

# GEOCHEMICAL FORECAST OF ACID MINE DRAINAGE TO EVALUATE CORRECTIVE ACTION PLANS FOR MINE RECLAMATION<sup>1</sup>

by

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**Abstract.** A geochemical model was developed as part of the site investigation to characterize current geochemical conditions in coal refuse disposal areas and to support a modification to the reclamation plan at a closed underground coal mine in southern Illinois. The model provided significant insight into the geochemical processes which impact the development of a reclamation plan for the mine. Specifically, the geochemical model was designed to simulate the actual chemical reactions between infiltrating water and coal refuse and/or soil. The modeled acid mine drainage (AMD) was calibrated to observed conditions. Once these chemical reactions were understood, new geochemical models were developed to predict the effectiveness of proposed reclamation activities on ground-water quality. Development of the geochemical model proceeded in two steps: (i) construction of a detailed conceptual model which accounted for all reaction paths; and (ii) computer geochemical modeling to confirm the validity of each reaction path using MINTEQA2 and PHREEQE. Mineralogical analysis of the coal refuse confirmed that pyrite was the mineral responsible for the AMD, therefore the conceptual model focused on pyrite dissolution and the generation of sulfate. The computer modeling accurately predicted the resulting sulfate concentrations in the AMD observed for all reaction paths in the conceptual model. Once the system was adequately characterized by a geochemical model, new models were generated and validated via comparison to ground water analyses, followed by computer modeling to forecast the impact of a range of corrective action scenarios on the ground water. The forecast models were then used in conjunction with a ground-water flow model to evaluate the overall effectiveness of each component of the reclamation plan. The selected reclamation plan consists of hydraulic control of impacted ground water by pumping and construction of an enhanced cover system comprising a compacted clay liner overlain by a soil cover. This paper demonstrates how geochemical modeling is a valuable tool to use in evaluating and developing solutions for surface mine reclamation.

Additional Key Words: Leaching, ground water, modeling

## Introduction

Successful reclamation of a mine site does not necessarily end with the aesthetic restoration of the local landscape. Regulatory agencies must also

be convinced that the site will not adversely impact the environment in the future, particularly water resources. The site must be closed in such a manner that a monitoring system and protective measures are in place to evaluate ground-water conditions and prevent degradation of those resources.

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Effective evaluation of reclamation alternatives requires the integration of engineering-feasibility assessment and hydrogeologic/geochemical modeling. Each component of the study impacts the others: such that the final reclamation strategy may have required numerous iterations of modeling various combinations of engineered-covers and ground-water control scenarios (Gentile, et al; 1997). This paper discusses an approach to modeling the geochemical conditions at a site marked by acid

mine drainage (AMD) and using this model to forecast the impact of different reclamation strategies. This work was part of a larger, integrated study also involving surface-water infiltration and ground-water flow modeling as well as engineering design. The objective of this study was to formulate a reclamation plan for the site that would be protective of the environment and acceptable to state regulators.

### Integrated Site Characterization

#### Location

The mine site is located on a 250 acre (118 hectare) tract of land approximately one mile (1.6 km) northwest of Shawneetown, Illinois, as shown in Figure 1. The mine operated as an underground coal mining facility from approximately 1968 until July 1993. The surface operations consist of coal refuse management impoundments (used for disposal of coarse coal mine waste (gob) and coal slurry from coal washing), the tippel area (underground mine access), lakes and ponds, water supply wells, and ground-water monitoring wells.

#### Hydrogeology and Ground-Water Chemistry

The mine site is located at the eastern edge of the Saline Valley, a broad valley which is drained by the Saline River, its tributaries, and several artificial drainage channels. The Saline Valley is filled with fluvio-glacial sands and gravels of the Pleistocene-age Henry Formation (Nelson and

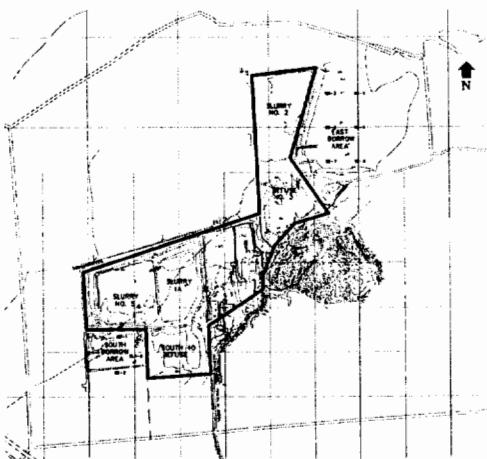


FIGURE 1. Site location map with the coal refuse impoundments outlined. The site sits in the Saline Valley, with the Shawneetown Hills adjacent to the Southeast.

Lumm, 1983). The Henry Formation is also the local aquifer (Henry Aquifer) which could be adversely impacted by refuse disposal activities. Ground water in the Henry Aquifer can be characterized as hard to very hard, slightly oxidizing, with moderately high alkalinity (Table 1). This ground water can also be considered to have significant buffering capacity.

The site is bounded to the east by the Shawneetown Hills, which rise approximately 230 ft (70m) above the valley floor. The rock comprising the Shawneetown Hills and underlying the Saline Valley fill consists of Pennsylvanian sandstones, siltstones, limestones, shales, clays, and coals. The finer sediments, particularly adjacent to coal seams, are marked by abundant pyrite.

### Coal Refuse and Acid Mine Drainage

#### Coal Refuse Characteristics

Coarse Coal Refuse. The coarse coal refuse (gob) consists of rock (shale) and sub-grade coal removed during coal washing operations. Early in the development of the mine, gob was disposed in trenches excavated approximately to the water table. Gob was also used to construct berms for the slurry impoundments. Two representative samples of gob were collected from the refuse impoundments.

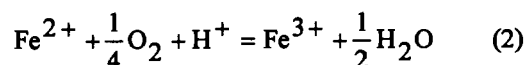
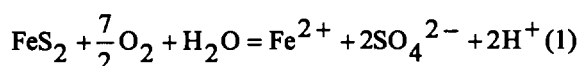
Mineralogic analyses of the samples using x-ray diffraction show that the gob is about 60 percent clay of which about 50 percent is mixed layer illite/smectite and about 10 percent is kaolinite (Table 2). Pyrite is the next most abundant mineral ranging in concentration from 9 to 19 percent. Calcite, sodium feldspar (albite), quartz and gypsum are present at concentrations of 5 percent or less. The gypsum is believed to be a secondary mineral resulting from weathering of pyrite and calcite (Weaver, 1995). The remaining 10 to 15 percent is primarily coal.

Coal Slurry. The coal slurry consists of sand-sized coal, rock, and mineral particles which are a waste product from coal washing operations. The coal washing waste is pumped as a slurry to the impoundments constructed on site. As the particles eventually settle, the supernatant is recirculated and returned to a make-up lake. Depending upon economics, slurry ponds are sometimes "mined" for recoverable coal (carbon recovery).

Mineralogically, coal slurry is similar to gob. Major differences are that the content of pyrite is lower (ranging from 8 to 11 percent) and that calcite and gypsum were not present in the samples. Mineralogical analytical results of two representative slurry samples are summarized on Table 2.

### Acid Mine Drainage

The acidic and sulfate-rich leachate generated in mining or mining waste areas is termed AMD. AMD forms when sulfide minerals in mine waste are weathered in oxidizing conditions (e.g., in the presence of water and oxygen). In coal regions, pyrite and marcasite (FeS<sub>2</sub>) are the most common iron sulfides. As the principal sulfide mineral observed at this site is pyrite, only the oxidation of pyrite is considered in this study. The oxidation of pyrite and generation of AMD occurs through numerous reactions, the four most significant of which are as follows.



Constituent	Concentration
Cl (mg/l)	47
SO <sub>4</sub> (mg/l)	17.32
Fe-total (mg/l)	12.42
Mn-total (mg/l)	0.114
TDS (mg/l)	487
Redox Potential (mv)	+87
Alkalinity (as CaCO <sub>3</sub> mg/l)	358
pH	7.38

<sup>1</sup>Values are a summary of data from four townships surrounding the site as compiled from the Illinois State Water Survey database (1938-1992).

Table 1. Summary of ground water quality in the Henry Aquifer, Saline Valley area.

Sample	GW-6	GW-9	GW-4	GW-11
Sample Type	Gob	Gob	Slurry	Slurry
Sample Depth (ft)	15	12	10	10
Quartz	5	5		5
Albite	5		5	5
Calcite	3	1		
Gypsum	3	1		
Pyrite	9	19	11	8
Illite I/S <sup>3</sup>	54	55	59	54
Kaolinite	9	8	15	18

<sup>1</sup> Results are expressed as relative percents

<sup>2</sup> Values do not equal 100 Percent due to varying levels of non-mineral components in each sample

<sup>3</sup> Denote mixed-layer illite/smectite

Table 2. Mineralogic analyses of coal slurry and gob

Equation 1 details the oxidation of pyrite to form ferrous (reduced) iron, sulfate, and acidity. In Equation 2, ferrous iron is oxidized to ferric iron. The ferric iron then follows two possible (and not mutually exclusive) reaction paths: (i) the ferric iron is hydrolyzed to generate ferric hydroxide and acidity; or (ii) the ferric iron can act as an oxidant and react with pyrite, a reaction much like that described in Equation 1.

Equation 2 is known to be the rate-limiting step because abiotic chemical conversion of ferrous iron to ferric iron is kinetically slow at low pH's. Iron-oxidizing bacteria (specifically *Thiobacillus ferrooxidans*) have been observed to enhance and accelerate iron oxidation (Kleinman, et al., 1981; Leathen et al. 1953).

From the four equations presented above, it is observed that oxygen and water are required for the AMD-generation process to proceed. Isolation of the mine waste from either air or water effectively ceases AMD generation.

### Facility-Related Effects on Geochemistry

The facility-related effects of interest to this study are those that result in: (i) weathering of the unstable minerals in the coal slurry and gob; and (ii) infiltration of the mineralized water (AMD) to the ground water.

Gob Disposal Activities. Gob first removed from the mine was initially deposited in trenches which were dug with a dragline approximately to the water table. The gob was also used to create coal slurry pond berms and as a cover material for inactive coal slurry ponds. Placement of the gob in the above areas occurred over long periods (years in some cases) resulting in lengthy exposure to the elements air and precipitation. As a result of the exposure to the elements and the high pyrite content (9 to 19 percent) of the gob, AMD surface runoff from the gob disposal area into a collection sump showed total dissolved solids (TDS) values up to 9,000 mg/l, sulfate up 5,200 mg/l and pH values as low as 2.7.

AMD is also generated by infiltrating precipitation. Mixing of AMD with recharge water results in a high TDS (mineralized) ground-water plume beneath the disposal areas. The primary AMD-related component of the TDS is sulfate as it is the domination species.

Coal Slurry Disposal Activities. Coal slurry disposal also generates AMD which can impact ground water. The slurry was placed in ponds over periods of several years, allowing the reactive pyrite to be exposed to water and air. Samples of the supernatant from slurry pond sumps show TDS values up to 6,800 mg/l, sulfate concentrations up to 4,200 mg/l and pH values as low as 2.9. The somewhat lower TDS and sulfate concentrations in coal slurry-derived AMD compared to gob-derived AMD may be due to the observed lower pyrite concentrations in the slurry or relatively lower concentrations of more soluble pyrite forms (e.g., lower framboidal or granular pyrite concentrations).

### Geochemical Model - Development of Existing Conditions

#### Overview

The geochemical model was constructed to attain three principal goals:

- closely match actual ground-water analyses for each water being modeled;
- allow for variability in actual conditions that influence ground-water composition; and
- form a basis for predictive modeling of coal refuse material and ground-water interactions as a result of the Reclamation Plan.

It was particularly important to replicate and predict sulfate and TDS concentrations as these are the most significant factors leading to possible ground-water quality degradation. Furthermore, as sulfates generally account for approximately 50 percent of the elevated TDS concentrations, the modeling focused primarily on sulfates.

The geochemical model was also required to be constrained by the following:

- realistic input parameters for the water composition and mineral assemblage in the gob and coal slurry;
- the presence or absence of atmospheric gases as appropriate; and
- realistic thermodynamic parameters for near-surface conditions.

#### Modeling Software

Two geochemical modeling software programs were used in this study: (i) MINTEQA2, developed by the U.S. Environmental Protection Agency (USEPA) (Allison, et al, 1991); and (ii) PHREEQE, developed by the U.S. Geological Survey (USGS) (Parkhurst et al, 1980). Although both programs were written to produce essentially similar results, each has unique features which are required to generate the overall geochemical models. Specifically, MINTEQA2 was used to model fluid-mineral interaction in coal refuse and soil due to the superior calculation and presentation capabilities of the program. PHREEQE was used to mix different proportions of AMD and ground water modeled in MINTEQA2. Only PHREEQE is capable of mixing waters and simultaneously calculating the chemical and thermodynamic equilibrium of the resulting mix. Both of these software packages generate thermodynamic models: reactions continue until thermodynamic equilibrium is reached. Neither is capable of considering kinetic constraints on reactions. Therefore, it is critical to compare the results of modeling with observed conditions to assess the relevance of each particular modeled scenario.

#### Conceptual Model

Prior to actual computer modeling, a conceptual model had to be generated that predicted the reaction paths to be accounted for in the geochemical modeling (Figure 2). In this conceptual model, the site is vertically divided into the coal

refuse (i.e., gob and slurry) and the aquifer. Furthermore, the coal refuse is divided into three zones: surface, vadose, and saturated. The modeling process must begin at the top - rain percolating through the waste and eventually mixing with local ground water. Rain water initially reacts with coal refuse in the surface zone, forming the initial AMD. This AMD should closely match the composition of surface water run-off collected at the site from the gob impoundments. A portion of this AMD will continue to travel through the vadose zone of the coal refuse, eventually reaching the saturated zone. Some of the initial AMD will evaporate, resulting in precipitation of gypsum and other salts (Caruccio, et al, 1981; Ziemkiewicz, et al, 1990). Rain water also reacts with coal refuse which includes precipitated gypsum and salts, dissolving some or all of these minerals as shown on the right side of the figure. Mineralogic analysis of the coal refuse indicates that gypsum is the only precipitated mineral not entirely consumed in actively leaching refuse. Water (AMD) resulting from this secondary leaching reaction will also travel through the vadose zone and eventually reach the saturated zone.

AMD generated in the surface and vadose zones continues to react with water-saturated coal refuse. It is predicted that this reaction will

contribute very little TDS or acid to the AMD, therefore this water can be considered to have the same chemical composition as vadose AMD. Ground water also reacts with the saturated coal refuse. The resulting water from this reaction mixes with the vadose AMD, forming the final AMD which leaves the refuse and mixes with local ground water. This last reaction occurs in a variety of mix-ratios, dependent on infiltration rates, ground-water flow velocities, and local ground-water stratification.

### Assumptions

**General.** Several assumptions were used in the mathematical simulation of fluid-mineral and fluid-fluid interactions. Some of the assumptions were used to substitute for unavailable data regarding the water and coal refuse properties. Others were required to simplify the geochemical system so that it could be modeled. The general assumptions were as follows:

- temperature of 25°C;
- complete equilibrium for all reactions;
- homogenous mineral phases;
- oxygen (O<sub>2</sub>) and carbon dioxide (CO<sub>2</sub>) at atmospheric partial pressures (where present);
- complete mixing of fluids, and fluid and mineral phases;
- substitute halite for connate chlorine and sodium in the coal refuse material; and
- restrict mineral precipitation to likely minerals based upon kinetic data.

The substitution of halite for connate chlorine and sodium in the coal refuse material allows for the model to reach equilibrium with all coal refuse components, solid or liquid, simultaneously. Otherwise an intermediate step mixing infiltrating water and connate water would be required and equilibrium calculations would not occur simultaneously for all phases. The restriction on likely mineral precipitation is based on the results of similar studies, both published and not published, and experience.

**Gob Modeling.** The gob currently is found in two hydrogeologic regimes at the mine: (i) vadose zone; and (ii) saturated zone. Therefore, two basic gob models were selected: (i) inclusion of gaseous O<sub>2</sub> and CO<sub>2</sub> (i.e., vadose conditions); and (ii) absence of gaseous O<sub>2</sub> and CO<sub>2</sub> (i.e., saturated conditions).

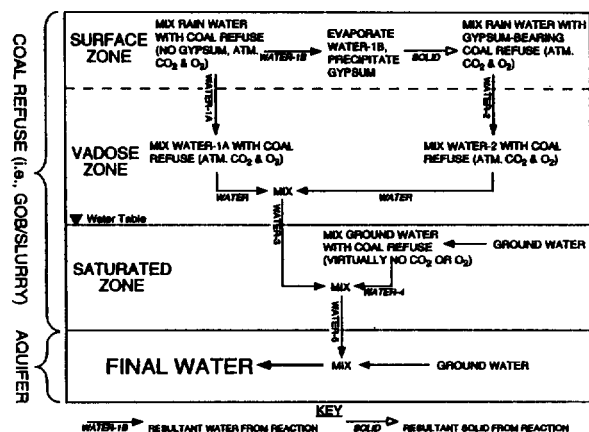


FIGURE 2. Conceptual model for the leaching of coal refuse and mixing of leached waters and ground water. The vertical scale is undefined. Reaction paths are indicated with arrows.

Mineralogic analysis of two gob samples using X-ray diffraction are presented in Table 2. Kinetic data and modeling experience indicate that quartz, illite, illite/smectite, and kaolinite are non-reactive in situations where water has relatively short residence time within a porespace (i.e., days to tens of years) and pH is relatively low. As these minerals are reactive in the long-term, MINTEQA2 would automatically equilibrate the waters with these minerals, and therefore, these minerals were not included in the modeling.

Discussions with mine personnel suggest that the gob is relatively homogeneous and probably did not change in composition with time. To make the models applicable to each waste area, an average gob composition was chosen for all modeling consisting of:

- 5 percent albite;
- 5 percent calcite;
- 1 percent gypsum; and
- 11 percent pyrite.

Additionally, approximately 0.007 percent (2.824E-02 mol/kg) of halite (NaCl) was included to generate chlorine concentrations in modeled water of 1,000 mg/l. This served two purposes: (i) to model waters with concentrations similar to those observed near the leachate sources; and (ii) assess whether chlorine (Cl<sup>-</sup>) and sodium (Na<sup>+</sup>) are reactive in the modeled system. The remaining fraction consists of clays and coal particles.

The reactive fluid in the gob modeling originates as rainfall. Both a typical rainwater (Snoeyink and Jenkins, 1980) and pure water were modeled as the reactive fluid, yielding essentially the same results.

Coal Slurry Modeling. Like the gob, coal slurry is currently found in the vadose and saturated. Table 2 details the mineralogic composition of the coal slurry. As the mineralogy is similar to that of gob, the same percentages of the minerals were chosen for modeling the coal slurry. A significant portion of the coal slurry is coal dust. MINTEQA2 cannot model complex organic phases, therefore the coal dust could not be included in the models. Leaching of the coal dust may result in weak organic acids which might enhance the dissolution rates for the minerals. To compensate for these weak acids, slurry modeling included a lower pH of the initial reactant water than in the gob modeling.

AMD - Ground-Water Interaction Modeling. Water which flows through the coal slurry and gob mixes with the local ground water beneath the impoundments. The chemical composition of the ground water was obtained from an analysis a test well located approximately 1/2 mile (0.8 km) south and upgradient of the site. Data from the sample collected and analyzed from this well was chosen because it is located in an area believed to be unaffected by mining operations. As the rates of ground-water flow and infiltration in the coal refuse vary, the coal refuse-derived water (AMD) and ground water were mixed in a range of proportions determined to include realistic maximum and minimum contributions of each water.

### Geochemical Modeling Results

GOB vs. Slurry. The geochemical models were successful in replicating the range of concentrations of the constituents of concern (sulfate and TDS) The model results are detailed in Table 3. One of the most important results of this modeling was the assessment that gob and coal slurry react similarly and that the end-products of the respective reactions are virtually indistinguishable (i.e., both contain pyrite in concentrations greater than necessary to reach equilibrium). Therefore, in the remainder of this document, gob and coal slurry are treated as a single matrix and waters which react with the waste are described as originating from rainfall infiltration either in the vadose or saturated zones.

Vadose Zone. The vadose zone is the site of the most significant water-coal refuse interaction because O<sub>2</sub> levels are sufficient to oxidize sulfide minerals and therefore create AMD. As gypsum is predicted to precipitate in the surface zone (as is indeed observed at the site), the initial reaction between rain water and the coal refuse was accounted for by including gypsum as a mineral phase in the vadose zone models. The residence times of other precipitated salts appears to be too short to impact the model, and therefore these phases were allowed to dissolve immediately after precipitation during model runs. Table 3 shows the ranges of pH and key constituent concentrations based on three models described below:

- Model A: Unlimited availability of all mineral phases and chemical (i.e., abiotic) conversion of ferrous to ferric iron;
- Model B: Limited availability of all mineral phases (percentages as presented in Table 2)

and chemical conversion of ferrous to ferric iron; and

- Model C: Limited availability of all mineral phases and biotic conversion of ferrous to ferric iron.

It is observed that sulfate and TDS values vary by more than one order of magnitude (from 1,176 mg/l to 23,248 mg/l for sulfate, and 3,383 to 38,379 mg/l for TDS). The range of pH was relatively narrow (i.e., 7.8 to 8.3). These results compare favorably with chemical analyses of surface runoff collected in sumps at the site, detailed earlier in this paper. As the runoff also contains a substantial fraction of fresh rain water, it is expected to have ion concentrations somewhat lower than the maximum modeled. The principal controls on each parameter are as follows:

- sulfate - rate of oxidation of pyrite, dissolution of gypsum;
- TDS - dissolved sulfate; and
- pH -  $\text{CO}_2$  and  $\text{CO}_3^{2-}$  from calcite dissolution and atmospheric  $\text{CO}_2$ .

**Saturated Zone Water.** The vadose zone modeling indicated that all of the gypsum present in the coal refuse was soluble, therefore gypsum is not included as a mineral in the saturated zone modeling. As the pore space in the saturated zone contains water and essentially no gaseous  $\text{O}_2$  and  $\text{CO}_2$ , pyrite is oxidized by dissolved oxygen in the water, which is kinetically a much slower reaction than oxidation in the presence of free oxygen. Table 3 shows the results of geochemical modeling of waste in the saturated zone.

Model	pH	$\text{SO}_4$ (mg/l)	TDS (mg/l)
<b>Vadose Zone Model</b>			
A	7.809	1,176	3,363
B	7.945	2,241	7,902
C	8.32	23,248	36,379
<b>Saturated Zone Models</b>			
D	8.963	23,287	36,369
E	6.503	23,316	36,339
F	5.76	2,256	7,837
G	8.006	2,242	7,901

Table 3: Summary of vadose zone and saturated zone modeling

These models were constrained by the following criteria:

- Model D: Unlimited availability of all mineral phases and limited dissolved oxygen;
- Model E: Limited availability of all mineral phases and limited dissolved oxygen;
- Model F: Limited availability of all mineral phases and no dissolved oxygen; and
- Model G: Unlimited availability of all mineral phases and no dissolved oxygen.

Although similar maximum sulfate and TDS concentrations can be attained in the saturated and vadose zones, the kinetics of the reaction under hydraulically saturated conditions preclude complete oxidation of pyrite given the relatively short residence-time of pore waters in the waste. As described above, the presence of iron-oxidizing bacteria can greatly enhance and accelerate iron oxidation rates which in turn accelerates acid generation. Other mine waste reclamation studies (Grim and Hill, 1974; Nawnot, 1985) have shown that submerged coal refuse is generally not acid-generating because pyrite reactivity and microbacterial activity are minimized. Since non-equilibrium reactions cannot be modeled directly, the use of more constrained models (i.e., model F) can approximate the observed conditions.

**Development of Existing Conditions.** The current levels of sulfate and TDS in ground water at the site were perhaps most strongly influenced by early coal refuse disposal operations. A combination of factors acted on the coal refuse which resulted in varying impacts at different areas of the site. The initial weathering of gob and coal slurry results in leaching of the most unstable pyrite and produces the majority of the sulfate and TDS from that material. Evaporation of the water generated in these conditions results in precipitation of gypsum and other salts, some portion of which may later be dissolved, remobilizing aqueous sulfate. When the coal refuse is first placed in a new impoundment, it is uncompacted and expected to be characterized by relatively high permeability and more rapid infiltration rates. Therefore the high-TDS water (i.e., AMD) is expected to enter ground water more quickly and in greater volumes. As more coal refuse is added, both the coal slurry and gob become more compacted and infiltration decreases, slowing the contribution of AMD. Eventually, no new coal refuse is added and the majority of the easily leached

pyrite has dissolved, leaving mostly more stable (perhaps more coarse) pyrite and a reduced potential for AMD generation. Figure 3 is a conceptual graph of TDS or sulfate contribution with time for a typical individual waste impoundment. The effects of microbacterial activity, although not considered by MINTEQA2, may tend to continue AMD generation from less soluble pyrite.

### Geochemical Model - Forecast

#### Overview

Once a satisfactory model explaining the existing conditions is generated, the impact of various reclamation strategies on the local ground water can be assessed. The existing AMD within the coal refuse cannot likely be neutralized or removed in a cost-effective manner. Therefore, the forecast model involves two steps: (i) mix the existing AMD with the local ground water in proportions that vary depending on the reclamation strategy; and (ii) examine the long-term development of AMD chemistry and its contribution to the ground water under different reclamation scenarios. The first step is well-constrained from a chemistry standpoint, but the physical mixing ratios could vary widely during the initial reclamation activities. The second step assumes that the engineering and hydrologic controls are established and performing to expectation, and therefore the infiltration and ground-water flow rates are well-constrained. The geochemical conditions, however, cannot be predicted as precisely as in the initial model, as the system is more strongly impacted by the kinetics of the reactions.

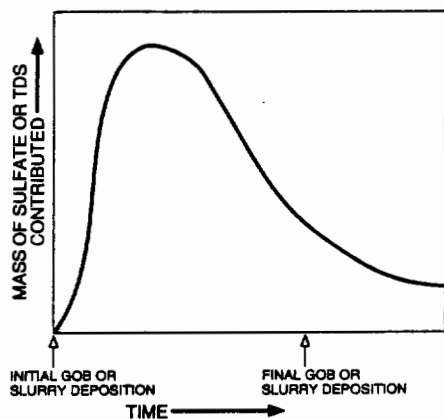


FIGURE 3. Graph showing the conceptual mass-contribution of sulfate and TDS to ground water with time (e.g., the development of existing conditions in ground water beneath the site). The vertical and horizontal scales are undefined but linear.

### AMD-Ground Water Mixing

Two types of fluid mixing were modeled: (i) the mixing of vadose and saturated zone waters; and (ii) the mixing of coal refuse-derived waters (AMD) with ground water. The final composition of water moving beneath the site is controlled by the ratio of contribution from each source (Figure 2). The possible chemistries of waste-derived waters are presented in Table 3. The ratio of vadose to saturated zone water controls the final composition of the AMD. The sulfate and TDS concentrations in the AMD are likely to be less than or equal to the maximum possible values that can be generated in the vadose zone.

The modeled mixing of AMD and ground water does not result in a water with an intermediate composition directly proportional to the mix ratio. Table 4 shows the results of mixing as modeled by PHREEQE. In this mixing model, ground water was mixed with leachate (as predicted by Model D, presented in Table 3) in five ratios of ground water to leachate: (i) 9999:1, (ii) 999:1, (iii) 99:1, (iv) 90:1, and (v) 1:1. These ratios cover the likely relative contributions of leachate to the local ground water system. The variation from perfect proportionality in mix waters is due to ion complexing which occurs during mixing. This can have a potentially significant impact on the resulting waters chemistry. In the case of the model presented in Table 4, the modeled sulfate concentration is about 82 percent of the expected value with a 50 percent fraction of ground water mixed with leachate (i.e., equal mixture of leachate and ground water). Table 5 presents selected ground water analytical results as measured on 22 June 1995. Comparison of the mixing model results with the actual analytical data from wells located below or downgradient of the refuse areas indicates that the range of mix ratios modeled accurately mimic observed conditions.

### Reclamation Impacts

Overview. The results of the conceptual and predictive geochemical modeling were used in the development of the reclamation plan. The process by which the proposed reclamation plan was generated was iterative, and involved extensive ground-water flow modeling and engineering design, in addition to the geochemical modeling. A full discussion of this work is beyond the scope of this paper, therefore, only the selected reclamation alternative is discussed in conceptual terms: the application of lime and an



Ground-Water to ARD Leachate Mix Ratio <sup>(1)</sup>	Sulfate		Chloride	
	Modeled (mg/l)	Proportional Mix <sup>(2)</sup> (mg/l)	Modeled (mg/l)	Proportional Mix <sup>(2)</sup> (mg/l)
9999:1	17	18	4	4
999:1	36	39	5	5
99:1	230	249	15	14
90:1	2108	2343	107	104
1;1	9587	11652	521	503

<sup>1</sup> Mixing of Model D (sulfate = 23,287 mg/l, chloride = 1,001 mg/l) and ground water (sulfate=16 mg/l, chloride=4 mg/l).

<sup>2</sup> Proportional mix of Model D and ground water at ratios indicated.

Table 4. Summary of mixing model results.

engineered soil cover with continuing ground-water pumping. This reclamation will impact the coal refuse chemistry, infiltration rate of water in the coal refuse, AMD generation, and local water table. The mitigation of the effects from these impacts is addressed below.

**Coal Refuse Chemistry Impact.** The addition of lime to the impoundments increases the potential for acid neutralization and decreases the rate of pyrite dissolution in the near surface. Additionally, the excess calcium will reduce the solubility of gypsum and therefore decrease the availability of sulfate.

**Infiltration Impact.** Due to the expected relatively low permeability of weathered gob and the moderate permeability of coal slurry, current rainwater infiltration rates in the impoundments are estimated to be about 8 in./yr (20 cm/yr). An engineered compacted soil cover would decrease infiltration, thereby reducing the length of time that saturated coal refuse would require to dewater and minimizing the discharge of water from the coal refuse into ground water. Although the residence time for pore water would increase, leading to increased sulfate and TDS concentrations within the pore water, very little of this water would enter the ground-water system because the engineered soil cover would effectively shut-off the hydraulic head which mobilizes the sulfate and TDS.

**Local Water Table Impact.** It is likely that if the pumping from on-site withdrawal wells is discontinued, the local water table will rise and saturate some portion of the buried coal refuse. As discussed earlier in this paper, saturated conditions are expected to retard the dissolution of pyrite. A rise in the water table would also tend to reduce the

amount of coal refuse available for vadose leaching. A rise in the water table into deeply buried coal refuse is not expected to significantly increase the ground-water contamination.

Geochemical data can be used to support the proposed enhanced pumping strategy. The ground-water monitoring data from site characterization activities show that the highest concentrations of TDS and sulfate are limited to the upper portion of the aquifer beneath the site. TDS and sulfate concentrations in samples collected from the deep on-site pumping wells suggest that impacted ground water is being drawn downward toward the well screens near the bottom of the aquifer.

Table 6 shows an estimate of the TDS being removed from the aquifer by the existing on-site pumping wells. The estimation is based on the current pumping rates for the wells and the water quality data from a recent monitoring round. About 19,000 pounds (8,700 kg) per day of TDS is removed from the aquifer. A projection of the quantity of TDS which could be removed using three proposed shallow wells is also shown on Table 5. The projection assumes that wells will pump at the rates described in the conceptual model above and that the concentration of TDS will be the same as the nearest monitoring well. Based on the calculations for the projection, it is estimated that the new wells could remove about 14,300 pounds (6,500 kg) per day of TDS from the aquifer. Despite the lower pumping rate of the new wells (about 275 gpm or 17 l/s) compared to the existing wells (about 1,075 gpm or 68 l/s), the strategic location and design of the new wells removes nearly as much impacted ground water in terms of TDS as the existing wells. Mitigation of

the impacted ground water at the site should therefore be accelerated by the additional wells.

### Conclusions

Based on the results of the geochemical modeling, the evolution of AMD is understood to occur as described in Figure 2. Surficial leaching produces the most concentrated AMD and the highest sulfate and TDS concentrations. Other vadose zone waters contribute significant sulfate and TDS and only minimally dilute the AMD. Mixing of vadose zone waters with those from the saturated zone, where present, results in further dilution of the AMD. This water then mixes with the ground water through vertical and lateral dispersion, as modeled by PHREEQE.

From this model, two typical scenarios were generated. Figure 4 is an idealized representation of the flow of AMD from a refuse impoundment area into a sump and then down into the aquifer. As the leachate mixes with the ground water it forms a zone of high sulfate and TDS waters, as has been observed through ground-water sampling and analysis. Similarly, Figure 5 illustrates the situation within a typical waste impoundment. Note in both scenarios the large vertical interval of high sulfate generation potential.

Implementation of the reclamation measures (i.e., engineered reclamation cover on coal refuse areas) significantly changes the system. Figure 6 presents a conceptualization of the impoundment presented in Figure 5 after reclamation. Not only will the lime significantly reduce the potential for

Well	Relative Location	Alkalinity (as CaCO <sub>3</sub> )	Chloride	pH	TDS	Sulfate
MW-6	Upgradient of Site	358	3.7	7.62	575	12
MW-21	Beneath slurry pond	342	40.4	7.24	1025	318
GW-6	Downgradient of Sump	522	292.7	6.90	5889	2747
GW-27	Beneath buried gob	538	70.1	7.07	1905	958
MW-14	Downgradient of Site	400	44.6	7.36	1025	354

Table 5: Selected ground water analytical results from 22 June 1995

Pumping Well No.	Pumping Rate			TDS Removed by Pumping		
	(gpm)	(gpd)	(gpy)	Discharge TDS (mg/l)	(lb/day)	lb/yr
<b>Existing Wells</b>						
A	535	770,400	281,196,000	1,728	11,100	4,052,000
B	100	144,000	52,560,000	1,876	2,300	822,000
C	400	576,000	210,240,000	1,100	5,300	1,929,000
D	20	28,800	10,512,000	370	90	33,000
E	20	28,800	10,512,000	1,710	400	146,000
Subtotal	1,075	1,548,000	565,020,000	-	19,200	6,982,000
<b>Proposed Wells</b>						
1	100	144,000	52,560,000	3,200	3,800	1,387,000
2	100	144,000	52,560,000	3,130	3,800	1,387,000
3	75	108,000	39,420,000	7,395	6,700	2,446,000
Subtotal:	275	396,000	144,540,000	-	14,300	5,220,000

Table 6: Estimate of TDS removed by onsite pumping wells

sulfate generation, the low infiltration rate decreases the volume-contribution of AMD to ground water. The higher local water table created by cessation of on-site pumping will flood some gob areas and reduce their chemical reactivity.

The reclamation measures proposed for this site should effectively isolate the coal mine refuse as a source for further significant effects on local ground water quality. Remediation of the existing TDS plume by mitigating elevated concentrations and reclamation of the surface coal refuse should mitigate the potential for future degradation of local ground water.

In this study, geochemical modeling has proven itself to be a cost-effective and defensible means to understand and forecast the impact of reclamation activities on ground-water quality.

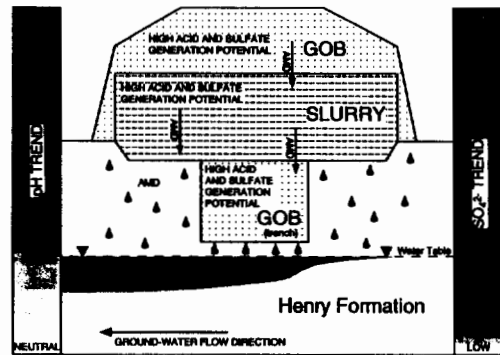


FIGURE 5: Illustration of a typical coal refuse impoundment and the associated AMD. This figure illustrates conditions at the site prior to reclamation. Note that the entire refuse column is contributing to AMD.

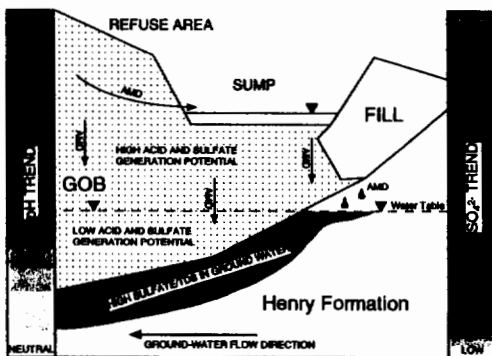


FIGURE 4. Illustration of the generation, movement, and chemical characteristics of AMD in a coal refuse impoundment containing a sump to collect run-off. The results from geochemical modeling of the vadose zone closely matched analytical data from water collected from such sumps at the site.

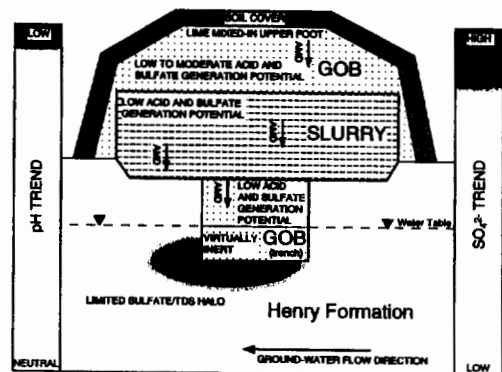


FIGURE 6. Illustration of the same coal refuse impoundment as shown in Figure 5 after reclamation is complete. Although AMD is still generated in the unsaturated coal refuse, the virtual elimination of rainwater infiltration results in an overall reduction of AMD-generation potential and minimizes the transport mechanism.

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