (Al) concentrations of 50 to 75% of original discharge quality.

Each mine-pool is now in a maturation process with continuing declines in chemical concentrations, less variation in composition, and increasing metals attenuation in the mine-pool aquifer. The flooded mine-pool turned net alkaline after pumping about 21 pool volumes. After 35 years, Fe and SO₄ are 5 to 10% of initial composition. Equilibrium calculations show that Fe may be controlled by poorly crystalline oxyhydroxides. Mine-pool oxidation reduction potential (ORP) is < +250 mv. The free draining mine still has pH < 3 after discharging about 25 pool volumes. Iron and SO₄ concentrations are still 25 to 40% of original composition and Al is unchanged since the initial flush. Equilibrium calculations show that Fe may be controlled by oxyhydroxides or K-jarosite. Mine-pool ORP is +500 to 700 mv. Al is near apparent equilibrium with jurbanite. Declining Fe to SO₄⁻² ratios in both mine-pools indicate that 60 to 80% of Fe dissolved from pyrite is being attenuated in-situ, probably by precipitation, exchange or adsorption.

Flooding has suppressed, but not eliminated pyrite oxidation in one mine-pool. The free draining mine water chemistry is still controlled by sulfide oxidation. Both mine-pools may contain dissolved Fe from continuing mineral dissolution in the mine-pool aquifer indefinitely.

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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). Long term chemical composition of mine-pools is of interest to government, industry, and environmental organizations who estimate cost and duration of treatment, and select optimal mine closure techniques. The rate of improvement or pollution abatement and the steady-state composition of mature mine-pools are not readily predicted, although the controlling hydrologic and geochemical processes are recognized. In general, coal mine-pools discharge the poorest water quality in the initial flush, followed by a gradual improvement in composition. 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 (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.

Flooding of pyritic mine wastes and tailings has been advocated as an effective technique for reducing or eliminating acid drainage in coal and metal mines for at least 75 years (Leitch et al, 1930; Temple and Koehler, 1954; Fraser and Robertson, 1994; Tremblay, 2000). Flooding should limit the availability of O₂ and Fe⁺³ iron, the two principal oxidants of pyrite. Success of this technique is dependent on the exclusion of oxygen, or at least maintenance of O₂ levels below a threshold concentration. Hammack and Watzlaf (1990) suggested that pyrite oxidation should be limited by maintaining O₂ levels below 1%. They concluded that inundation below a permanent water table was the best method to suppress pyrite oxidation. Williamson and Rimstidt (1994) summarized data from several studies and their own experiments and formulated three rate laws to describe pyrite oxidation. In the pH range of 2 to 10, pyrite reaction is described as a function of dissolved oxygen and pH. Their rate equation is:

$$R = 10^{-8.19} (m_{D,O}^{0.5} / m_{H^+}^{0.11}) \quad (1)$$

Equation 1 shows that pyrite oxidation is most influenced by dissolved oxygen and secondarily by pH. Williamson and Rimstidt also formulated two rate laws in the pH range of 0.5 to 3.0 that include Fe⁺² iron and Fe⁺³ iron and pH, based on the presence or absence of dissolved oxygen. They also found good correlation between Eh and the rate of aqueous oxidation of pyrite with dissolved oxygen and Fe⁺²/Fe⁺³ ratio.

The purpose of this study is to compare the effects of flooding and oxygen control on long term water quality data from two closed abandoned underground coal mines in Appalachia, one mine mostly flooded, the second mostly unflooded. Both mine-pools initially discharged acidic water of pH 3 or less and high concentrations of Fe, Al and other metals. One mine-pool, Lancashire 15, is about 80% flooded and turned from acid to net alkaline after pumping about 21 pool volumes. Metals and SO₄⁻² concentrations declined about 80% from initial conditions. The second mine-pool, T&T 2, is only about 20% flooded, and has a gravity discharge at the down-dip end mine entries. After discharging about 25 pool volumes, the mine-pool is still about pH 3 and shows less improvement in overall water quality than the Lancashire 15 mine-pool.

Geologic and Hydrogeologic Setting

Lancashire 15 mine-pool(mostly flooded)

The Lancashire 15 (L-15) mine-pool is located in Cambria County, Pennsylvania and is contained within an enclosed basin defined by the Barnesboro syncline, and Nolo anticline on the west and Laurel Hill anticline to the east (Fig. 1). The axes of the syncline and anticlines are oriented about N 30° East, and form an elongated basin about 24 km long. This geologic structure influences extent of flooding and the flow direction of water in the mine-pool. The L-15 mine-pool is controlled by pumping from the Duman plant at the low point of the basin (Fig. 1). The L-15 mine-pool is in the Lower Kittanning coalbed, and is partially overlain by a second set of flooded mine-works in the Lower Freeport coalbed. The vertical interval between coals is around 50 m. The two mine-pools are hydraulically connected as shown by pumping and other data (Hawkins et al., 2005). Mine-works located near the crest of the two anticlines are not fully flooded, and water in these areas flows down-dip to recharge the main pool. The L-15 mine-pool is also recharged by leakage through barrier pillars from adjoining flooded or partially flooded mines. About 30% of the flow at Duman is estimated to be barrier seepage from another mine-pool located to the east (Hawkins et al., 2005). Some ground water also enters the mine-pool through unmined strata. The total mine-pool covers about 5937 Ha, of which an estimated 4690 Ha, or 79%, are flooded (Hawkins et al., 2005). The mine-pool holds about 6.4 billion liters of ground water. Ground water flow paths within the flooded part of the mine-pool are as much as 9 km long. Overburden thickness is 100 to 150 meters over most of the mine-works. The mine has been closed and flooded for 35 years.

The rocks are Pennsylvanian age, Allegheny group, consisting in descending order of the Freeport, Kittanning and Clarion formations. Rock strata in this area are characterized by sandstones interbedded with shales, mineable coal beds and thin but persistent limestones near the Lower Freeport coalbed. Rocks in the Kittanning formation generally lack carbonates. The Lower Kittanning coal seam averages about 1 m thick, and the Lower Freeport coal is about 1.4 m. Area geology is described in more detail by McElroy (1998).

T&T Mine 2(mostly unflooded)

The T&T Mine 2 is located in Preston County, West Virginia and is part of a complex of three adjacent underground mines covering a total of about 600 Ha (Fig 2). All three mines are located above the local base level drainage and dip to the southeast at about 8% toward the axis of the nearby Kingwood syncline. Barrier pillars of varying thickness separate the three mines, and the barrier is known to be breached in at least one location. Leakage from the adjacent Ruthbelle and T&T 3 mines contributes part of the drainage that discharges from the T&T 2 mine (Fig 2).

This mine, T&T 2, is at the lowest elevation of the three workings. The entries were developed along strike and mining proceeded up-dip from that location. This design allowed gravity drainage of the mine-works during operation. After closure, about 20% of the lower mine-works flooded to the elevation of the entries. The mine-pool contains about 300 million liters of ground water and discharges at the entries as shown in Fig. 2. The mine has been closed and partly flooded for 10 years. In an attempt to treat the acid water in-situ, about 72,000 metric tons of limestone by-product(70 % CaCO₃ Eq.) were injected into the mine between late 1999 to 2001. The Upper Freeport coal, located at the top of the Allegheny Group and stratigraphically above the Lower Kittanning coalbed, was mined at the T&T 2 mine using room and pillar

recovery. The coal bed is about 1.3 meters thick, and is overlain by several massive sandstones up to 20 meters thick, interbedded with thinner shale units. The section contains few carbonates and maximum overburden thickness is about 80 meters. Subsidence cracks have been found in lands overlying the mine complex.

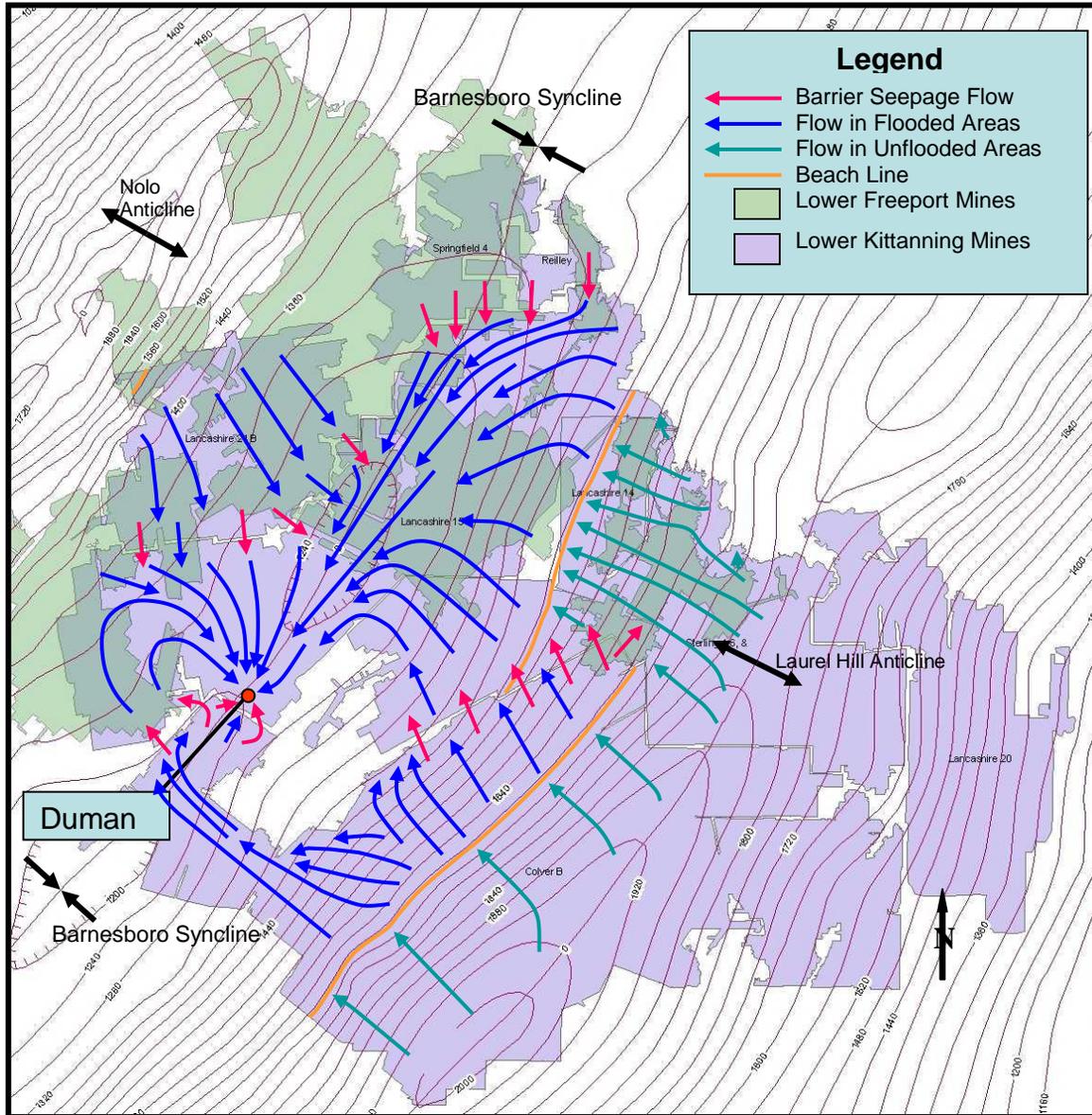


Figure 1. Hydrogeologic Setting of the Lancashire 15 Mine-pool.

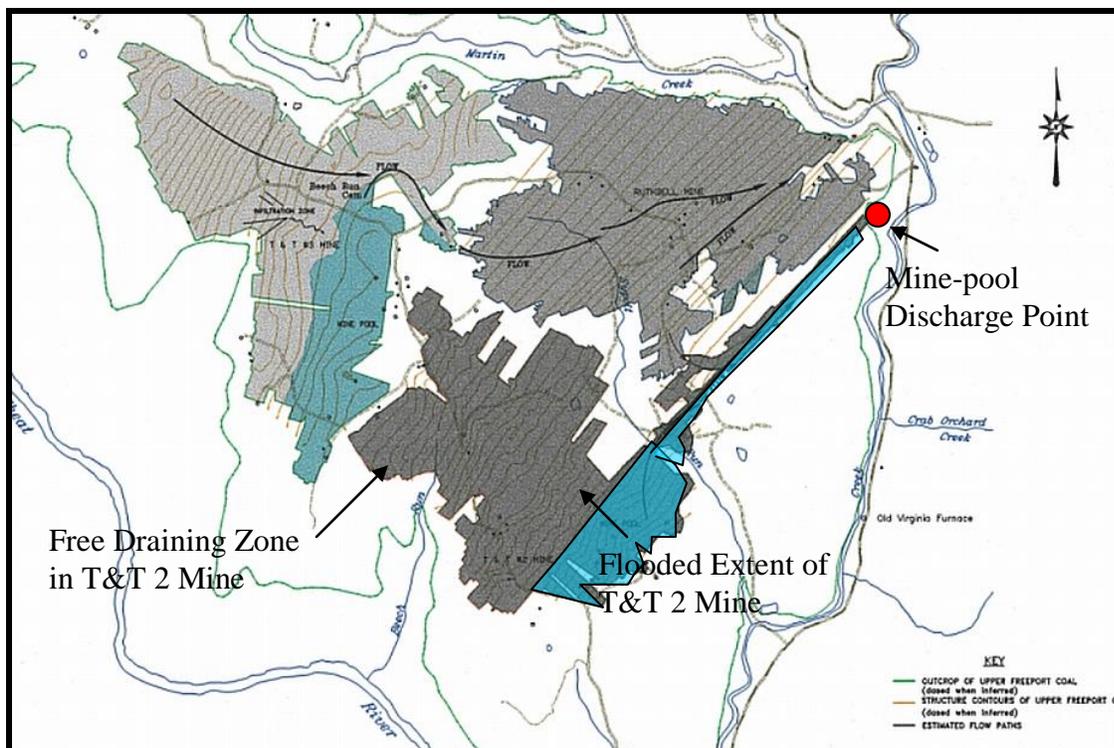


Figure 2. Hydrogeologic Setting of the T&T 2 Mine-pool

Methodology

Mine water quality data were compiled for the two sites from offices of the Pennsylvania Dept of Environmental Protection (PADEP), West Virginia Dept of Environmental Protection (WVDEP) and supplemented with samples collected by the first author. Pumping, discharge, mine-pool head measurements and weather data were also compiled. The water quality analyses vary in reported parameters, in particular for the Lancashire 15 mine-pool, and were run by different laboratories. Iron, pH and acidity are the most consistently reported parameters. Values for SO_4^{-2} , Mn, and Al were reported for some, but not all samples in the Lancashire 15 mine-pool, but are reported for most samples from T&T 2. Acidity was calculated from reported pH, Fe, Al and Mn concentration, counting all iron as Fe^{+2} , as suggested by Kirby and Cravotta, (2004), and Cravotta and Kirby, (2004). Calculated acidity was determined as:

$$\text{Acidity Calc} = 50*((\text{Fe} *2/55.85)+ (\text{Al}*3/27) + (\text{Mn}*2/54.94)+1000*(10^{-\text{pH}})) \quad (2)$$

The calculated acidity values were used in subsequent analysis.

To supplement the historical data, complete suite samples of the Lancashire 15 and T&T 2 raw water were collected at different seasons of the year. Water quality samples included field filtered, acid preserved, sub-samples for major cations (Ca, Mg, Na, K), metals (Fe, Mn, Al), trace elements(As, Ba, Be, Cd, Co, Cr, Cu, Ni, Pb, Sb, Se, Zn), raw unpreserved sub-samples for anions (SO_4^{-2} ,Cl) and general chemistry (pH, acidity, alkalinity, specific conductance, Total Dissolved Solids, and Total Suspended Solids). A few waters were also sampled and acid preserved for Fe^{+2} determination. Field measurements included pH, specific conductance,

temperature, oxidation reduction potential (ORP or Eh), and dissolved O₂. Geochemical calculations of mineral saturation indices were performed using PHREEQC (Parkhurst and Appelo, 1999) for waters with complete major ion analysis, temperature and Eh data.

A regression equation was developed from samples with complete major ion analysis and specific conductance measurements to estimate ionic strength on waters with fewer analyzed parameters. Sulfate typically comprised >95% of the anion charge. These features allowed us to determine an approximate charge balance on samples that did not include all major ions. For samples that did not have all major ion analyzed, ionic strength was estimated from the regression relation and approximate charge balance. These data were then used to estimate activity coefficients, and calculate selected mineral saturation indices. Statistical analyses were performed using Statgraphics for Windows, version 5.1.

Results and Discussion

The Lancashire and T&T 2 mines both produced acidic drainage immediately after closure, followed by a gradual decline in pollutant concentrations. Table 1 shows median water quality for the two discharges for the first few mine-pool volumes after closure and water quality after discharging about 25 pool volumes. The 25 volumes correspond to the maximum period of record for the T&T 2 mine. The Lancashire 15 mine-pool began to accumulate alkalinity almost immediately after closure and flooding in spite of high pollutant concentrations. Thus, within the first year of flooding, median pH was 5.1 and has since stabilized at about 6.5. Total acidity and Fe eventually declined in the Lancashire 15 mine-pool to less than 10% of original concentrations in the initial discharge. Sulfate declined more slowly to about 18% of original concentration. The declining trends have continued in more recent monitoring data for Lancashire 15. Metals and acidity are now about 5% of initial conditions, and SO₄⁻² about 10% (Perry et al, 2005).

Table 1. Median Water Quality for the Lancashire 15 and T&T 2 Mine-pools after Closure and After Discharging 25 Pool Volumes.

Site	pH (S.U.)	Total Acidity ⁽¹⁾ (mg/L CaCO ₃ Eq)	Alkalinity (mg/L CaCO ₃ Eq)	Fe (mg/L)	Al (mg/L)	Sulfate (mg/L)
Lancashire 15 After Closure	5.1	1500	40	837.5	N.R.	3432
Lancashire 15 After 25 Pool Volumes	6.53	113.5	120	63.4	N.R.	614
T&T 2 After Closure	2.6	968	0	313.5	82	2400
T&T 2 After 25 Pool Volumes	2.9	340	0	72.4	27.3	905

(1) Acidity based on pH and Fe only for Lancashire 15, and pH, Fe and Al for T&T 2.

The T&T 2 mine, which is only about 20% flooded, has shown little change in pH after 25 pool volumes and 10 years of monitoring. Acidity and Al concentrations have declined to about one third of initial concentrations; Fe is about one fourth of initial conditions, and SO₄⁻² about

38%. Limestone injection into the T&T 2 mine-pool had little or no discernible effect on pH or acidity. After leaching an equivalent number of pool volumes over about 16 and 10 years respectively, the mostly flooded Lancashire 15 mine-pool showed proportionally greater improvement in water quality than the mostly unflooded T&T 2 mine-pool.

Iron Temporal Behavior

Figure 3 is a scatter plot of iron concentration for the T&T 2 mine-pool. The initial discharge shows extreme variation in iron content for a period about two years or approximately two pool volumes, followed by a relatively rapid overall decline. A similar trend, that is, a period of extreme fluctuation, followed by a rapid concentration decrease also occurred for total dissolved solids, Al and SO_4^{-2} content. The Lancashire 15 mine-pool also displayed a similar initial flush with large short term variation in composition and rapid decline in pollutant concentrations. The initial flushing period lasted about 8 years or 12 pool volumes in the larger Lancashire 15 mine-pool. Figure 3 also shows a rapid increase in Fe concentration occurring in early 2003, followed by an equally rapid decline in the T&T 2 mine-pool. The increase in Fe concentration was accompanied by about a 10 meter decline in water level in one mine-pool monitoring well, increases in mine-pool discharge rate and annual precipitation that was more than 25% greater than the long-term average. Water level in the monitoring well did not recover to previous elevations. These data suggest that mine-pool flow paths changed permanently, and a portion of the mine-works released stored acid products. Sulfate and other mine water parameters exhibited behavior similar to the Fe data in Fig. 3.

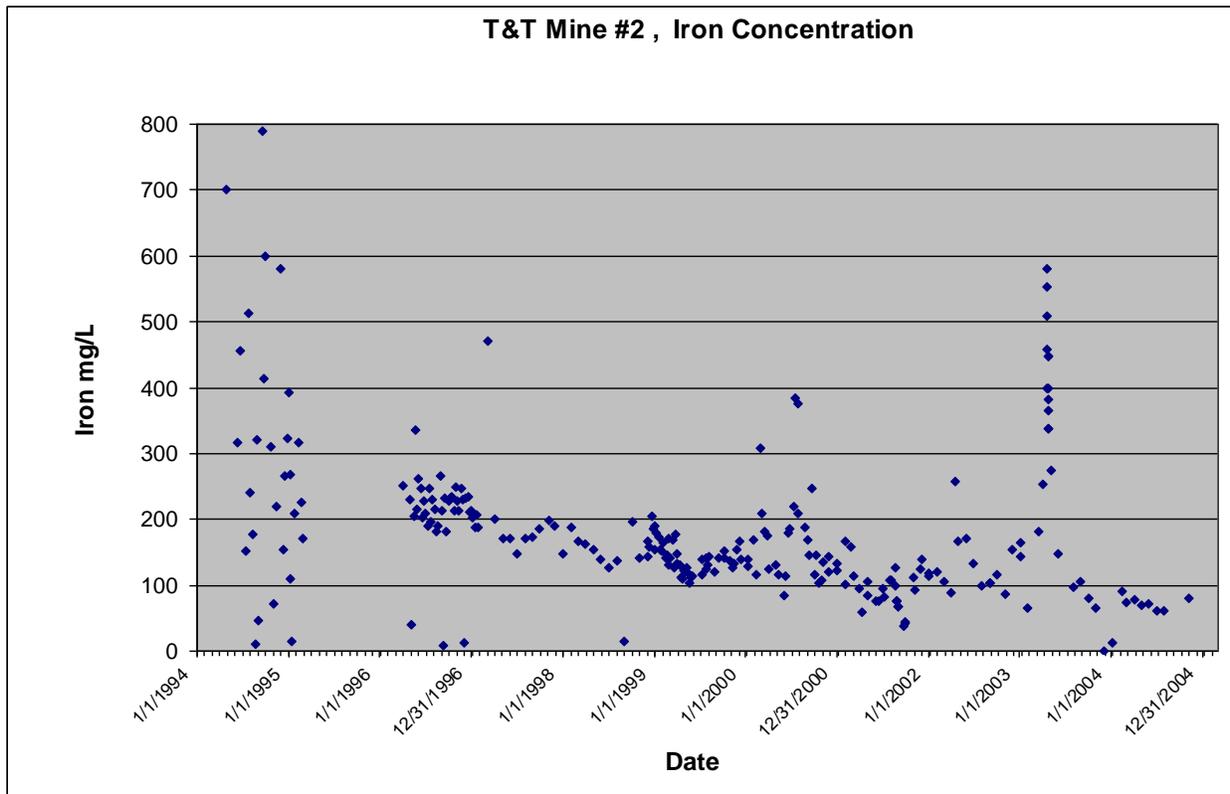


Figure 3. Time Series Scatter Plot, Fe Concentration, T&T 2 Mine-pool.

Sulfate Temporal Behavior

Figure 4 is a time series scatter plot of SO_4^{-2} concentration for the T&T 2 mine-pool. After the initial flushing, sulfate concentrations declined from about 3000 to about 1000 to 1500 mg/L. Limestone injection into the mine began in late 1999 and continued for about 2 years. During this period sulfate concentrations increased and displayed more variation. The limestone injection apparently displaced stored acid weathering products, including SO_4^{-2} minerals, and mobilized them into the mine-pool flow system. Inhibition of pyrite oxidation as a result of the limestone injection is not apparent in any of the compiled water quality data. A comparable effect was observed with grout injection in another mostly unflooded underground coal mine in a similar hydrogeologic setting (Perry and Rauch, 2004). Aggressive reclamation techniques like injection into underground mine-works may cause short-term deterioration in water quality, before beneficial effects of the treatment are seen.

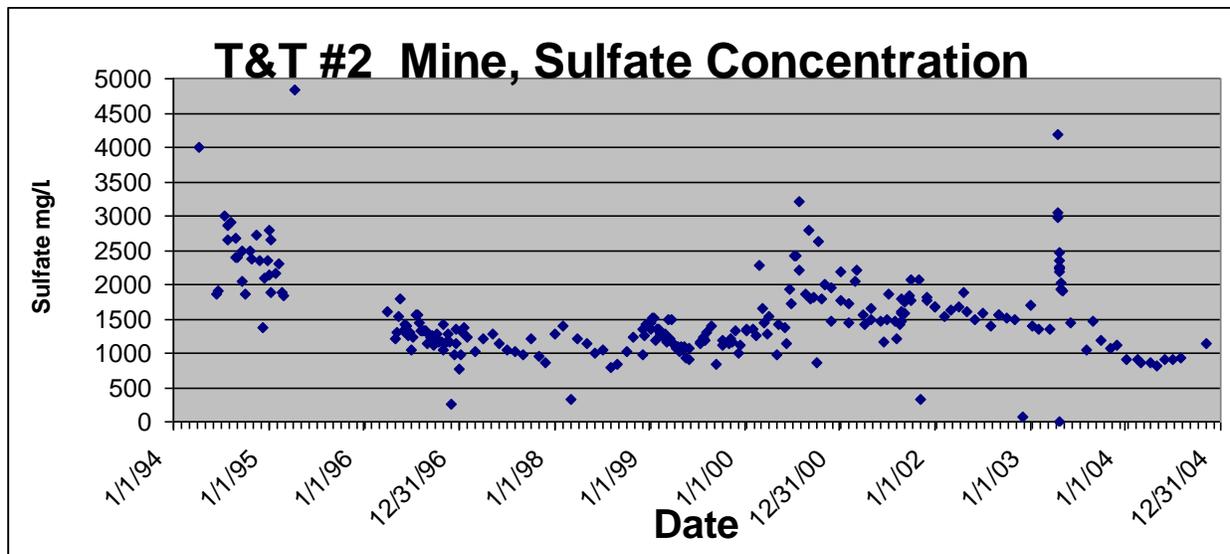


Figure 4. Time Series Scatter Plot, Sulfate Concentration, T&T 2 Mine-pool.

A rapid increase and decline in sulfate concentration occurred in 2003 along with a large increase in flow. This behavior corresponds to the spike and decline in Fe concentration observed in Fig. 3. It is believed that flow path conditions within the mine-pool changed abruptly due to subsidence or failure of barrier pillars. A rapid change in water level in one portion of the mine complex was measured at the same time flows increased 3 to 10 times typical conditions. The effect was like that observed for the limestone injection, an increase in chemical concentrations occurred as stored weathering products were flushed from the mine-pool. Because the T&T mine-pool discharges by gravity flow, its chemical composition and discharge rate can be affected by large recharge events, seasonal variation and other stresses. In contrast, the Lancashire 15 mine-pool is a pumped discharge, and variation in recharge and other stresses can be dampened by controlling pumping rates.

Aluminum Temporal Behavior

Figure 5 is a time series scatter plot of Al concentration in the T&T 2 mine-pool. Since the initial flushing concluded in 1996, there has been little change in the long term trend. Aluminum concentrations remain fixed in the range of about 30 to 40 mg/L. Limestone injection

and the flushing event in 2003 affected Al behavior in a manner similar to that described for SO_4^{2-} ; short term increases and variable composition, followed by a return to the underlying long-term trend. Under current conditions, Al concentration shows the slowest rate of improvement of the mine drainage parameters examined. Similar trends were found in another acidic unflooded mine (Perry and Rauch 2004) where a half life for Al in mine drainage was 2 to 3 times longer than other metals. So long as mine-pool pH remains below about 4.0, dissolution of alumino-silicate minerals and Al hydroxides could occur. Thus there is a large source for soluble Al, and concentrations may continue to decline more slowly than other constituents. The Lancashire 15 mine-pool contains only minor quantities of Al, since its waters are about pH 6.5.

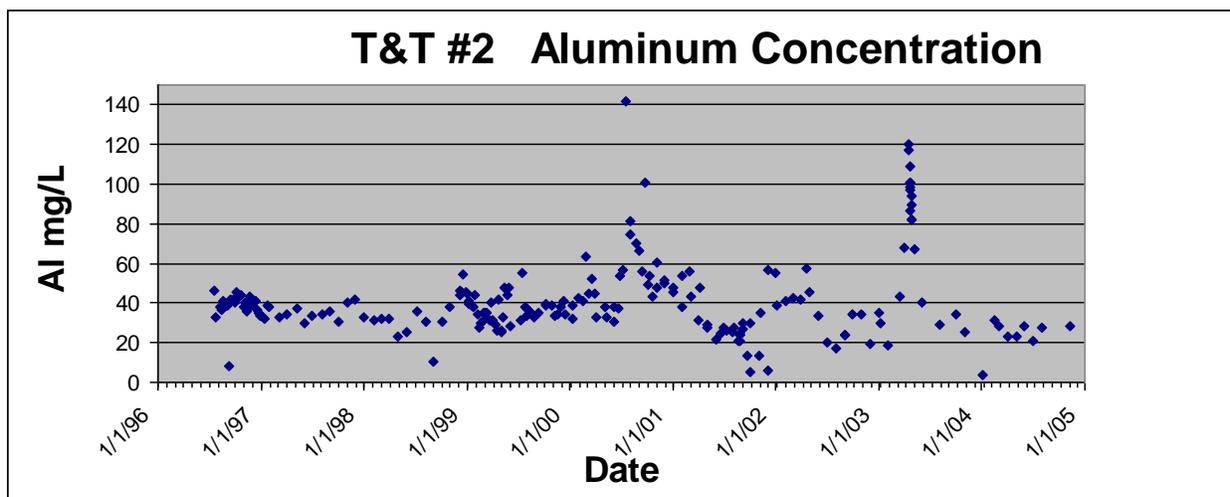


Figure 5. Time Series Scatter Plot, Aluminum Concentration, T&T 2 Mine-pool.

Figure 6 is a plot of saturation index for jurbanite, an aluminum hydroxyl sulfate mineral, in the T&T 2 mine-pool. For most samples, the waters are slightly supersaturated for jurbanite or an Al bearing mineral with similar properties. The slight jurbanite oversaturation suggests the mineral is not actually forming; the reaction rate is slow, a slightly more soluble poorly crystalline phase is forming, or the “dissolved” fraction on which the calculations were based, contains colloidal Al. Our current knowledge of the mine precludes identification of which of these variables is allowing slight jurbanite supersaturation. Jurbanite is stable in acidic waters (Nordstrom, 1982) in the pH range of zero up to 3 to 5 in sulfate rich waters. Jurbanite could form from kaolinite alteration as reaction 3 shows:

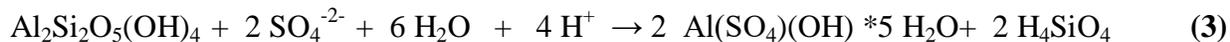


Figure 6 also shows a cyclic variation in jurbanite saturation index from 1996 to 1998. Higher values occur in late summer and autumn, characteristically the driest period of the water year in this region with the lowest mine-pool flows. Values are lowest in the spring, the period of major recharge and mine-pool flow. The inverse relation between saturation index and flow suggests mine waters are diluted during seasonal recharge and more concentrated at drier periods of the year. Mineral saturation and precipitation should be favored during dry periods, and dissolution promoted during high flow conditions. We observed similar trends in another

unflooded mine-pool (Perry and Rauch, 2004). The jurbanite saturation index is more scattered beginning in 1999, and corresponds to limestone injection. The in-situ treatment apparently disrupted the quasi steady-state conditions that had developed.

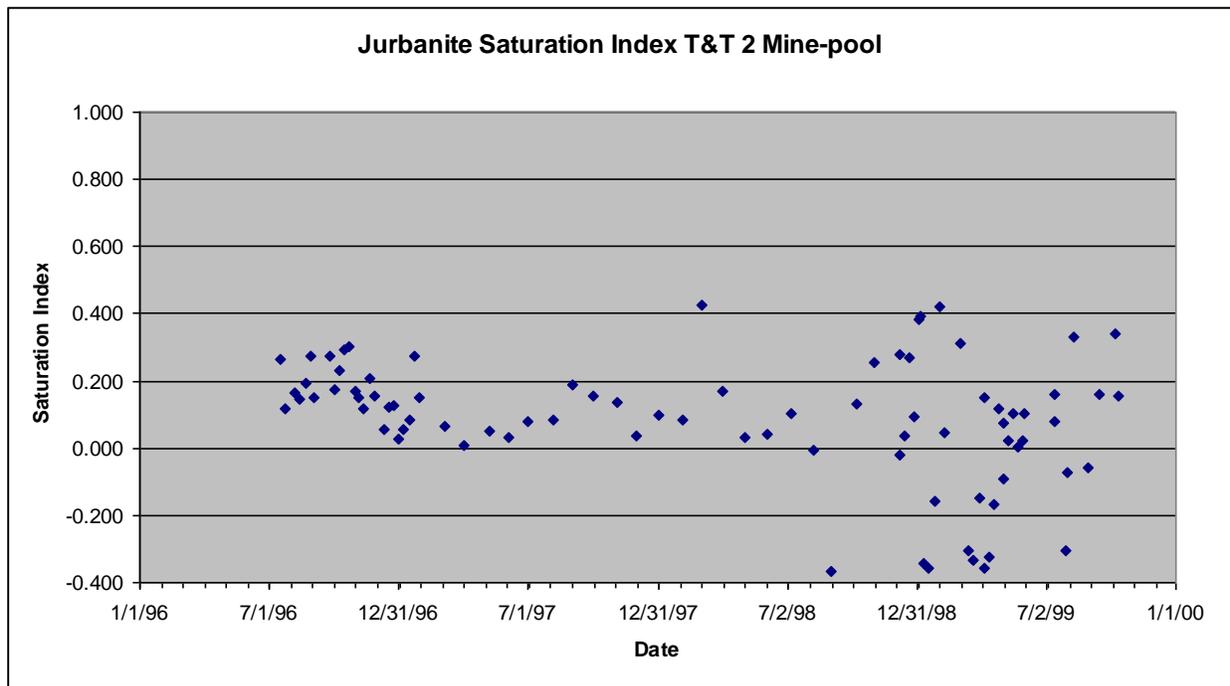


Figure 6. Jurbanite Saturation Index, T&T 2 Mine-pool

The presence of jurbanite or other Al and Fe-bearing SO_4^{-2} minerals in the mine-pool cannot be directly confirmed because the mine-works are not accessible for sampling and observation. However, since most of the T&T 2 mine is not flooded, conditions are favorable for the formation of sulfate and hydroxysulfate minerals that characteristically occur in acidic, metal and sulfate-rich environments. Melanterite, copiapite, halotrichite, pickeringite, gypsum, schwertmannite, various jarosites, and others are commonly present in the vadose zone of 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.

Iron and Sulfate Mole Ratio

The initial chemical weathering of pyrite should yield an Fe to SO_4 mole ratio of 0.5, as shown in reaction (4):

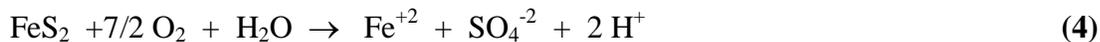


Figure 7 is a plot of Fe to SO_4^{-2} mole ratio based on average annual data for the Lancashire 15 mine-pool. The ratio declines over a 35 year period to around 0.2. Assuming SO_4^{-2} behaves as a mostly conservative ion in the L-15 mine-pool, and Fe and SO_4^{-2} are derived mainly from pyrite; about 60% of the Fe is now being attenuated in the mine-pool by adsorption, precipitation or other reactions. In the first few years after flooding, less Fe was retained in the mine-pool aquifer matrix. The T&T 2 mine-pool shows similar behavior with Fe to SO_4^{-2} mole ratio

declining to 0.1 to 0.2 after 10 years. Thus, even in the very acid mine-pool environment of the T&T 2 site, an estimated 60 to 80% of the Fe produced from pyrite oxidation is being attenuated, or at least temporarily stored in the mine-works.

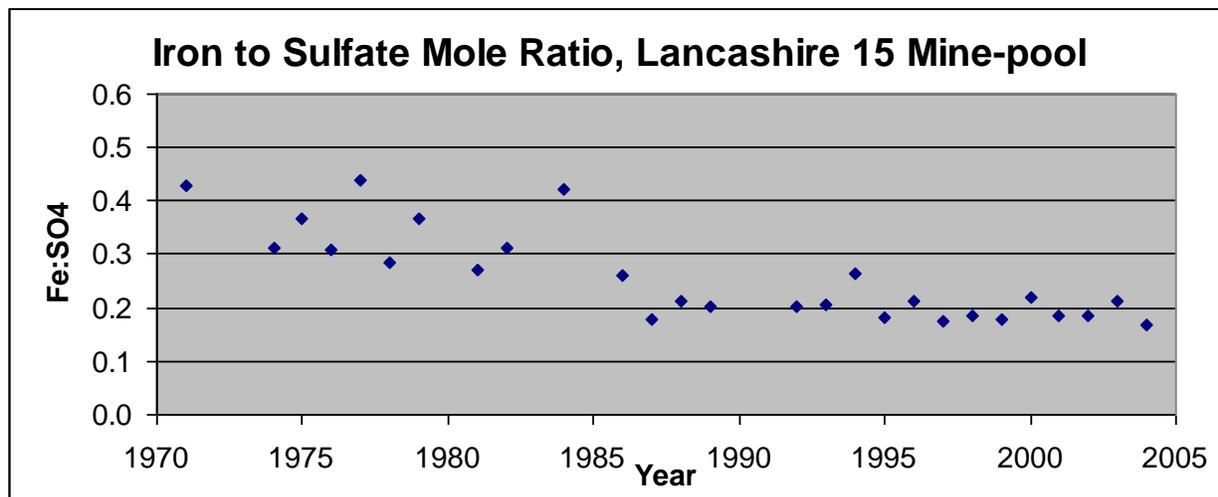


Figure 7. Plot of Average Annual Iron to Sulfate Mole Ratio, Lancashire 15 Mine-pool.

Dissolved Oxygen, Eh and Iron

A limited number of Eh, dissolved O₂ and Fe⁺²/ Fe⁺³ measurements have been collected from the two mine-pools. The mostly flooded Lancashire 15 mine-pool discharge has Eh between about 0.165 and 0.255 V. Reliable dissolved O₂ measurements have been difficult to obtain, but the mine-pool seems to have less than about 0.2 mg/L D.O, or pO₂ of about 0.5%. Mineral saturation indices, examination of sediments and an Eh/pH plot (Fig. 8) show that the water is slightly super-saturated for a poorly crystalline Fe oxyhydroxide. Based on pH, solubility considerations and speciation calculations using PHREEQC (Parkhurst and Appelo, 1999), the Fe⁺² species should comprise almost all of the soluble Fe. The Fe⁺³ species are present only in small concentrations and little soluble Fe⁺³ should be available for continuing oxidation of pyrite.

The mostly unflooded T&T 2 mine has Eh between about 0.650 and 0.725 V. Dissolved O₂ is consistently greater than 2.5 mg/L, or a pO₂ of about 7 to 8%. These data indicate that O₂ is not limiting for pyrite oxidation. Air probably circulates freely into the mine-works, since air has been observed to flow into an unsealed opening when barometric pressure increases. Eh calculated from Fe⁺²/ Fe⁺³ measurements and observed Eh were generally within 0.050 V for the T&T 2 mine-pool. This suggests that solution Eh reflects the Fe⁺²/ Fe⁺³ couple and provides a measure of Fe activities in acid mine waters. Nordstrom et al (1979) obtained good agreement between measured and computed Eh values in an acid, Fe rich waters at values between about 0.600 and 0.800 V. Williamson and Rimstidt (1994) also reported a good correlation between Eh and the Fe⁺²/ Fe⁺³ couple in acid solutions.

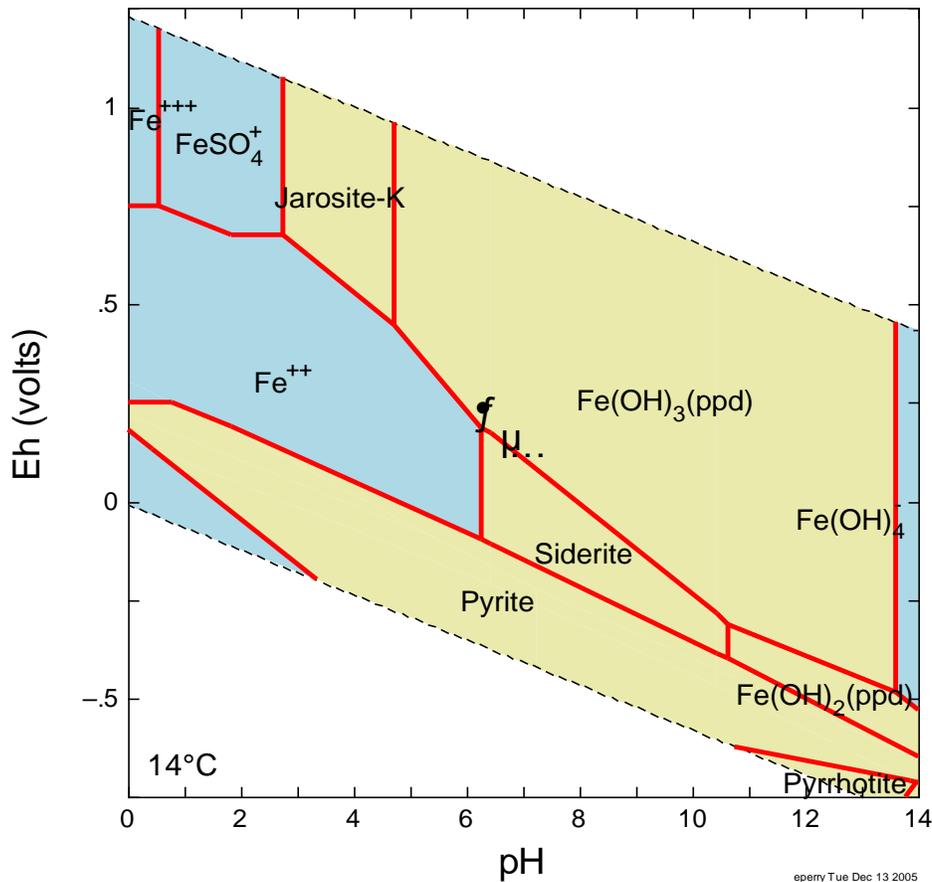


Figure 8. Eh/pH plot for Selected Iron Minerals, Lancashire 15 Mine-pool

Figure 9 is an Eh/pH plot of waters from the T&T 2 mine. These waters are at apparent equilibrium with the Fe SO_4^{-2} mineral K-Jarosite, or another mineral with similar properties. Thus, in the unfllooded mine, Fe activity may be controlled by K-Jarosite or similar Fe hydroxysulfates that are stable in acid oxidizing conditions, while poorly crystalline Fe oxyhydroxide may control Fe activity in the flooded mine-pool. Although we cannot access either mine-pool for mineralogical sampling, mineral precipitates that look like K-Jarosite and copiapite are present on outcrops near the T&T 2 mine entries, and small amounts of suspended material with characteristic appearance of Fe oxyhydroxides are present in the Lancashire 15 pumped discharge.

Sulfate Production and Flooding State

Chemical concentration and flow or pumping data were combined to estimate the total production of SO_4^{-2} and Fe from the two mine-pools. The cumulative production of SO_4^{-2} from the Lancashire 15 and T&T 2 mine-pools are plotted against pool volumes in Fig. 10 and 11. Assuming SO_4^{-2} production represents pyrite oxidation within each mine-pool, the plots show chemical weathering proceeding in two different modes. Sulfate production in the flooded Lancashire 15 mine-pool is undergoing a logarithmic decay as the slope of the plot approaches zero. This may indicate that flooding has mostly suppressed oxidation and the mine-pool is undergoing leaching and some continuing chemical reaction. Production of SO_4^{-2} from T&T 2

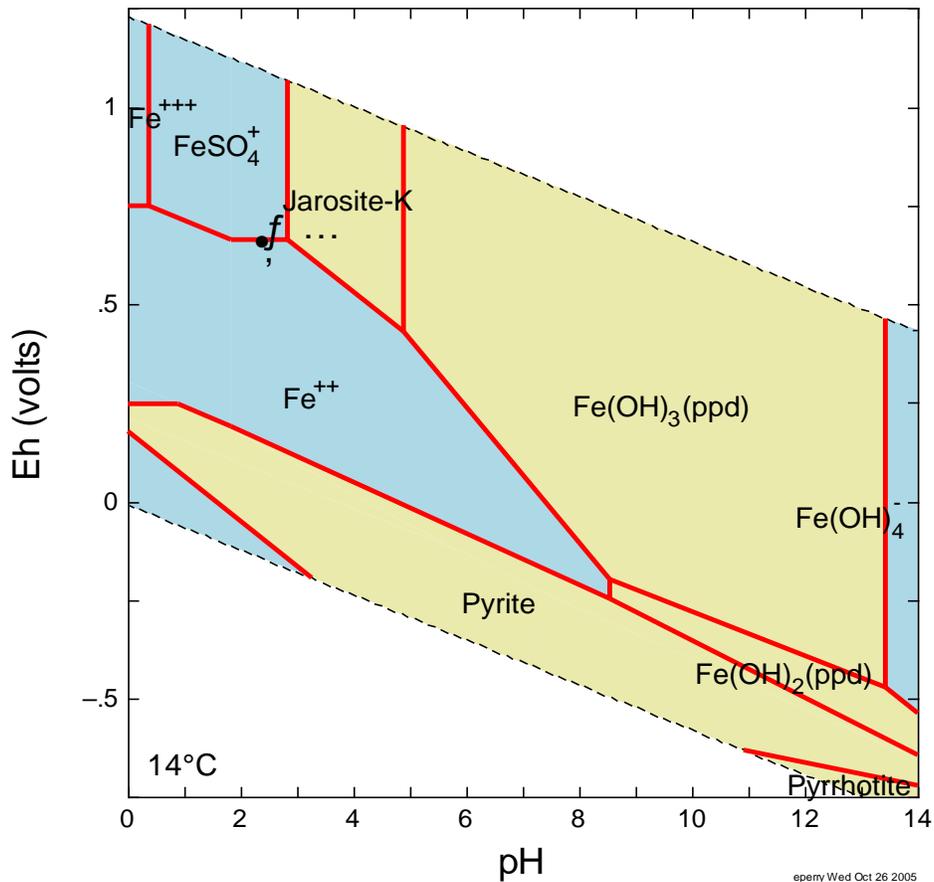


Figure 9. Eh/pH plot for Selected Iron Minerals, T&T 2 Mine-pool.

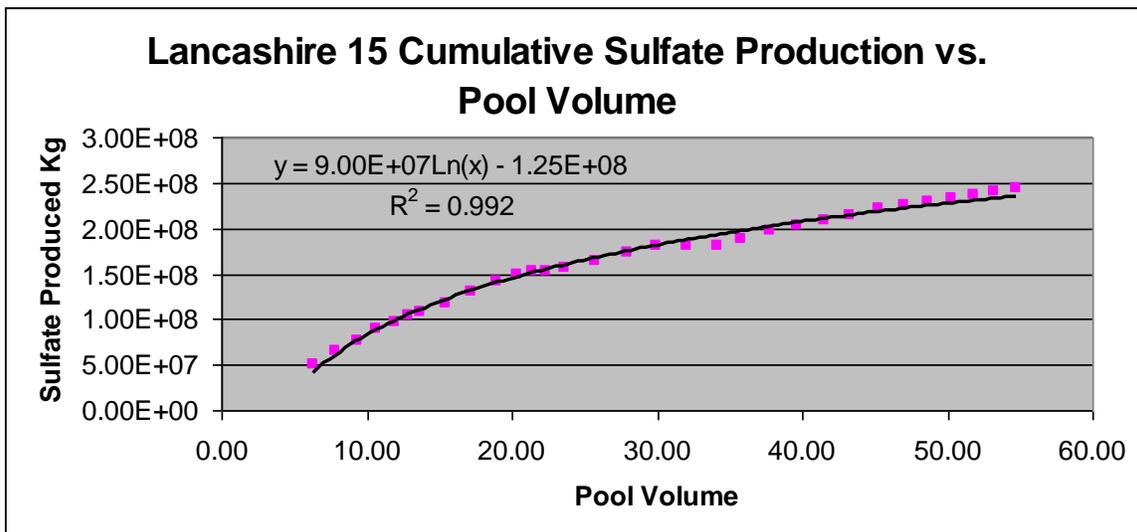


Figure 10. Cumulative Sulfate Production (Kg), Lancashire 15 Mine-pool (mostly flooded).

mine continues on a straight line plot with no apparent change in slope. This may indicate that oxidation and acid production is proceeding with few constraints. The T&T 2 mine-pool produced about two times as much sulfate per Ha of mine-works as the flooded Lancashire 15

mine-pool for an equivalent number of mine-pool flushings. Initial pyrite content of the mined strata are not well characterized at either site, but are believed to be of similar range and magnitude. The greater normalized sulfate production from the unflooded mine probably reflects continuing oxidation, while pyrite weathering in the flooded mine is suppressed in the flooded Lancashire 15 mine-pool.

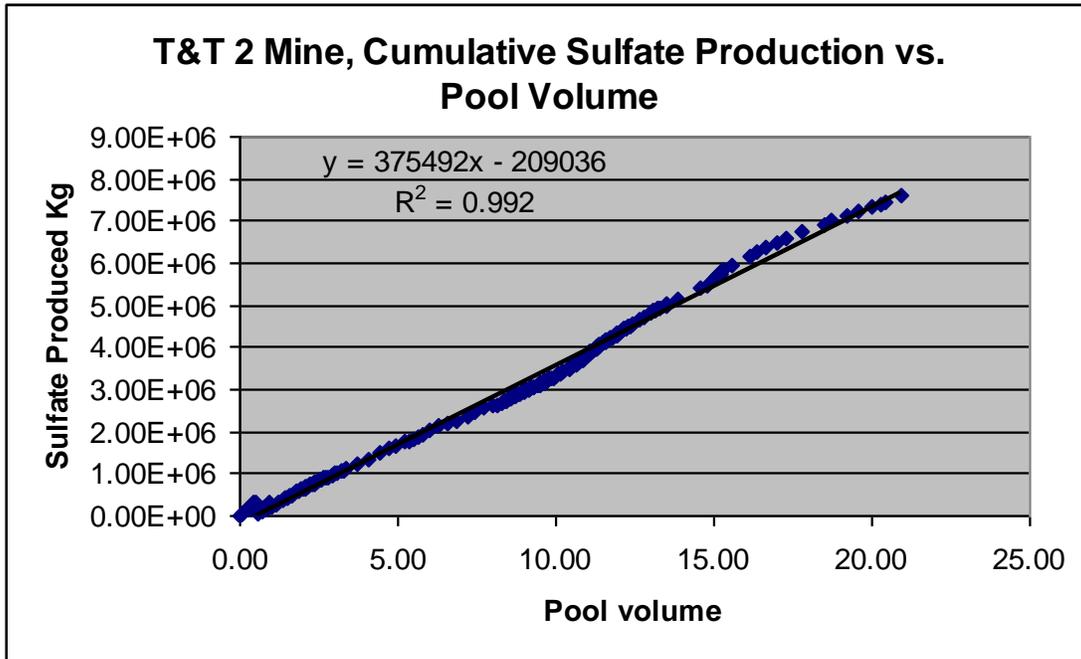


Figure 11. Cumulative Sulfate Production (Kg),T&T2 Mine-pool (mostly unflooded).

Summary and Conclusions

Water quality and flow data from two closed underground coal mines were examined for temporal trends and apparent controls on pyrite oxidation. The Lancashire 15 mine-pool is about 80% flooded, while the T&T mine is only about 20% flooded. For both mines, mine-pool chemistry evolves through two stages, including an initial flushing with extreme fluctuation in chemical concentration and poor quality. Both mine-pools also have a second maturation phase where chemical concentrations decline, composition changes more slowly and begins to approach a steady state condition. Similar behavior has been described for closed coal mines in Great Britain (Wood et al, 1999; Younger, 2000). Both mines underwent an initial period of flooding, characterized by a discharge of acidic water with variable, but high, concentrations of iron and sulfate. The initial flush lasted about 8 years, or 12 pool volumes in the larger Lancashire 15 mine-pool. In the T&T 2 mine-pool, the initial flush lasted about 2 years or 4 pool volumes. This may indicate greater leaching efficiency in the smaller free draining mine.

Both mine-pools underwent a rapid decline in chemical concentrations in the initial flush. However, the decrease was more pronounced in the flooded Lancashire 15 mine-pool. Both mine-pools are now in a maturation phase characterized by a continuing slow decline in most chemical concentrations and less short term variability in composition. The T&T2 mine-pool

however is controlled by gravity drainage and is therefore more responsive to large recharge events and seasonal variation. Stresses on the Lancashire 15 mine-pool are dampened by controlling pumping rates. An estimated 60 to 80 % of the iron produced by pyrite oxidation is now being retained in both mine-pools, probably by a combination of adsorption, exchange and precipitation reactions.

Flooding of the Lancashire 15 mine-pool seems to have suppressed pyrite oxidation. A large portion of the mine-pool has very low dissolved O_2 concentration ($<0.5\text{mg/L}$ or $pO_2 <1\%$) and moderately reducing conditions, as shown by Eh measurements. Thus the supply of the pyrite oxidants, O_2 and Fe^{+3} iron, should be limited. The measured dissolved O_2 and apparent suppression of pyrite oxidation are consistent with Hammack and Watzlaf's (1990) recommendations to maintain O_2 concentration below 1%. Some chemical reactions are probably continuing in unflooded parts of the mine-pool. Stortz et al. (2001) also found that mine flooding results in more rapid water quality improvement. They noted significant increases in pH, and decreases in acid load, dissolved solids and other parameters in a mine that was mostly flooded compared to a nearby unflooded mine in the same geologic and hydrologic setting.

Pyrite oxidation is continuing with few constraints after 10 years and about 25 pool volumes in the T&T 2 mine. Dissolved O_2 is more than 2.5 mg/L , corresponding to pO_2 of about 7 to 8%, and oxidizing conditions prevail with Eh values greater than 0.65 V. Oxygen content is significantly greater than Hammack and Watzlaf's (1990) recommended 1% threshold. Both dissolved oxygen and some Fe^{+3} iron are therefore available to continue the oxidation process.

Injection of limestone byproducts in the T&T 2 mine had little discernible effects on acid generation, and in fact caused a short term increase in chemical concentrations by displacing stored acid weathering products. Other disruptions in the flow system including subsidence, barrier pillar failures, large recharge events or other significant stresses may also cause short-term surges and pollutant slugs.

Iron activity in the flooded mine-pool appears to be controlled by poorly crystalline Fe oxyhydroxide, while waters in the unflooded mine are at apparent equilibrium with the acid sulfate salt K-Jarosite. Aluminum has been largely removed from the flooded mine-pool system as pH has stabilized at about 6.5 and the water is net alkaline. Reaction (pH) in the T&T mine is has changed very little from initial conditions. As long as pH remains below about 4, significant Al concentrations are likely to persist in the mine-pool. The waters are at apparent equilibrium with jurbanite or a mineral with similar properties.

Comparison of sulfate production rate as an indicator of pyrite oxidation showed little change in the unflooded mine-pool, while a logarithmic decrease in sulfate production rate is occurring in the flooded mine-pool. The unflooded mine-pool has produced about two times as much SO_4^{-2} per Ha of mine-works as the flooded mine. Hydrogeologic conditions must be suitable for flooding of underground mines to succeed. In the dissected Appalachian landscape, this usually requires the mine to be below the local base level drainage to maintain a flooded condition. Even with pyrite oxidation suppressed, flooded mines may discharge elevated concentrations of Fe, SO_4^{-2} and dissolved solids for an indefinite period, while oxidation continues in unflooded mines. The time period required for either mine-pool to produce water that does not require treatment is uncertain.

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