WATER QUALITY TRENDS IN A FLOODED 35 YEAR OLD MINE-POOL[1]

Eric F. Perry[2], Jay W. Hawkins, Mike Dunn, Robert S. Evans, and John K. Felbinger

Abstract: Thirty five years of water quality data from a pumped, mostly flooded, mine-pool were examined for trends in mine drainage parameters. At the start of pumping in 1970, the Lancashire 15 mine-pool discharged acidic water with average iron (Fe) concentration exceeding 900 mg/L. Average sulfate (SO_4) concentration was about 3700 mg/L. After 14 years of pumping about 21 mine-pool volumes, Fe and SO_4 were about 20% of their initial concentrations. Alkalinity had increased from less than 50 to about 120 mg/L, and pH was about 6.0. In 1986, an overlying mine complex closed and flooded. Its' waters have low concentrations of Fe and SO_4, and are hydraulically connected to the Lancashire 15 mine-pool. The combined mine-pool waters reduced Fe by about 50% in Lancashire 15. Since 1986, Fe and SO_4 concentrations have continued a slow, irregular decline at the rate of 1 to 2 mg/L/yr for Fe and about 10 to 15 mg/L/yr for SO_4. Short term fluctuations due to seasonal and pump rate variations occur, but long term concentration trends can be described with curvilinear models.

The Lancashire 15 discharge is sodium-sulfate (Na-SO_4) type water. Geochemical calculations show that cation exchange of calcium (Ca) for Na is a feasible explanation for the observed water composition. Mixing calculations show that mine-pool composition can be explained by cation exchange; continuing dissolution of iron and sulfur bearing minerals, iron oxyhydroxide formation and about 80% of recharge as leakage from adjacent and overlying mines, and 20% recharge from unmined strata.

The Lancashire 15 mine-pool quality has improved significantly since closure and flooding. After leaching an estimated 55 pool volumes, Fe concentrations are about 5% of original values, and the waters are net alkaline. Continued mineral dissolution, and inefficient leaching due to dispersion and short circuiting, are likely responsible for current water quality conditions.

Additional Key Words: acid mine drainage, mineral solubility, pyrite, Eh

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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). Mine-pool quality is controlled by geochemistry of the immediate roof and floor rock, residual coal, composition of recharge water, and extent of flooding of the mineworks. Mine-pool quality changes after closure with the poorest water quality discharged in the initial flush, followed by a gradual, (i.e. years to decades) improvement in composition. Skousen et al. (2004) reported that iron concentration had decreased an average of 80% in 44 free draining underground mine discharges over a 30 year period. 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 concentrations would decline to 30 mg/L or less within 40 years. The final chemical composition of initially acidic, highly polluted mine-pools is uncertain after early flushing. In the long term, these mine-pools may also be important ground-water resources, because they are frequently transmissive enough to sustain relatively large yields when pumped (Donovan et al., 2004; Perry and Hawkins, 2004).

In this paper we describe water quality trends and geochemical processes for iron and sulfate in a 35 year old mine-pool, Lancashire 15, that is about 79% flooded (approximately 4690 Ha). The physical hydrogeology is detailed in a companion paper (Hawkins et al., 2005) and information on pool volume and storage are used to interpret observed chemical trends. The mine-pool has one principal pumped discharge that yields over 24,000 L/min and has been sampled since closure and initial flooding.

Geologic and Hydrogeologic Setting

The Lancashire 15 (L-15) mine-pool is located in Cambria County, Pennsylvania and is largely 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 pumped from the Duman plant at the low point of the basin (Fig. 1). The main 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 presence or absence of complete flooding also influences water chemistry. Unflooded or free draining areas are more likely to undergo continuing pyrite oxidation and leaching and produce acid drainage, while fully flooded mineworks may yield water with circumneutral pH and net alkaline conditions.

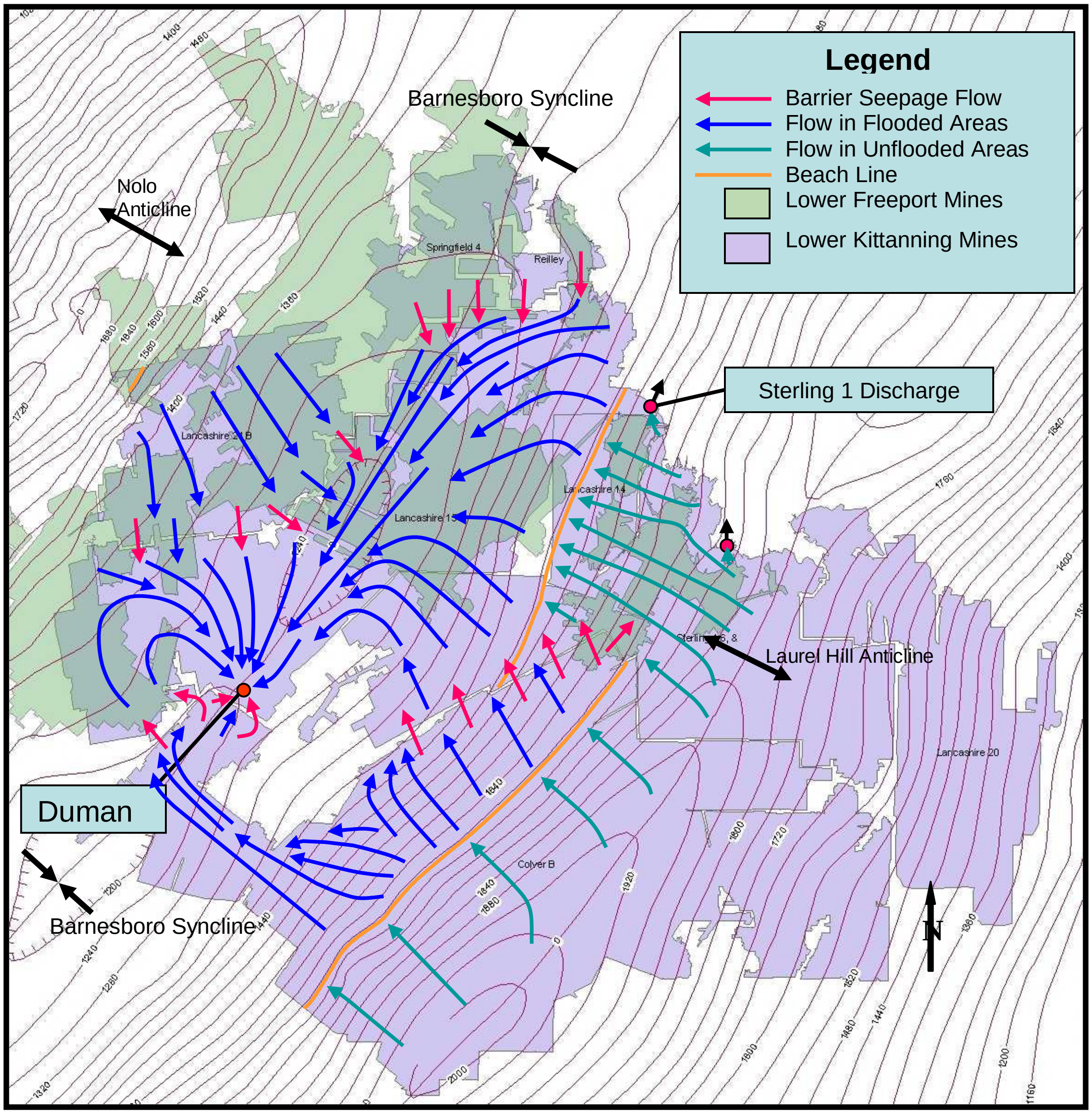

Figure 1. L-15 Mine-pool Flow Paths and Geologic Structure.

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 the Colver mine-pool located to the east (Hawkins et al., 2005). Some ground water also enters the mine-pool through unmined strata.

The rocks are Pennsylvanian age, Allegheny group, consisting in descending order of the Freeport, Kittanning and Clarion formations. Rock strata of 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 seam elevation varies from a high of about 610 m on the Laurel Hill anticline to a low of about 366 m near the Duman treatment plant. The Lower Kittanning seam averages about 1 m thick, and the Lower Freeport is about 1.4 m. Area geology is described in more detail by McElroy (1998) and references cited therein.

Mine Closure and Flooding History

The L-15 mine-pool formed in adjacent and interconnected mineworks of about 15 different mines (Hawkins et al., 2005). Coal development began in the late 1800's by room and pillar methods, and many areas had retreat mining. Later mining included longwall extraction. By the mid 1980's all significant underground mining was completed. The L-15 mine-pool began to form after the closure of several larger mineworks in the Lower Kittanning seam in 1969. At that time, dewatering was halted and the mineworks were allowed to flood. About one year later, a major blowout occurred at the north end of the mine-pool, discharging an estimated 4000 to 8000 L/min into the West Branch of the Susquehanna River. Discharge quality was extremely poor with iron and total acidity concentrations ranging from 2500 to 4000 mg/L, and about 7000 to 10,000 mg/L, respectively. A major fish kill occurred, and the Commonwealth of Pennsylvania began emergency treatment of the West Branch of the Susquehanna River. The mining company began pumping and treating at the Duman facility until water level was below breakout elevation and discharge to the West Branch of the Susquehanna River ceased.

In 1986, mines in the overlying Lower Freeport seam and one Lower Kittanning seam mine closed and flooded. Closure of these mines increased the required pumping rate at Duman by about 60% (Hawkins et al., 2005) indicating they contribute part of the recharge to the L-15 mine-pool. The L-15 mine-pool has been pumped and treated since 1970. As shown in Fig.. 1, flow within the mine-pool is from northeast to southwest along the synclinal axis, and from the anticlinal axes toward the center of the basin. The northern end of the mine-pool is unflooded (about 1246 Ha). The Sterling 1 discharge (Fig. 1) drains a portion of the unflooded mineworks.

Methodology

Over 1400 analyses of Duman raw water quality from offices of the Pennsylvania Dept of Environmental Resources (PADEP) (Kernic, 1999), and mine drainage reports for Blacklick Creek and West Branch of Susquehanna (Michael Baker Consulting Engineers, 1978; Gwin, Dobson and Foreman, 1972) and unpublished data (Lloyd, 2004) were used in this study. Sampling frequency ranged from daily to monthly to quarterly, and there were several years for which no data were located. However, a good record of initial water quality conditions at Duman was available, and continuous sampling of monthly frequency exists for about the last 7 years.

The compiled analyses vary in reported parameters, and were run by different laboratories which may not have used identical analytical methods. Iron, pH and acidity are the most consistently reported parameters. Values for sulfate, manganese and aluminum were reported for some but not all samples. Acidity was calculated from reported pH and iron concentration, counting all iron as Fe(II), based on theoretical and practical considerations of iron speciation in mine waters (Kirby and Cravotta, 2004; Cravotta and Kirby, 2004). Calculated acidity was determined as:

$$\text{Acidity Calc} = 50*((\text{Fe}*2/55.85)+1000*(10^{-\text{pH}})) \quad \textbf{(1)}$$

The available analyses show relatively small amounts of manganese present (generally less than 2 mg/L), and except in acid waters, concentrations of soluble aluminum are low. Therefore, for most samples, iron should represent most of the acidity. The calculated acidity values were used in subsequent analysis.

To supplement the historical data, four complete suite samples of the Duman raw water were collected at different seasons of the year in 2004. Samples from the unflooded works of the Sterling 1 mine (Lower Kittanning seam), and the upper mine-pool (Lower Freeport seam) and several other mine discharges were also collected. 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,Cl) and general chemistry (pH, acidity, alkalinity, specific conductance, Total Dissolved Solids, and Total Suspended Solids). Field measurements of pH, specific conductance, temperature, oxidation reduction potential (Eh), and dissolved oxygen were also collected. Geochemical calculations of mineral saturation indices, inverse modeling and solution mixing were performed using PHREEQC (Parkhurst and Appelo, 1999). Statistical analyses were performed using Statgraphics for Windows, version 5.1.

Results and Discussion

Temporal Trends

During the initial year of treatment at the Duman plant, overall water quality was very poor. Influent water pH varied from strongly acidic (~ 3.5) to circumneutral (~6.3); alkalinity from zero to a maximum of about 100 mg/L and acidity was usually in excess of 1000 mg/L. Iron and sulfate concentrations also showed short term fluctuation, but were typically in excess of 500 and 3000 mg/l, respectively. Table 1 summarizes median water quality conditions for initial conditions from August, 1970 to December 1971, and recent data from February, 1998 to May, 2004 at the Duman plant.

Table 1. Median Water Quality, Historical and Current Conditions, Duman Treatment Plant(1)

Date	pH	Acidity(2)	Alkalinity	Fe	SO_4
8/70 to 12/71	5.10	1500	0	837.50	3432
2/98 to 5/04	6.51	98.3	172.9	43.75	397

(1) pH in Standard units, acidity and alkalinity in mg/L $CaCO_3$ Eq, iron and sulfate in mg/L.
(2) Acidity is calculated from iron and pH data as described in text.

After about 35 years of leaching, L-15 mine-pool quality has improved substantially, although treatment is still required. The raw influent water is now typically net alkaline and median iron concentration has declined to about 5% of initial values. Fig. 2 shows the trend in average annual iron concentration at Duman from 1970 to present. Concentrations exceeded 900 mg/L during initial flooding and discharge, but declined rapidly afterwards, dropping to about 200 mg/L after about 8 years. This period likely represents active flushing of soluble metal sulfate salts and stored acidity. After 1986 when the overlying mine-pool flooded, iron declined further to current values of around 40 mg/L. Sulfate concentration initially declined more slowly, to about 1000 mg/L over a 10 year period, and is now about 11% of initial conditions.

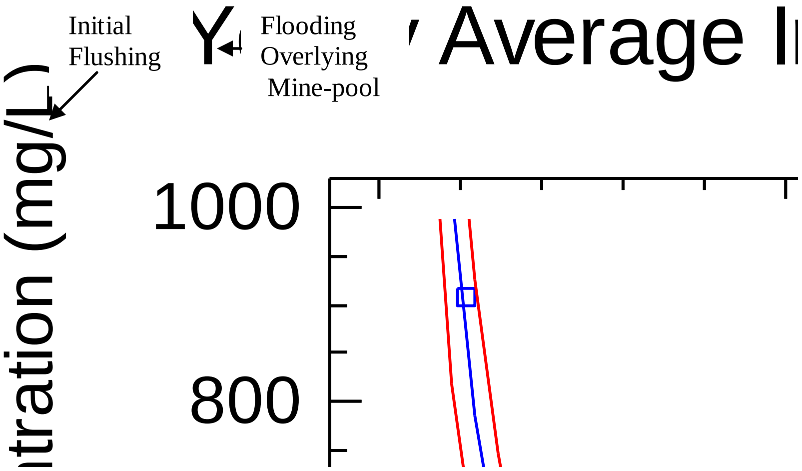

Figure 2. Plot of Average Annual Iron Concentration with Fitted Regressions, Duman Site.

The iron data in Fig. 2 from 1971 to 1986 can be fitted to a reciprocal model of the form:

$$\text{Fe Average (mg/L)} = 82.5 + (1579.8/\text{Years since flooding}) \qquad r = 0.92 \qquad \textbf{(2)}$$

In 1986, the L-15 mine-pool was affected by closure and flooding of mines in the overlying mine-pool (Lower Freeport seam). The resultant influx of water of differing chemical composition, generally containing iron of less than 5 mg/L, changed the long term chemical behavior of the L-15 mine-pool. As seen in Fig.. 2, average iron concentration dropped abruptly from about 200 to 60 mg/L from dilution and mixing with the overlying mine-pool. In addition to dilution, increased precipitation of iron oxyhydroxides and/or carbonates may also have occurred. Flooding of the Lower Freeport mine-pool increased average alkalinity in the L-15 mine-pool from 120 to 290 mg/L and pH increased from 6.0 to 6.7. No Eh or iron speciation measurements are available for the 1986 flooding period. However, the 2004 water samples are slightly oversaturated for both siderite and poorly crystalline iron oxyhydroxides, indicating these minerals could precipitate. The post 1986 iron data can be fitted to a model of the form:

$$\text{Fe Average (mg/L)} = 1/(7.59 * 10\text{^}^{-4} * \text{Years since Flooding}) \qquad r = 0.83 \qquad \textbf{(3)}$$

After 1986, iron concentration continues to decline with time, but more slowly.

Younger (1997, 2000) and Wood et al. (1999) have reported similar discharge chemistry behavior of iron concentration in closed underground mines in the United Kingdom. Younger (1997) reports on several discharges where iron follows an exponential decay function. He attributes this behavior to depletion of “vestigal” or stored acidity, similar to the 8 year flushing period in the L-15 mine-pool. After 10 to 20 years, the curves in the British mines become asymptotic and solution iron is controlled by juvenile or ongoing acid generation. Younger (2000) concluded the main period of flushing of stored acidity is about four times as long as the flooding period, and that short-term to long term iron concentrations are about 8:1 (mg/L basis) with some site specific variation. For the L-15 mine-pool, flushing appears to be about 8 times as long as the flooding period, and is a function of flow path length and tortuosity, residence time, and extent of flooding. Initial iron to longer term concentrations is about 4:1 before the 1986 flooding, and about 19:1 when compared to current conditions. The 4:1 ratio suggests a slower rate of iron removal than observed by Younger, or greater ongoing acid production in L-15. The 19:1 ratio is influenced by the 1986 flooding, and shows that the quality of the recharge water can significantly affect iron behavior.

Yearly average sulfate concentration data and fitted regressions are shown in Fig.. 3. The pre- 1986 sulfate data has a best fit model of:

$$\mathrm{SO_4}\ \text{Average (mg/L)} = 1/(2.93*10^{\wedge -4} + 6.04*10^{\wedge -5}\ *\text{Years since Flooding}) \qquad r = 0.91 \qquad \mathbf{(4)}$$

The post 1986 sulfate model is similar with a best fit regression of:

$$\mathrm{SO_4}\ \text{Average (mg/L)} = 1/(6.14*10^{\wedge -5}\ *\text{Years since Flooding}) \qquad r = 0.73 \qquad \mathbf{(5)}$$

Unlike iron, sulfate concentration shows a small response to the 1986 mine flooding. Slopes of the pre and post flooding regressions (equations 4 and 5) are nearly the same. The small response in sulfate concentration to the 1986 flooding reflects its' conservative behavior in L-15. Gypsum and other common sulfate minerals are one or more orders of magnitude under-saturated in flooded sections and do not control sulfate concentration.

The curvilinear models and post 1986 flooding behavior for both iron and sulfate suggest that the system will approach long term geochemical equilibrium slowly, on the order of decades.

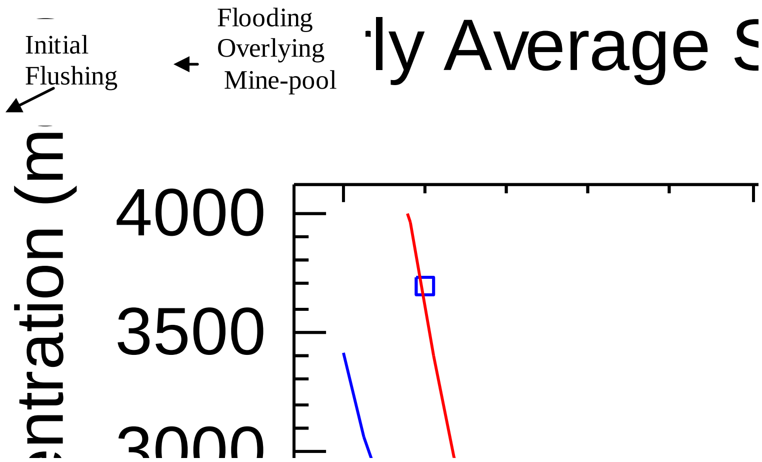

Figure 3. Plot of Average Annual Sulfate Concentration With Fitted Regressions, Duman Site.

Fig. 4 is a plot of simple moving average and raw data for iron concentration at the Duman plant for recent conditions (2000-2004). The overall trend has a current rate of decline of 1 to 2 mg/L-year but there are short term and seasonal fluctuations in concentration. Most of the raw data are within about 25% of the trend line. Sulfate exhibits similar behavior, displaying a slow irregular decline of about 10 mg/L-year in concentration over time. It is not known whether the trends will continue to decline or become asymptotic and approach equilibrium where iron is maintained at elevated concentrations indefinitely. Even if the current trends continue, it will be decades before water quality approaches some acceptable criteria. The curvilinear function derived for iron, based on post 1986 data, projects approximately 131 years from mine closure for iron to reach 10 mg/L, assuming current hydrologic and geochemical conditions are still applicable in the future. The curvilinear function for sulfate based on post 1986 data, projects approximately 65 years from mine closure for sulfate to reach 250 mg/L.

The L-15 mine-pool has been pumped at a rate equivalent to about 2 pool volumes a year based on storage calculations reported by Hawkins et al. (2005), and is approaching a total of 60 pool volumes. If the mineworks function as a simple flow through system, then soluble constituents should have been rapidly leached from the L-15 mine-pool within the first few years or pool volumes, when most flushing took place. In fact, both iron and sulfate persist in the mine-pool, suggesting that the flow system has elements of dispersion, short circuiting and no-flow zones, and that some chemical reactions are continuing.

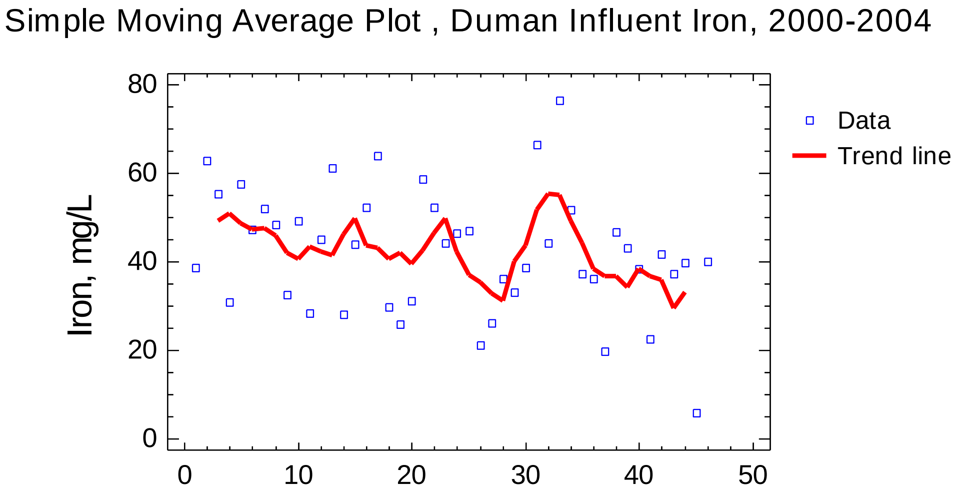

Figure 4. Plot of Simple Moving Average and Recent Iron Concentration, Duman site.

Pyrite oxidation in theory yields an Fe to SO_4 mole ratio of 0.5. Fig. 5 is a plot of Fe to SO_4 mole ratio based on average annual data for the Duman site. The ratio declines over a 15 year period to around 0.2. Assuming sulfate behaves as a mostly conservative ion in the L-15 mine-pool and is derived from pyrite; about 60% of the iron is now being attenuated in the mine-pool by adsorption, precipitation or other reactions. In the first few years after flooding, less iron was retained in the mine-pool aquifer matrix.

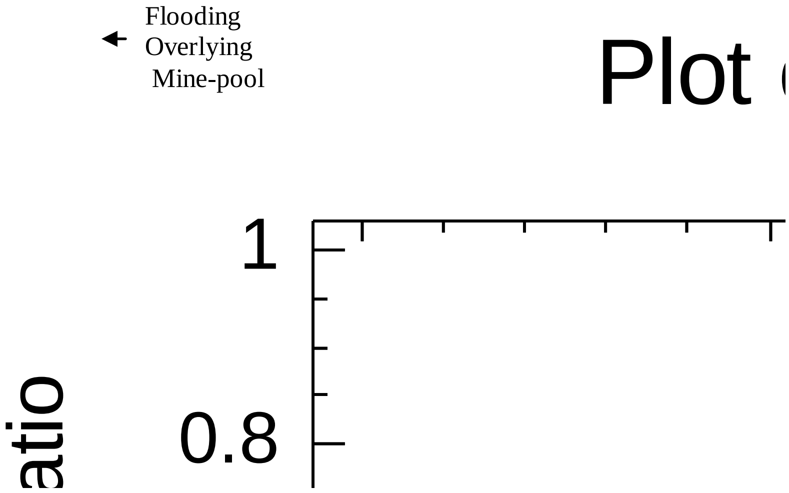

Figure 5. Plot of Average Annual Iron to Sulfate Mole Ratio, Duman Site.

Fig. 6 is a plot of average annual alkalinity for the Duman discharge. For at least 6 years after flooding, corresponding to the period of initial flushing, alkalinity remained at about 50 mg/L or less. After the initial flushing of the L-15 mine-pool, alkalinity continued to increase to over 100 mg/L and peaked at about 300 mg/L after flooding of the overlying Lower Freeport mines. Since that time alkalinity has remained around 200 mg/L and pH has stabilized at about 6.5.

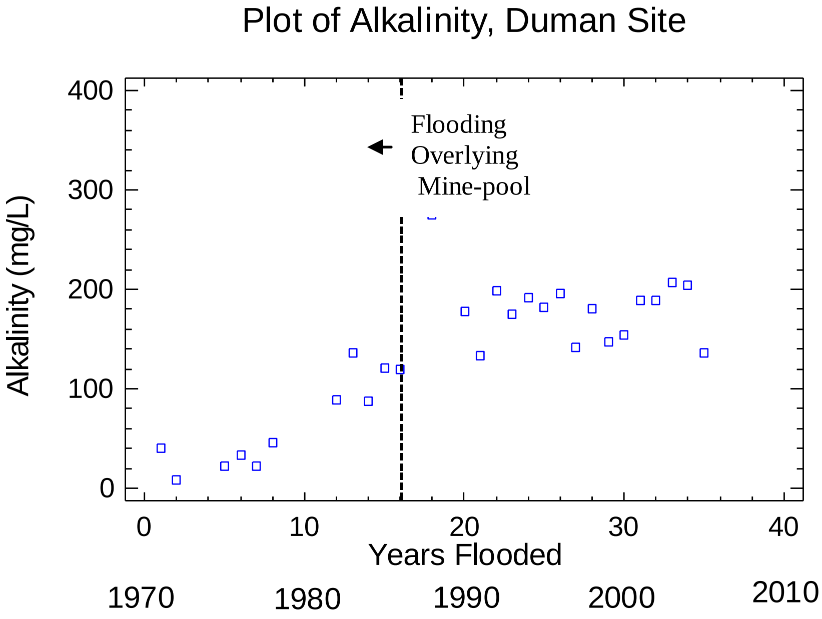

Figure 6. Plot of Average Annual Alkalinity at Duman Site

Mine-pool Chemical Composition

The Duman influent is a combination of several source waters that have mixed and reacted with the aquifer matrix as they flow toward the pump station. From the discussion of quantitative hydrogeology (Hawkins et al.,2005) and examination of water quality data, the following waters contribute to the Duman influent in varying fractions: a) leakage through a barrier pillar from the Colver mine-pool, located east of the main L-15 pool, estimated as approximately 30% of the influent, b) leakage from the overlying Lower Freeport seam mines, estimated to be about 40 to 50% of the influent, c) ground water recharge from unmined strata, and d) acidic water from unflooded areas at the northern end of the mine-pool and flanks of the two anticlines that are the eastern and western boundaries of the Lancashire 15 mine-pool. Representative analyses of each of these waters collected during 2004 are shown in table 2.

The Duman influent represents the end of the flow system for the Lancashire 15 mine-pool. It is a Na-SO_4 type water and is usually net alkaline. Iron and sulfate concentrations are about 40 and 400 mg/L, respectively. On several site visits, dissolved oxygen (D.O.) and/or Eh were measured on the raw influent. Fig. 7 is an Eh/pH diagram for iron in the Duman influent waters. Two samples are plotted against iron oxyhydroxide, siderite and pyrite, based on field measured pH and Eh. The samples are slightly oversaturated for poorly crystalline iron oxyhydroxide, and well outside the pyrite stability field, indicating that pyrite could undergo dissolution and iron oxyhydroxide could precipitate. The dominant soluble iron species is Fe^{2+}. Speciation calculations using the geochemical code PHREEQC (Parkhurst and Appelo, 1999) show that Fe(II) species comprise almost all of the soluble iron, and Fe(III) species are present only in small concentrations.

Table 2. Representative Full Suite Analyses of Mine-pool Waters, 2004 (1)

Source water	pH	Alkalinity	Acidity	Fe	Al	Mn	Ca	Mg	Na	K	SO_4	Cl
Duman (L. K.) (2)	6.55	137	75	40	0.19	1.0	39.9	15.1	159	1.89	390	7.0
Colver (L. K.)	6.35	63	114	62	0.05	1.17	95.7	30.2	69.8	4.63	417	8.0
Lower Freeport	6.32	124	2	0.26	0.21	0.34	75.2	19.4	11.2	2.4	157	4.0
Ground water(3)	7.0	142	1	0.32	0.14	0.03	42.9	6.2	1.7	1.64	27	6.3
Sterling 1 (Unflooded L. K.)	2.78	0	574	113	43.7	1.7	85	33.9	34.8	1.44	767	5.3

(1)pH in S.U., alkalinity and acidity in mg/L $CaCO_3$ Eq.; all others in mg/L.
(2)L. K. = Lower Kittanning coalbed.
(3)Ground water from unmined area strata. Data from McElroy,1998.

The Colver mine water composition is similar to the Duman influent with respect to mine drainage parameters, with iron and sulfate concentrations of about 60 and 400 mg/L, respectively

(Table 2). It contains less sodium than the Duman discharge however, and is a Ca-Na-SO_4 type water. The Sterling 1 sample was collected from the unflooded free draining north end of the mine-pool (Fig. 1). Its' composition differs sharply from waters in the flooded part of the mine-pool. It is strongly acidic with pH less than 3.0, total acidity of near 600 mg/L, and higher concentrations of iron and sulfate, with significant quantities of soluble aluminum. Both Eh and dissolved oxygen measurements (+786 mv and 8.1 mg/L, respectively) indicate a well aerated, oxidizing environment. Acid generation is ongoing in this portion of the mineworks.

Water from Lower Freeport seam mines can contain 100 to 200 mg/L alkalinity, with metal concentrations of about 5 mg/L or less. These waters, if mixed with the Lower Kittanning seam mine-pool, would have a net dilution effect on metals concentrations, and add alkalinity to the L-15 mine-pool. The Lower Freeport seam sample in table 2 is mixed composition Ca-Mg-SO_4-HCO_3 type water.

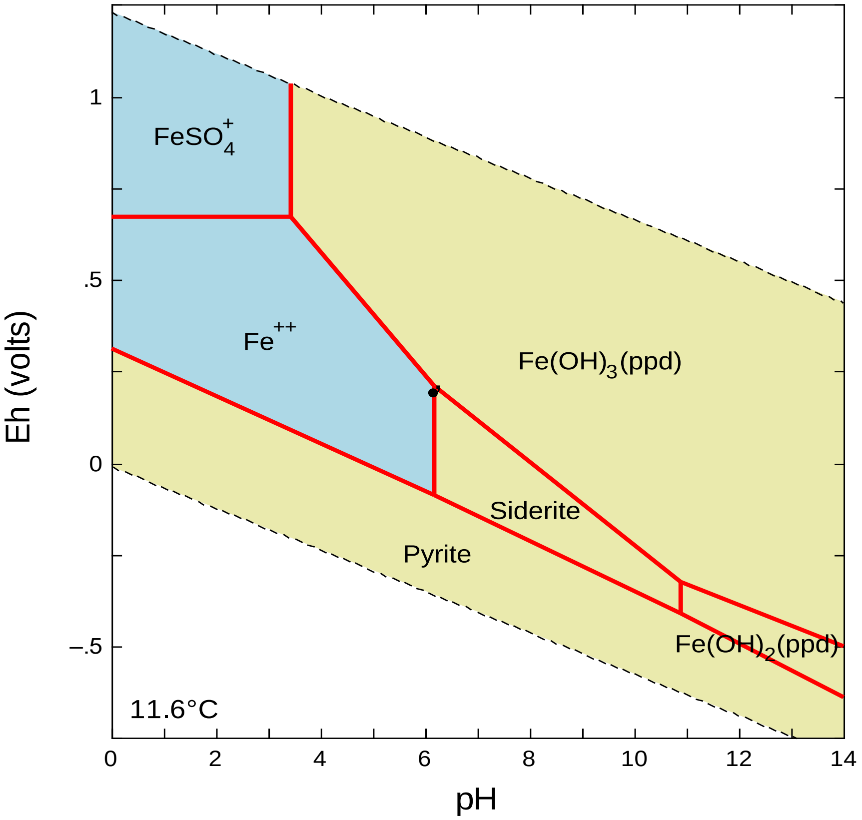

Figure 7. Eh/pH plot of Duman site mine waters for two sample events, 2004.

McElroy (1998) reported on ground water quality and quantity for Cambria County, Pennsylvania including wells in rocks above and adjacent to the L-15 mine-pool. Ground water in the Allegheny group contains about 150 to 300 mg/L dissolved solids, and the waters are mixed Ca-Mg-HCO_3 or Ca-Mg-HCO_3-SO_4 type waters. Unlike the Duman plant influent, ground waters in unmined strata contain low concentrations of sodium. Median composition data from McElroy's report was used to represent ground water from unmined areas in geochemical modeling simulations.

Geochemical Modeling of Mine-pool Water Composition

A conceptual geochemical model of mine-pool quality at the Duman plant was developed and tested with PHREEQC using inverse and forward modeling. The purpose was to determine which geochemical processes were likely to generate water of the observed composition in table 2 for the Duman site, by mixing fractions indicated by quantitative data, and using the simplest possible models. The analyses in table 2 show that most elemental transfer in mixing and reacting involves iron, calcium, magnesium, sodium and sulfate, and in acid waters, aluminum. Simulations were therefore focused on these elements.

The Duman influent is enriched in sodium and depleted in calcium and magnesium compared to the Colver mine-pool and Lower Freeport seam waters, which are the two principal components of the Lancashire 15 mine-pool. Cation exchange of adsorbed sodium for dissolved calcium and magnesium is a feasible explanation for the observed behavior, and has been postulated in ground water flow systems (Back, 1964; Stoner et al., 1985). To obtain the concentrations of iron and sulfate found in the Duman influent, additional sources of these elements were needed when Colver mine water, Lower Freeport seam and ground waters were mixed. Based on Eh measurements and other calculations, pyrite could still be dissolving in the mine-pool (see Fig.. 7) and is the likely source of additional iron and sulfate. Other geochemical processes were considered as alternatives to cation exchange and pyrite dissolution. They were abandoned as unlikely if they produced unrealistic solutions in numeric modeling or required minerals not likely to be present in these rocks.

Inverse modeling solved for all possible mathematical solutions and produced a large set of potential mixes and reactions. The results were screened for mixing fractions that were consistent with pumping records and other quantitative data, and that invoked reactions consistent with mine-pool chemistry and mineralogy. Many inverse model simulations showed that Lower Freeport seam and Colver mine waters comprise most of the source water for Duman. Acid water from the unflooded area was typically included in very small amounts of less than 1%. Scenarios with infeasible mixing fractions or very large mineral transfers were rejected.

Based on the initial screening with inverse modeling, a forward model was developed using cation exchange and adsorption, pyrite dissolution and formation of goethite, a common iron oxyhydroxide mineral. In forward modeling, a starting solution is allowed to undergo specified reactions to produce final water. Element and mineral amounts were adjusted until the final solution had a composition similar to the Duman influent. The comparison of simulated and actual water is shown in table 3. The principal constraints and conditions used in the forward model are:

Mixing Fractions – Lower Freeport seam water 50%, Colver water 30%, ground water 19%, "acid drainage" water 1%.

Mineral reactions – Dissolve pyrite $9x10^{-4}$ moles/liter solution; precipitate goethite if oversaturated, fix partial pressure CO_2 $10^{-1.4}$ atm.

Cation Exchange – add exchangeable cations, calcium $3x10^{-2}$ moles, magnesium $1.3x10^{-2}$ moles, sodium $1.3x10^{-2}$ moles, total exchange capacity $9.9\ x10^{-2}$ moles.

Table 3. Forward Modeling Simulation and Actual Composition of Duman Influent (1)

Solution	pH	Fe	Ca	Mg	Na	SO_4
Simulation	6.69	35.7	37.3	15.1	146	388
Actual	6.55	40.0	39.9	15.1	159	390

(1) pH in S.U., all others in mg/L

In general the simulated and actual concentrations were in close agreement. The quantities of pyrite dissolved, goethite precipitated, and cation exchange capacity were small in comparison to the aquifer matrix encountered along a flow path of several km or more in length. The simulation showed that some of the dissolved iron was removed by exchange and adsorption. Additional iron was removed by the formation of goethite. These results were consistent with the Fe to SO_4 mole ratio plot (Fig.. 5) showing that about 60% of the iron dissolved from pyrite was attenuated within the mine-pool. Exchange also decreased the amount of dissolved calcium and magnesium and increased dissolved sodium. A second forward model using the calcium sulfate salt gypsum and pyrite dissolution also produced a good match between simulated and actual waters. However, solubility calculations showed that all mine waters were at least one order of magnitude or more undersaturated for gypsum. These saturation indices suggest that gypsum is not controlling sulfate concentration, and we have no mineralogical data to confirm or refute its' presence.

The initial modeling efforts showed that the Duman influent mine waters could be satisfactorily described as a product of mixing several source waters, cation exchange, pyrite dissolution and goethite formation. These modeling results were similar to work reported by Chen et al. (1999), who found that mixing, pyrite oxidation, calcite dissolution and goethite formation were the main processes controlling mine water evolution at a Scottish colliery. There are undoubtedly additional mineral reactions and processes taking place in the L-15 mine-pool, but they seem to influence water chemistry and composition to a lesser extent.

Flooded versus Free Draining Mineworks

There are large contrasts in water chemistry between flooded mineworks at the Duman site versus unflooded mineworks at the Sterling 1 discharge. These two sites discharge water from adjoining mines in the same Lower Kittanning coalbed. The unflooded works, which have been abandoned for more than 50 years, still discharge acid water, while the Duman site began discharging circumneutral alkaline water within 10 years after flooding. Water quality data collected in 1984, 1994 and 2004 from the Sterling 1 discharge are summarized in table 4 and compared to the Duman site for the same years. Median sulfate and pH concentrations in the unflooded mineworks are essentially unchanged for the period. In the flooded mineworks, median pH increased about 0.6 units, and sulfate concentrations declined about 50%. Total acidity has declined from about 700 to 500 mg/L at the Sterling discharge in 20 years, and the difference is statistically significant at p=0.01. Acidity at Duman in 2004 is 68 mg/L or about 20% of its' 1984 concentration. The unflooded Sterling 1 mine-water parameters of sulfate, iron and acidity remain 2 to 7 times greater than concentrations than at Duman, even though the Sterling mines have been abandoned for a longer time. Flooding inhibits pyrite oxidation and increases the rate of natural remediation occurring in mine-pools. Stortz et al. (2001) also found that mine flooding results in more rapid water quality improvement. They noted significant increases in pH, and reductions 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.

Table 4. Median Annual Water Quality at unflooded Sterling 1 Discharge and Flooded Duman L-15 Minepool, 1983-2004(1)

Year	Location	pH	T. Acidity	Alkalinity	Fe	SO_4
1983-84	Sterling 1	2.62	710	0	85	850
1994	Sterling 1	2.7	604	0	60	920
2004	Sterling 1	2.7	497	0	102	837
1984	Duman	5.98	340	121	190	775
1994	Duman	6.48	131	182	73	478
2004	Duman	6.58	68	136	38	388

(1) pH in S.U., acidity and alkalinity in mg/L $CaCO_3$, Eq, others in mg/L.

Summary and Conclusions

Water quality in the 35 year old mostly flooded L-15 mine-pool has improved significantly since closure. Changes in water quality occur in two phases, a short term initial flushing of stored relatively soluble acid products, and long term leaching of additional materials and continuing geochemical reactions. Younger (1997) characterizes this process as production of vestigial (stored) and juvenile (continuing pyrite oxidation) acidities. In the L-15 mine-pool, the main period of flushing lasted about 8 years, and iron and sulfate concentrations declined to about 20 to 25 % of their initial values. In 1986, closure and flooding of mines in the overlying Lower Freeport coalbed introduced water of different water chemistry into the L-15 mine-pool. Mixing of these waters abruptly lowered iron concentration from about 200 to 60 mg/L, while sulfate concentration was less affected. Composition of the recharge water influences mine-pool chemistry. The Fe to SO_4 mole ratio rapidly declined in the L-15 mine-pool to around 0.2. About 60 % of the iron dissolved from pyrite is now attenuated by precipitation, cation exchange or other reactions within the mine-pool. Iron attenuation was much less in the initial flushing phase.

The temporal declines in iron and sulfate concentration can be described using curvilinear models. Current mine-pool behavior shows a decline of about 1 to 2 mg/L-year and 10 to 15 mg/L-year for iron and sulfate, respectively. This behavior suggests that geochemical equilibrium will be approached slowly, over a period of decades.

Long term predictions of iron, sulfate or other mine drainage parameters at future dates can be generated from curvilinear models of the current data. However, long term predictions are uncertain because slope of the curvilinear function is a statistical estimate; there may be changes in the mine-pool aquifer and flow system, and mineral solubility constraints could control solution chemistry at low concentrations. The estimated slopes for functions derived for iron and sulfate have standard errors of about 13 to 16%, thus any future projected concentration values should be expressed as a range. A small change in the predictive function can change the estimated time to achieve a target concentration by years.

Mine-pools are young aquifers that are undergoing rapid physical and chemical changes. These changes can include continuing physical breakdown of rocks, collapse or subsidence of roof rock and coal pillars, and opening or closing of other mines nearby. These features may change flow paths, tortuosity, residence time and pumping and seepage rates, all of which may influence mine-pool chemistry. Predicting the exact composition of mine waters as they approach long term equilibrium requires detailed knowledge of the mineralogy and flow characteristics of the aquifer; information which may not always be available. While a local equilibrium condition seems to exist at a given sample point, overall mine-pool composition can be heterogeneous (Perry and Hawkins, 2004).

The L-15 mine-pool is actually a mixture of seepage water from the adjacent Colver mine-pool (about 30%), leakage from the overlying Lower Freeport mine-pool (about 40 to 50%), acid waters from the unflooded northern end of the mine complex, and ground water from unmined strata. Inverse modeling with PHREEQC (Parkhurst and Appelo, 1999) was used to develop and test models of the L-15 mine-pool. The goal was to approximate mixing percentages and geochemical reactions that produce the water quality of the Duman discharge. Simple mixing alone does not explain Duman's chemistry. Forward modeling showed that the continuing dissolution of small quantities of pyrite and formation of goethite provided a close match of modeled and actual water quality.

The Duman discharge is a Na-SO_4 type water, while the waters that contribute to it are of mixed cation composition, where Na is a secondary cation. Cation exchange of dissolved calcium and magnesium for adsorbed sodium provides a feasible explanation for the observed dominance of sodium at Duman. The presence of small amounts of exchangeable sodium along a flowpath as much as 8 km in length would be sufficient to produce a Na-SO_4 solution. Back (1966) in a study of water quality evolution in Coastal Plain aquifers, observed increasing dominance of sodium over calcium and magnesium the further ground water moved along its flowpath.

Comparison of mine waters from flooded and unflooded sections of the L-15 complex shows that the rate of water quality improvement is much more rapid when the mineworks are inundated. Drainage from unflooded sections remains strongly acidic 50 years after closure, while the Duman site began discharging circumneutral water within 10 years of flooding. Chemical concentrations are higher in the free draining section.

The L-15 mine-pool has been pumped at a rate equivalent to about 2 pool volumes a year and is approaching a total of 60 pool volumes. The persistence of iron and sulfate in the mine-pool after this amount of leaching suggests that dispersion, short circuiting and no-flow zones are important, and that some chemical reactions are continuing. The L-15 mine-pool is expected to continue slow improvement in water chemistry, but is likely to require treatment for an extended period.

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Literature Cited

Back, W. 1966. Hydrochemical Facies and Ground-Water Flow Patterns in Northern Part of Atlantic Coastal Plain. US Geological Survey Professional Paper 498-A.

Chen, M., C. Soulsby and P Younger. 1999. Modelling the Evolution of Minewater Pollution at the Polkemmet Colliery, Almond Catchment, Scotland, p 351-362, Quarterly Journal of Engineering Geology, 32.

Cravotta, C. A. III and C. S. Kirby. 2004. Acidity and Alkalinity in Mine Drainage: Practical Considerations, Proceedings America Society of Mining and Reclamation, 2004 pp p334-365. http://dx.doi.org/10.21000/JASMR04010334

Donovan, J and B. Leavitt. 2004, The Future of Mine-Water Discharges From Underground Coal Mines of The Pittsburgh Coal Basin, WV-PA, Proceedings America Society of Mining and Reclamation, 2004 pp 518-528 . http://dx.doi.org/10.21000/JASMR04010518.

Gwin, Dobson, & Foreman. 1972. West Branch Susquehanna River Mine Drainage Pollution Abatement Project, Operation Scarlift, prepared for Commonwealth of Pennsylvania, 181 p.

Hawkins J., E. Perry and M. Dunn 2005, Hydrologic Characterization Of A Large Underground Mine Pool In Central Pennsylvania, Proceedings America Society of Mining and Reclamation, 2005 pp 487-503

https://doi.org/10.21000/JASMR05010487

Lloyd, D. 2004. personal communication, unpublished water quality data for Lancashire 15 mine-pool and associated mines, Lloyd Environmental Services, Commodore, PA.

McElroy, T. 1998. Groundwater Resources of Cambria County Pennsylvania, 49pps, Water Resources Report 67, Pennsylvania Dept of Conservation and Natural Resources, Bureau of Topographic and Geologic Survey, Harrisburg, PA.

Kernic, J. 1999. Barnes and Tucker Company, Lancashire 15 and 20 Mines, Cambria County, Mine Pool and Discharge Report, unpublished report prepared for Pennsylvania Dept Environmental Protection, McMurray District Office, 11 pages.

Kirby, C.S. and C.A. Cravotta. 2004, Acidity and Alkalinity in Mine Drainage: Theoretical considerations, Proceedings America Society of Mining and Reclamation, 2004 pp 1076-1093 .http://dx.doi.org/10.21000/JASMR04011076.

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

Michael Baker Consulting Engineers. 1978. Operation Scarlift Report SL-185, Blacklick Creek Watershed, Indiana Cambria Counties, prepared for Pennsylvania Dept of Environmental Resources, 152 p.

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

Perry, E.F. and J. Hawkins. 2004, Ground-Water Flow and Quality in A Fully Flooded Underground Mine Complex, Proceedings America Society of Mining and Reclamation, 2004 pp 1460-1479. http://dx.doi.org/10.21000/JASMR0401460.

Skousen J., L M. McDonald and J. Demchak. 2004, Longevity of Acid Discharges From Underground Mines Lying Above the Regional Water Table, Proceedings America Society of Mining and Reclamation, 2004 pp 1769 . Abstract

Stoner, J. D., D. R. Williams, T. E. Buckwalter, J. K. Felbinger and K. L. Pattison. 1987. Water Resources and the Effects of Coal Mining, Greene County, Pennsylvania, prepared by the US Geological Survey Water Resources Division, Pennsylvania Geological Survey Water Resources Report 63, Harrisburg, Pa.

Stortz, M., M Hughes, N. Wanner and M. Farley. 2001. Long Term Water Quality Trends at a Sealed Partially Flooded Underground Mine, p 51-65, Environmental and Engineering Geoscience, Vol VII, No.1. https://doi.org/10.2113/gseegeosci.7.1.51

Wood, S.C., P. Younger and N. Robins. 1999. Long-term changes in the Quality of Polluted Minewater Discharges from Abandoned Underground Coal Workings in Scotland, p 69-79, Quarterly Journal of Engineering Geology, 32. https://doi.org/10.1144/GSL.QJEG.1999.032.P1.05

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

Younger, P. 2000. Predicting Temporal Changes in Total Iron Concentrations in Waters Flowing From Abandoned Deep Mines: A First Approximation, p 47-69, Journal of Contaminant Hydrology, 44(2000). https://doi.org/10.1016/S0169-7722(00)00090-5