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APPLICATION OF GEOCHEMICAL MODELING AND HYDROLOGIC TECHNIQUES TO INTERPRET SOURCES, MIXING AND EVOLUTION OF MINE DRAINAGE[1]

by

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Abstract The geochemical code PHREEQC was used in an investigation of potential recharge sources to a flooded pit affected by acid drainage. Pit water quality had been alkaline with low metals and moderate dissolved solids content for at least 15 years. A decline in water quality occurred with a decrease in pH, and increase in dissolved aluminum, manganese and sulfate. The recharge area for the flooded pit included a coal refuse pile, flooded underground mine works, flyash pile, surface minespoil and a sediment pond. A set of water quality samples were analyzed for mine drainage parameters, major dissolved constituents and some trace metals. These data were inverse modeled using the flooded pit water as the end product. Mixing of several possible sources and single source recharge scenarios were run along the inferred ground water flow path. Mixing of coal refuse pile leachate with leakage from the sediment pond or minespoil provided acceptable characterization as the principal sources controlling pit water chemistry. These results were consistent with the ground water flow path interpreted from water level measurements in wells, structure, air photos and mining history. The dominant rock-water interactions modeled were dissolution of carbonate minerals and stored sulfate salts. Simple binary mixing was not adequate to describe the reaction path and resultant water chemistry. Geochemical models were useful for assessing mine drainage sources, and can be included as one of a collection of investigative tools.

Additional Key Words: geochemical models, coal refuse, ground water flow path, mine drainage, water quality

Introduction

This study was performed to identify the pollution source that caused a fish kill in a farm pond, located in Preston county, West Virginia. The main water source for the farm pond is discharge from existing "final cut ponds" on abandoned surface mines, located at the head of the watershed. Mining activity was suspected of causing the adverse change in water chemistry because of an increase in several mining related water quality parameters. These changes included a decrease in pH of about three S.U., an increase in soluble aluminum, sulfate, manganese and titrateable acidity. The final cut pond, locally referred to as the "blue pond" had been in existence for more than forty years and was used for swimming and fishing before being affected. It had been reported to be of "good quality" as verified by sporadic sampling over a 15 year period. The Office of Surface Mining Reclamation and Enforcement (OSM) technical staff were asked to determine if any of the following recent mining activities, including flyash and coal refuse placement, surface mining, and underground mining, were causing the adverse impact; or if the effects were attributable to abandoned mines.

Site Conditions

Discharge from the "blue pond" forms the headwaters of a perennial stream. A farm pond with the reported fish kill is located approximately one half mile downstream and is sustained mostly by flow from the "blue pond." The inferred recharge area for the "blue pond" includes a coal refuse pile, flooded underground mine works, a flyash pile, surface mine spoil and a sediment pond. Locations are shown in figure 1. Potential recharge sources could produce waters of widely differing chemical composition, and control water quality independently, or as a mixture from several sources.

The "blue pond" has only one small feeder stream, and is recharged mostly by ground water. It has a maximum depth of about 15 feet. A large area to the east is covered by minespoil from extraction of the Bakerstown coal bed during the 1950's. Both the flyash pile and coal refuse pile are built directly on minespoil without underdrain or leachate collection systems. During the investigation, both the flyash and coal refuse piles were actively being worked. Ash was trucked in and placed on a daily basis. New material was also added to the refuse pile, while parts of it were simultaneously

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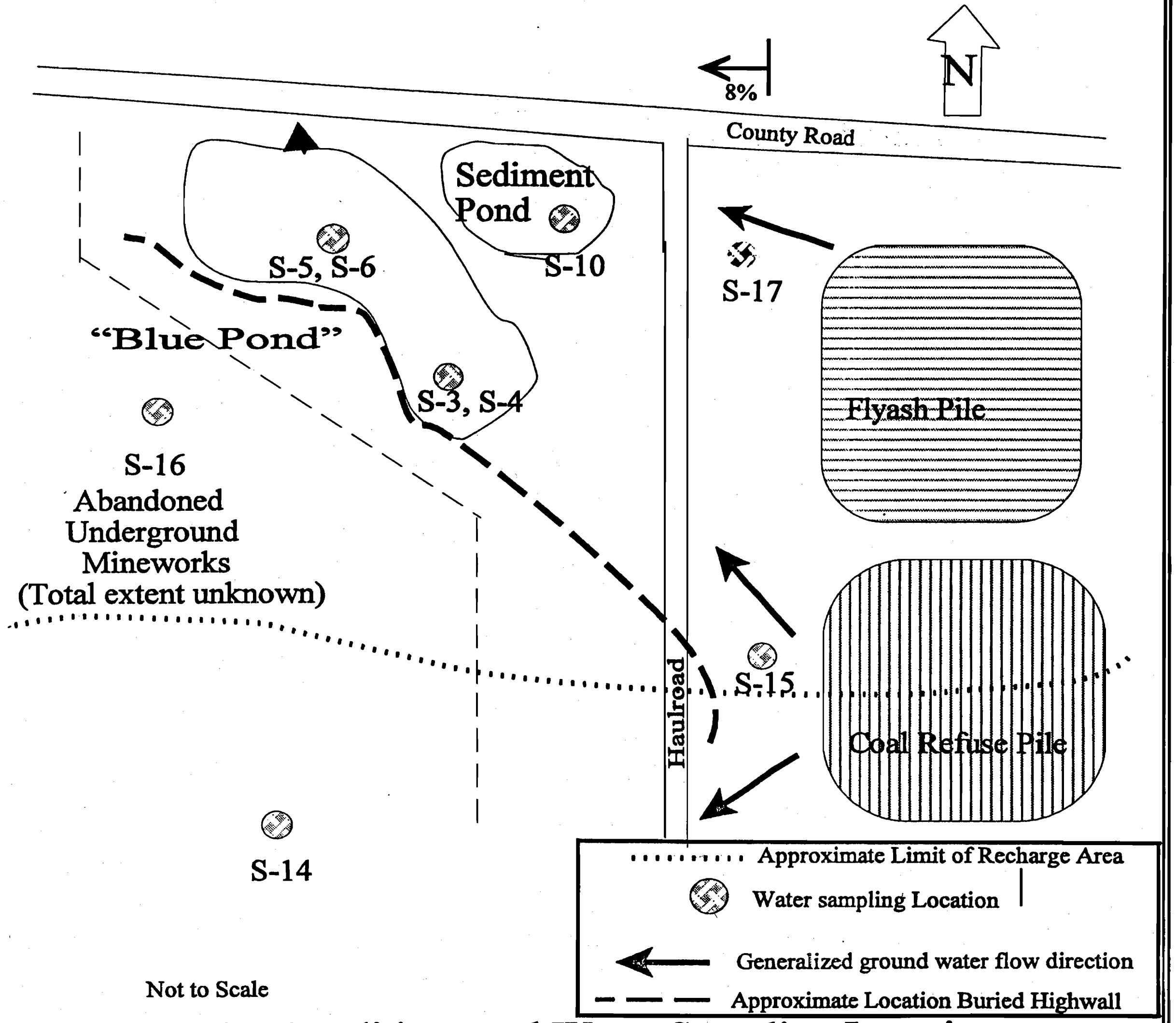

Figure 1 Site Conditions and Water Sampling Locations

being reprocessed.

The sediment pond is immediately adjacent to the "blue pond" (figure 1) and was built by excavating in minespoil. An embankment between the sediment pond and flooded pit is about 30 feet wide and constructed of minespoil. The sediment pond receives runoff from the ashpile and had been in place for more than three years. It has not discharged through the spillway during that time. Drainage is lost by leakage through the embankment or pond bottom.

Abandoned flooded underground mineworks in the Bakerstown coal bed are located west of the blue pond" Mine maps are incomplete and the total extent of the mineworks is unknown. A buried highwall is present approximately parallel to the haulroad and adjacent to the underground mine works. It is not known if surface mining intercepted the underground mine works. The entire area is underlain by deep mines in the stratigraphically lower Upper Freeport seam.

Surface and underground mining and coal refuse placement have occurred at various periods in both the Bakerstown and Upper Freeport coals since the 1940's, continuing into the 1990's. Timing and extent of mining were interpreted from mine maps, air photos and site examination.

Geology and Geochemistry

Strata in the study area include the Upper Freeport Coal (lowest mined coal) at the top of the Allegheny Formation. The Bakerstown Coal (Conemaugh Group) is approximately 195 feet statigraphically above the Upper Freeport Coal. The Conemaugh Group is composed of limey mudstones, gray shales, and limestone, with lessor amounts of sandstone. The rocks in the area strike almost due north with a corresponding dip of 8 % almost due west. The strike and dip of the coal seams and associated strata were controlled by anticlinal and synclinal features resulting from post-depositional tectonic activity. The axis of a small anticlinal structure passes underneath the refuse pile, and is oriented approximately east-west.

Geochemically, the Bakerstown minespoils and overburden are calcareous and generate moderately buffered waters. The coal refuse, generated from cleaning the Upper Freeport seam, is however pyritic, lacks carbonates and typically produces strongly acidic drainage. For this reason, Upper Freeport coal refuse is placed on the calcareous Bakerstown coal surface mine spoil as an acid prevention method. The flyash material is highly alkaline. Representative analyses of these materials are shown in Table 1.

Table 1 Representative Acid/Base Accounting Characteristics of Bakerstown Overburden and Minespoil, Upper Freeport Coal Refuse and Flyash

Material	Potential Acidity (From % Sulfur, (ppt $CaCO_3$ Eq)	Neutralization Potential (ppt $CaCO_3$ Eq)	Paste pH
Coal refuse, Upper Freeport seam	89.4	6.8	4.1
Shale, Bakerstown overburden	2.0	61.9	8.6
Bakerstown Minespoil	8.8	21.9	7.5
Flyash	0.5	727.1	12.4

Ground water Hydrology

Ground water flow at these mines is controlled by topography and the stress relief fracture systems that were created through erosional unloading. Ferguson (1974), and Wyrick and Borchers (1981), describe fracture flow path creation in rocks of the Appalachian coal basin. Surface mining within the fracture flow ground water systems serves as a ground water sink (center of a cone of depression) during mining and frequently as a ground water mound (recharge area) after reclamation occurs. Hydraulic conductivity of the mine spoil material and the rock unit (pavement) beneath the lowest coal mined in part controls the amount of mounding that will occur. Structure (dip) of the pavement also influences the size and direction of flow from the ground water mound. The pavement is frequently of lower hydraulic conductivity than the surrounding rock (Hawkins,1998) which leads to the development of a ground water mound that can discharge (as seeps or springs) at the coal outcrop area or recharge the coal aquifer.

At this site, the Bakerstown surface mine spoil is interpreted to act as the recharge area for the "blue pond" and abandoned underground mine works. A thin water table, about 2 to 4 feet thick, has developed in the minespoil, and is monitored in several wells. Based on well readings, location of seeps and buried highwall, and coal structure, the general ground water flow direction is from the coal refuse and flyash piles toward the "blue pond" (Figure 1). The small anticline beneath the refuse pile acts as a ground water divide. Ground water flow south of the divide is to the southwest, away from the "blue pond".

Methods

This hydrologic evaluation included airphoto interpretation, site reconnaissance, hydrologic and geologic data acquisition, graphical analysis of geologic and hydrologic information, and geochemical modeling using PHREEQC.

Airphoto Interpretation

Aerial photos from 1938, 1953, 1967 ,1980 and 1990 flights of the area were reviewed. The 1938 photos indicated no mining related disturbances in the study area. However, by 1953 surface mining had already occurred along the county road adjacent to the "blue pond". Surface mining was occurring in 1967 in the area that would later (in the 1990's) serve as the flyash and refuse placement areas. Refuse placement was also identified south of the "blue pond"..

Site Reconnaissance

Several site visits were made to establish the magnitude and extent of current and past mining practices. The field reconnaissance techniques included comparison of aerial photos to validate extent of mining and reclamation activities; field measurement (quality and quantity) of streams and ground water discharges; vertical profiling of specific conductance and temperature values for the "blue pond"; detection and measurement of unsealed coal exploration drill holes for water quality and water levels; and evaluation of the geochemical nature of the refuse, mine spoil, and flyash disposal areas.

Hydrologic and Geologic Data Acquisition

Existing water quality analyses for various mine sites, the "blue pond", ground water discharges and receiving streams were compiled to characterize site hydrology. From this baseline, field reconnaissance efforts were refined, and a sampling plan was developed to characterize current site conditions. A set of eighteen water quality samples from the "blue pond" and potential sources were analyzed for mine drainage parameters, major dissolved constituents and some trace metals.

Geologic data were compiled from maps, cross sections and drill logs and were validated, where possible, by field observations.

Water Chemistry and Geochemical Modeling

Water chemistry data were first examined visually, and by simple graphical methods including Stiff and trilinear plots (Hem, 1989). Dominant ions were identified and composition and concentration compared among samples. Then, PHREEQC (Parkhurst,1995) was employed to inverse model the "blue pond" water as an end product solution of one or more recharge sources. An initial modeling run was performed to calculate saturation indices for minerals potentially involved in reactions. A refined model was built using those minerals identified as possible participants in precipitation/dissolution reactions. The inverse model calculates the mass balance transfers of these minerals and gases to acccount for the difference between the starting and ending solutions, including mixing of two or more sources. Potential recharge sources were included as the starting solution, with PHREEQC calculating possible mixes and precipitation or dissolution of mineral phases. Model file output included aqueous phase speciation, mixing percentages, mole transfers for phase minerals involved in mass balance and mineral saturation indices

Modeling was conducted for six water samples using the options shown in table 2. Oxidation/reduction potential was not measured at sampling, so the default value of pe = 4 was used. Therefore speciation calculations performed by PHREEQC among valence states for redox sensitive species iron and manganese are not valid. Silica was not analyzed, and a value of 20 mg/l silica was arbitrarily specified for each solution to allow the consideration of silicate minerals in the model. Several runs were conducted without the minimal option, and other simulations were made that included defined ion exchange properties and a sampling point outside the recharge area.

Table 2 Inverse Model Parameters for Six Sample Solutions

Uncertainty Value	5% (11% for S-16)
Mineral Phases	calcite, dolomite, gypsum, jurbanite, rhodochrosite (all allowed to dissolve or precipitate)
Mass Balance Constraints	Sodium, Chloride in addition to elements in mineral phases
Phase Constraints	Minimal phases needed to satisfy mass balance constraints
Solution Composition	Specified for analytical parameters, field temperature, default pe =4
Mixing	Allowed
Evaporation	Not allowed

Results and Discussion

Ground Water Flow Path

A buried highwall, combined with structure directs ground water flow from the refuse pile toward the "blue pond" (Figure 1). Location of the buried highwall was inferred from several maps, drill logs, and air photos and close inspection of surface topography and soil conditions. A portion of the highwall is exposed on the southwest side of the "blue pond".

In spite of the relatively flat site topography and humid climate, only a thin water table (maximum thickness about four feet), is present in the minespoil. A thin saturated zone under relatively high recharge implies that the aquifer has moderate to high hydraulic conductivity. Hawkins(1998) has noted that hydraulic conductivity of bedrock is often a order of magnitude less conductive than the corresponding minespoil. With these conditions, the highwall can divert flow direction of ground water in the more conductive minespoil.

The final conceptual ground water flow model was : recharge from the refuse pile and minespoil was building a thin water table on the coal pavement and flowing down dip in a generally northwest direction. Upon reaching the buried highwall, flow was diverted and followed the highwall into the "blue pond". Some minor leakage into or from the highwall could occur along the flow path. Ground water recharge would enter the "blue pond" at its' southeast end.

About one year after we finished this

investigation , the "blue pond" was drained by the mining company. Ground water was observed to be discharging from the minespoil into the southeast end of the pond (Dixon,1998), as would be expected from the conceptual ground water flow model.

Water Quality

Chemical quality of the "blue pond" and several potential recharge sources is shown in table 3. Samples S-3 and S-4, and S-5 and S-6, are paired samples from two locations in the "blue pond", taken at the surface and at the bottom. Aluminum and manganese, not iron, are the dominant dissolved metals. Overall water composition is calcium-magnesium-aluminum sulfate. Water in the "blue pond" was found in field surveying to be stratified by chemistry and temperature. Vertical profiling of temperature and specific conductance showed the upper 2.5 feet of the water column (samples S-3 and S-5) to be distinct from deeper water (S-4 and S-6). The deep water is more mineralized with higher levels of dissolved constituents than the more dilute surface. Modeling the "blue pond" was therefore conducted for both the surface and bottom stratified waters. While the pit water is vertically stratified, samples within each layer show consistent composition, indicating the pond is well mixed.

Samples S-10 (sediment pond, calcium-magnesium-sulfate-bicarbonate water), S-15 (coal refuse pile, calcium sulfate water), S-16 (underground mine, calcium-magnesium-bicarbonate water) and S17(Bakerstown minespoil monitoring well, calcium-magnesium-sulfate-bicarbonate water) represent potential recharge sources to the "blue pond". Sample S-14 (calcium-magnesium-sulfate water) is an acid discharge located outside the recharge area. S-14 was included in the analyses as an additional check on the interpretation of recharge sources and mixing of waters

None of the recharge sources contain dissolved aluminum and magnesium in amounts that could explain the composition of the "blue pond" water. Dissolution of soluble aluminum and magnesium bearing minerals, ion exchange or mixing of several sources were considered the likely processes influencing evolution of the "blue pond" water quality.

Table 3 Water Quality Data of the "Blue Pond" and Potential Recharge Sources

Sample ID	S-3	S-4	S-5	S-6	S-10	S-14	S-15	S-16)	S-17
Field pH	4.42	4.20	4.38	4.20	8.3	3.2	3.7	6.8	7.0
Sp. Cond.	1668	2850	1689	2730	812	2150	3540	262	844
Alkalinity	0	0	0	0	78.3	0	0	106.7	166.1
Total Acidity	152	326	156	251	0	167	290	0	0
Ca	181.2	297.7	182.6	282.4	102.9	290.9	785.9	36.5	150.2
Mg	87.4	158.9	88.4	148	30.8	80.8	72.7	7.3	24.1
Na	39.6	65.1	40.1	61.9	20.	18.3	62.9	1.9	29.6
K	4.2	6.3	4.3	5.7	4.6	2.9	16.9	1.0	3.4
SO_4	1001	1860	1015	1731	297	1852	2603	16.9	317
Cl	10.6	12.3	10.6	12.1	29.7	3.	9.9	6.8	26.5
Dis Al	26.7	71.5	27.4	63.7	0.13	24.3	46.9	0.04	0.04
Dis Fe	0.29	0.24	0.35	0.27	0.02	46.0	2.86	0.02	6.25
Dis Mn	8.77	16.8	8.98	15.4	0.31	5.15	5.16	0.01	0.01

SEE FIGURE 1 FOR SAMPLE LOCATIONS. Field pH in standard units, specific conductance in umhos/cm @25°C. Alkalinity and Acidity in mg/L $CaCO_3$ Eq, all other parameters in mg/L. S-3 and S-5 are surface samples from the "blue pond", S-4 and S-6 are samples from the bottom of the "blue pond", S-10 is sediment pond, S-14 is mine water from outside the recharge area, S-15 is coal refuse pile leachate, S-16 is flooded underground mine works, and S-17 is minespoil monitoring well.

Table 3 shows the "blue pond" and refuse pile waters to be of similar composition. Since the pit water had been acidified, acidic refuse leachate was considered a likely cause. Other sources within the recharge area exhibited neutral to alkaline water quality, but mixing of several sources was considered possible based on location, inferred ground water flow directions and field observations..

The dominant ions in the "blue pond" include sulfate, calcium, magnesium, sodium and aluminum. Mineral phases were specified in modeling that contain all the dominant elements except sodium. Sodium and chloride were expected to behave conservatively. Sodium bearing minerals natrojarosite and mirabilite were examined for inclusion in the model, but were rejected when they caused mass balance errors, or were considered unlikely to be present in these rocks. Carbonate minerals calcite and dolomite were included because the Bakerstown overburden and minespoil contain as much as 20% carbonate. These carbonates probably are not pure calcite, as most water samples show significant concentrations of both calcium and magnesium. Gypsum was included as a potential precipitation product of calcium and sulfate.

Several aluminum bearing minerals were examined for inclusion in the model. Gibbsite was included, as the deep "blue pond" water is very near saturation for this mineral (saturation index +0.03) Saturation indices for selected minerals are shown in table 4 for the six waters included in modeling.. Two aluminum sulfate minerals, basaluminite and jurbanite, were examined for use in the model to satisfy mass balance transfers of aluminum from solid to liquid phase. Use of either mineral produced satisfactory mixing results. The coal refuse pile had observable metal sulfate minerals forming during dry periods. These salts would dissolve during precipitation events, thereby loading ground water with dissolved metals (aluminum and iron) sulfate and other species. The mineral rhodochrosite was included to provide a source/sink for manganese. Manganese has been shown to occur as a trace inclusion in siderite in Pennsylvanian coal measures (Morrison, 1990) as part of a solid solution series of carbonates. Mixed carbonates of indefinite composition are not included in PHREEQC.

Mixing Models Evolution of the stratified deep "blue pond" layer could be accounted for by mixing of refuse pile water (S-15) and a small amount of either leakage from the sediment pond (S-10) or minespoil ground water (S-16). Calculated mixing percentages and mineral transfers for the two models found are :

> Model 1- Refuse Sump(S-15), 88.3%; and Sediment Pond (S-10), 11.7%; calcite, gibbsite and gypsum precipitate; dolomite, jurbanite and rhodochrosite dissolve.
>
> Model 2-Refuse Sump (S-15), 90.7%; and Minespoil water (S-16), 9.3%; calcite, gibbsite and gypsum precipitate; dolomite, jurbanite and rhodochrosite dissolve.

Both models are reasonable representations. The sediment pond, adjacent to the "blue pond" does not discharge at the surface, but leaks through the bottom or sides. It's water level fluctuates but does not drop below the flooded pit water surface elevation. Bakerstown minespoil ground water flow direction is interpreted to be toward the "blue pond" based on structure and water level elevations. Due to its location and observed behavior, leakage from the sediment pond is considered the most feasible model.

Table 4 Mineral Saturation Indices in Six Waters

Sample	S-3	S-4	S-10	S-15	S-16	S-17
Calcite	-----	-----	0.69	------	-1.28	-0.43
Dolomite	-----	-----	1.20	-----	-3.13	-1.52
Gibbsite	1.59	0.03	0.90	-1.81	2.46	2.54
Basalumnite	1.69	0.90	-6.04	-5..20	5.45	6.71
Jurbanite	0.91	1.14	-7.16	0.45	-2.87	-2.01
Gypsum	-0.59	-0.29	-1.10	0.18	-2.48	-0.91
Rhodochrosite	-----	-----	0.49	------	-3.27	-2.13

SEE FIGURE 1 FOR SAMPLE LOCATIONS S-3 and S-4 are surface and bottom samples of "blue pond", S-10 is sediment pond, S-15 is coal refuse pile leachate, S-16 is flooded underground mines, and S-17 is minespoil well.

The apparent precipitation of calcite during modeling is due to the very high calcium levels present in one of the initial solutions; the coal refuse sump. This unlined basin is excavated in Bakerstown minespoil and collects acidic drainage from the coal refuse. It probably has already dissolved carbonate in the basin. The refuse sump is also slightly oversaturated with respect to gypsum and jurbanite (table 4), suggesting that calcium and aluminum may be at equilibrium with these minerals. The end product deep "blue pond" water (S-4) is slightly undersaturated for gypsum.

No mixing model was found that included the flooded underground mine works, except if evaporation was allowed, or by arbitrarily increasing the data uncertainty tolerance to more than 20 percent. In the humid climate of Appalachia, substantial evaporation is unlikely.

Five models were found that could account for evolution of the "blue pond" surface layer. Three explicitly include mixing with the deep stratified layer. The calculated mixing percentage and mineral transfers are:

> Model 1: Refuse sump (S-15) 59.1%, flooded underground mine works (S-16) 32.5%, sediment pond (S-10) 8.4%; calcite, jurbanite and gypsum precipitate, dolomite, rhodochrosite and gibbsite dissolve.
>
> Model 2: Flooded underground mine works (S-16) 42.5%, "blue pond" deep stratified layer (S-4) 57.6%, jurbanite and dolomite precipitate, gibbsite dissolves.
>
> Model 3 Refuse sump (S-15) 7.6%, flooded underground mine works (S-16) 42.7 %, "blue pond" deep stratified layer (S-4) 49.7%, calcite and jurbanite precipitate, and gibbsite dissolves.
>
> Model 4 "blue pond", deep stratified layer (S-4) 54.8%, flooded underground mine works (S-16) 45.2%, calcite and jurbanite precipitate, gibbsite and gypsum dissolve.
>
> Model 5 Refuse sump (S-15) 57%, flooded underground mine works (S-16) 32.9%, minespoil monitoring well (S-17)10.2%, calcite, gypsum and jurbanite precipitate, dolomite, rhodochrosite and gibbsite dissolve.

Model 2, 3 and 4 are regarded as feasible representations of evolution of the surface layer. Mixing percentages are considered reasonable based on site conditions, and the mineral reactions involve transfer of only aluminum, calcium, magnesium and sulfate. The two models which do not explicitly include some mixing from the deep stratified layer are regarded as hydrologically unlikely.

Modeling of the surface stratified water was conducted with and without minimal constraints. A minimal run produces models that contain the minimum phase and mass balance transfers needed to satisfy constraints and uncertainty. Sixty five models were produced from a run without minimal constraints. None differed greatly in mixing sources and percentage from the five minimal models. It was concluded that the minimal models provided satisfactory representation of geochemical processes.

Mixing Percentages The mixing percentages calculated by PHREEQC for evolution of the "blue pond" bottom water indicate about 90% of the recharge comes from the refuse pile. On the date of sampling, the"blue pond" was discharging about 10 gallons per minute (gpm), inferring the refuse pile should recharge the pit at about 9 gpm. This value appears high, based on the size and dimensions of the refuse pile. Thus the modeling supports the original hypothesis that the refuse pile was contributing acid drainage. However, the mixing percentages are interpreted as approximations and not exact values. The production of more than one feasible model shows that the solutions are nonunique.

Ion Exchange An attempt to include a defined ion exchanger in the model proved unsuccessful. An ion exchanger with a cation exchange capacity of 10 meq/100 g of solid was assigned various percentages of calcium, magnesium, sodium, potassium, aluminum and proton acidity. Significant charge balance errors resulted regardless of the assignments. From this exercise and inspection of the raw data, it was concluded that the ion exchange was not a significant process in "blue pond" water evolution.

Other Acid Sources A modeling simulation was also conducted which included an abandoned mine discharge (S-14) located outside of the recharge area for the mine pit. This discharge was modeled since it was acidic and was somewhat similar to the "blue pond" water. No feasible models were found that included this discharge as either a single source or mix component recharging the flooded pit. These results were consistent with field observations and hydrologic interpretation which excluded this drainage from the recharge area. No further modeling was attempted with this sample.

Metal Sulfate Mineral Phases The addition of an aluminum bearing mineral was necessary to mass balance the model of the deep pit water. Many metal sulfate minerals can form as intermediate products of pyrite oxidation; Nordstrom (1982) describes a series of iron sulfate minerals with varying stoichiometry and degree of hydration. Cravotta (1994) also refers to formation of iron sulfate minerals in acidic surface mine spoil in Pennsylvania, and Bayles and Olyphant (1993) identified copiapite, melanterite, rozentite szmolnokite at a coal refuse site in Indiana . A similar suite of aluminum sulfate minerals also occurs, including compounds such as jurbanite, alunite, and basalumnite. These minerals are contained in the Wateq4f database used by PHREEQC. The database is not however, all inclusive, especially for complex or unstable minerals. Other hydrated aluminum sulfate minerals such as halotrichite ($FeAl_2(SO_4)_4*22H_2O$ and pickeringite ($MgAl_2(SO_4)_4*22H_2O$) can form in acid minespoil. The inclusion of jurbanite in the model is interpreted as representing one, or perhaps several aluminum sulfate minerals not in the database, that dissolve and enter ground water system during recharge events. Model results are not interpreted to represent that jurbanite is actually present.

SUMMARY AND CONCLUSIONS

A flooded mine pit ("blue pond")that had "good" water quality for at least 15 years was acidified within a six month period. Total acidity, dissolved sulfate and aluminum increased and pH declined about three units. The "blue pond" is maintained mainly by ground water recharge. Within the recharge area, several possible sources were present including abandoned surface and underground mines, and active flyash and coal refuse piles. These sources could produce water of varying composition. The coal refuse pile was considered the probable source of acidification, but might be mixing with other ground water sources. Field reconnaissance, map and air photo interpretation were combined with mining and stratigraphic information to delineate a probable recharge area and flow path. The "blue pond", which was chemically stratified, was used as the end product solution in inverse modeling with PHREEQC. Modeling of the deep stratified layer produced two feasible solutions. Both models showed the refuse pile leachate was the dominant control on the deep "blue pond" chemistry, mixing with a small amount of leakage from an adjacent sediment pond, or minespoil ground water. Five models were produced that could describe evolution of the surface layer of pit water. Three included mixing of the flooded underground mine works and the deep "blue pond" layer. Dominant mineral reactions occurring in the system are the dissolution of carbonates and metal sulfates. Simple binary mixing was not adequate to describe evolution of water quality in the "blue pond".

Geochemical modeling produced results that were consistent with the physical flow system. The models produced are not necessarily unique, and should be interpreted as approximations, not exact solutions. Geochemical models can be useful as one of a collection of investigative tools to determine source waters .

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