

ACID MINE DRAINAGE AND MANAGEMENT OF EASTERN OIL SHALE
RESOURCES AND ASSOCIATED WASTE PRODUCTS

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Abstract.--The objectives of this research were to 1) understand the chemistry of acid mine drainage associated with oil shale resources and 2) suggest appropriate management options to minimize water quality problems. In this study, two eastern oil shales were collected. Each shale was retorted and combusted to produce waste products representative of potential mining and energy conversion processes. Each raw, retorted, and combusted shale was studied under the following laboratory conditions; 1) oxidizing equilibrium, 2) oxidizing nonequilibrium, and 3) reducing equilibrium. The Experimental results show that 1) the fundamental chemical equations that have been used to predict acid mine drainage are not correct, 2) using the new equations developed in this study, fundamental thermodynamic constants can be used to predict major and minor element activities, 3) the acid-base account method is not adequate for predicting acid potential, 4) simulated weathering methods should be used to predict acid potential, 5) combusted shales do not produce acid drainage under all disposal conditions, and 6) mineral weathering prior to the disposal of raw shales will significantly influence the acid potential of a material. These results suggest the following management implications 1) it is possible to predict leachate chemistry from waste and site specific data using thermodynamic constants, 2) placing weathered raw shale in a saturated environment can result in acid drainage, and 3) shales with a negative acid-base account should be combusted to minimize acid potential.

INTRODUCTION

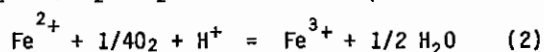
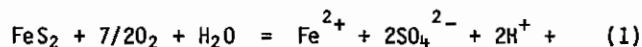
When geologic materials containing iron sulfides are exposed at the earth's surface, acid mine drainage may occur. Because many raw and processed oil shales contain iron sulfides suggests that these materials need to be characterized to determine their acid potential prior to mining or processing. This characterization is a critical step in selecting management methods for a specific waste and disposal environment to avoid water quality problems associated with low pH and high trace element concentrations (Martin 1974, Griffin 1980, Wahler 1978).

The extraction of eastern oil shale resources is a critical concern, since these shales contain iron sulfides. In addition to the raw shales,

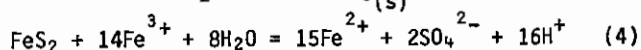
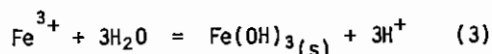
retorted and combusted oil shales may also contain iron sulfides (Paciorek et al. 1984). Each of these materials will generate a leachate that reflects the mineral properties of each shale and selected disposal environment. The ability to characterize both acid potential and trace element release of each shale in a selected environment begins with understanding the chemical reactions that are commonly used to describe iron sulfide oxidation.

Theory of Acid Generation

In a natural aerobic environment, iron sulfide compounds have the potential to oxidize and produce acidity. The best example of this natural process is the oxidation of FeS₂ (pyrite) that usually occurs in mining wastes, coal cleaning waste, spoil, and acid sulfate soils (Smith et al. 1974). The oxidation of pyrite in a natural environment is suggested by the following reactions (Stumm and Morgan 1981).



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After pyrite is oxidized by atmospheric oxygen (eq 1), ferric iron is produced extremely slowly (eq 2). This second reaction, however, can be accelerated by microbial catalysis (aerobic) to increase the overall rate of ferrous iron oxidation. With the generation of ferric iron, insoluble ferric hydroxide may form (eq 3). Pyrite can also be oxidized by soluble ferric iron (i.e., in saturated or unsaturated environments), resulting in the generation of more acidity and ferrous iron (eq 4).

With iron sulfide oxidation, Nordstrom (1982) proposes the formation of secondary iron phases that include ferrous iron sulfates, ferric iron sulfates (jarosite), and other ferric iron hydroxides and oxides. However, Nordstrom (1982) does not quantitatively show the environmental conditions in which these specific solid phases may be generated. Once these compounds are formed, Sullivan and Sobek (1982) have shown that soluble acidity in the form of ferric and ferrous iron will be released to solution. This is especially critical in evaluating the influence of geochemical weathering of iron sulfides prior to disposal.

Research Objective

Based on the discussion above, the objectives of this two-year study were to characterize the acid production of eastern oil shale waste products (i.e., raw shale fines, retorted shale, and combusted shale) as a function of process conditions, waste properties, and disposal practice and to recommend management practices. In order to understand acid production, each waste was characterized by determining the acid-base account and laboratory weathering studies to assess its acid potential and chemistry.

DESCRIPTION OF RESEARCH

Oil Shale Selection

A high pyrite shale, selected from the U.S. Department of Energy's reference shale E86, was collected by Terra Tek. The sample was collected from an unweathered section of the upper part of the New Albany Shale of the Borden Formation located in Bullitt County, KY. A shale with a low concentration of pyrite was collected from a weathered outcrop of the Chattanooga Shale located in the Chestnut Mound section of Smith County, TN.

Oil Shale Processing

Both oil shales were crushed to pass a 3-inch screen. All particles passing a 1/2-inch screen were rejected from the feedstock. Each feedstock was 1) retorted using the indirect-heated Paraho process by Western Research Institute and 2) combusted using a fluidized bed process by J&A Associates. When both shales were retorted by the Paraho process and were indirectly heated to 500°C for 12 minutes, the spent New Albany Shale retained 80% sulfur and had 28% organic carbon conversion. The spent Chattanooga Shale retained 76% sulfur and had a 26% organic carbon conversion when these shales were also combusted using a fluidized bed reactor in air at 760°C for 15 minutes, the

combusted New Albany Shale retained 43% of the sulfur and had an 87% organic carbon conversion. The combusted Chattanooga Shale retained 81% of the sulfur and had an 83% organic carbon conversion. The details of the retorting and combustion activities are given in Sullivan et al. (1987).

Laboratory Characterization

The acid-base account was determined for each shale using the method as given by Sobek et al. (1978). Laboratory studies were designed to simulate the following disposal environments, 1) oxidizing nonequilibrium leaching, 2) oxidizing equilibrium, and 3) reducing equilibrium. All solutions generated from these laboratory studies were analyzed for the following: pH, Eh (as mv), cations by ICP (Al, Ba, Ca, Cd, Co, Cu, Na, Fe, K, Mg, Mn, Ni, Pb, Sr, Zn) and anions by ICP and IC (As, Cl, Mo, S, Sb, Se, Si).

Oxidizing Nonequilibrium Studies

The humidity cell, developed by Caruccio (1968), can be used to simulate natural weathering of iron sulfides in an aerobic unsaturated environment. In this method, acid production will occur due to sequential leaching that allows oxidizing conditions to exist in a moist environment. In this study, the following humidity cell procedure was used. One kilogram of each shale (<2.00mm) was evenly spread out in the humidity cell, and the lid was tightly sealed. Dry air was passed over the samples for three days. From day four to day seven, humidified air was passed over the samples. On the seventh day, one liter of distilled-deionized water was added to each cell and allowed to equilibrate for one hour. After that time period, the solutions were extracted, filtered, and the sediments were returned to each respective cell. This cycle continued for 19 weeks. A solution of *Thiobacillus ferrooxidans* and *Thiobacillus thiooxidans* was added to each cell on the fifteenth week to increase acid production.

Oxidizing Equilibrium Studies

This method simulates waste disposal in a saturated groundwater environment that will be in contact with atmospheric oxygen (i.e., fluctuating watertable). In this environment, it is anticipated that the reaction in equation 1 will occur. However, the chemistry of the system will be determined by thermodynamic equilibrium conditions (i.e., no leaching).

Two hundred fifty-grams of each sample were placed into 500 mL Nalgene plastic bottles. Two hundred fifty milliliters of distilled-deionized water were added to these bottles and were capped tightly. A plastic tube was inserted through the cap to the bottom of the bottle to supply a constant flow of compressed air. Each sample bottle was placed into a water shaker bath at a constant temperature of 25°C. The samples were shaken at a constant rate of 60 rpm and were agitated manually four times a week. One bottle for each shale was removed from the water bath for analyses after 1, 4, 8, 16, 32, 64, 128, and 180 days of equilibration time. The samples were filtered, and the clear filtrates were analyzed for pH, Eh, and total acidity and alkalinity and split for analyses. Samples saved for anion analysis

were kept at 4°C, and those saved for metals analysis were adjusted with concentrated HNO₃ to a pH <2.

Reducing Equilibrium Studies

This method simulates waste disposal in groundwater conditions that would have limited contact with atmospheric oxygen. It would be expected that little or no oxidation of pyrite would occur from equation 1. However, it is anticipated that acid production could occur as a result of the reaction given in equation 4. There is no leaching so that chemical equilibrium will be established.

Two hundred fifty-grams of each sample were placed into 500 ml Nalgene plastic bottles. Two hundred fifty milliliters of distilled-deionized water were added to these bottles and were capped tightly and taped to limit oxygen diffusion into the bottle. Each sample bottle was placed into a water shaker bath at a constant temperature of 25°C.

The samples were shaken at a constant rate of 60 rpm and were agitated manually four times a week. One bottle for each shale was removed from the water bath for analyses after 1, 4, 8, 16, 32, 64, 128, and 180 days of equilibration time. The samples were filtered and the clear filtrates were analyzed for pH, Eh, and total acidity and alkalinity and split for analyses. Samples saved for anion analysis were kept at 4°C, and those saved for metals analysis were adjusted with concentrated HNO₃ to a pH <2.

RESULTS AND CONCLUSIONS

Potential Acidity

The results of the acid-base account are given in Table 1. These data show that the raw New Albany Shale, raw Chattanooga Shale and the retorted Chattanooga Shale have the potential to produce an acid mine drainage problem. Based on the work of Ferguson and Erickson (1986), it would also be predicted that these same materials would produce acidity in a field environment (i.e., acid-base account <+33).

Table 1.--Acid-base account of raw and processed shales.

Waste	%FeS-S	Acid (Tons of H ₂ SO ₄ /1000 tons of waste)	Base (Tons of CaCO ₃ /1000 tons of waste)	Balance*
Raw NAS	4.2	-131.3	4.9	-126.4
Retorted NAS	0.08	-2.5	65.0	62.5
Combusted NAS	0.04	-1.3	226.0	224.7
Raw CS	1.9	-58.4	24.1	-34.4
Retorted CS	0.8	-25.0	22.8	-2.2
Combusted CS	0.6	-18.8	170.9	152.1

* (-) indicates a net acid potential
NAS=New Albany Shale, CS=Chattanooga Shale

Humidity Cell

The humidity cell data represent a weathering environment that would stimulate maximum acid potential of a material. Humidity cell pH as a function of time is given in figure 1 for the New Albany Shale and the Chattanooga Shale in figure 2. These data clearly show that the New Albany and raw and spent Chattanooga Shales will produce acid leachates. This suggests that these materials can produce acid mine drainage in an unsaturated surface disposal environment.

When these data are compared to the acid-base account values of each shale, only the spent New Albany Shale was predicted to have a non-acid leachate (even in a field environment, i.e., value >+33). This suggests that the sources of neutralization in the spent shales were overestimated and/or not available for neutralization reactions during weathering.

During initial leaching (first 28 days), the raw Chattanooga Shale shows an acid pH and decreases rapidly. The raw New Albany Shale, however, demonstrates an initial neutralization and a steady decrease in pH. Because the raw Chattanooga Shale was weathered (but a lower concentration of pyrite than the New Albany Shale), some soluble acidity was released to show an acid pH with little available alkalinity.

Both retorted shales contain small concentrations of pyrite and both exhibit acid producing potential. After approximately 80 days, both shales establish a leachate pH below 4.0 after a loss of alkalinity. The combusted shales show a consistent decrease in pH with time. Like the retorted shales, the combusted shales have a small concentration of pyrite. However, because limestone was added to the combustion process, the combusted shales contain a higher neutralization potential. As a consequence, the leachate pH tends to remain higher. Even with this increased alkalinity, sulfide oxidation and dissolution of atmospheric carbon dioxide decreases leachate pH. When the pH was firmly established below 4.0 in the raw and retorted shales, microorganisms were added to the humidity cells. With this addition, the pH in both raw shales approached 2.0 (i.e., due to the increased rate of ferrous iron oxidation; equation 2). A corresponding rapid decrease of leachate pH associated with the retorted shale was not as evident due to a much lower concentration of sulfides.

Oxidizing Equilibrium

In the simulated oxidizing groundwater environment, it is assumed that the flow rate of groundwater in contact with a specific waste material will be slow enough to establish chemical equilibrium. Since leaching does not occur in this system, pH will be controlled by secondary mineral formation and hydrolysis but not iron sulfide oxidation. The oxidizing equilibrium pH as a function of time for the New Albany Shale is given in figure 3 and for Chattanooga Shale in figure 4.

The data for the raw shales show that the pH of the Chattanooga Shale extract is acidic and becomes more acidic with time, while the pH of the New Albany Shale extracts become alkaline and then pH decreases.

NEW ALBANY SHALE

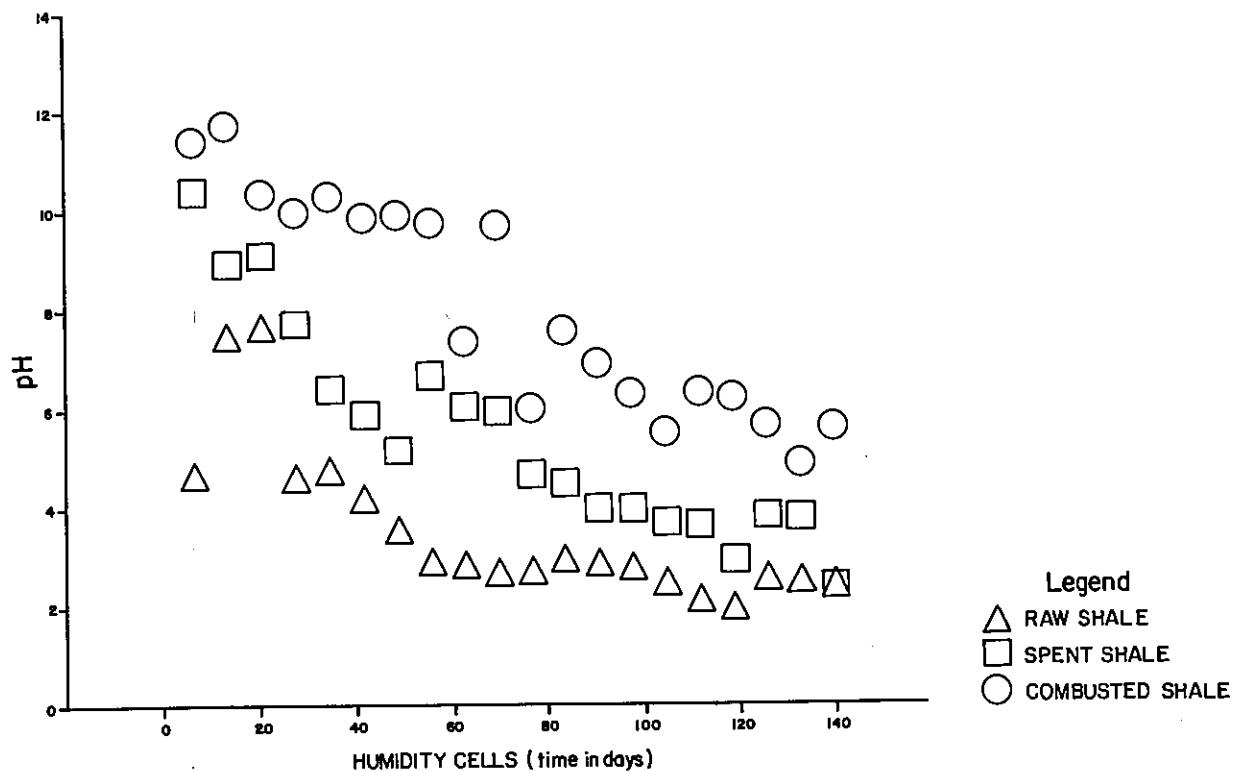


Figure 1.--pH data for the New Albany Shale humidity cell extracts.

CHATTANOOGA SHALE

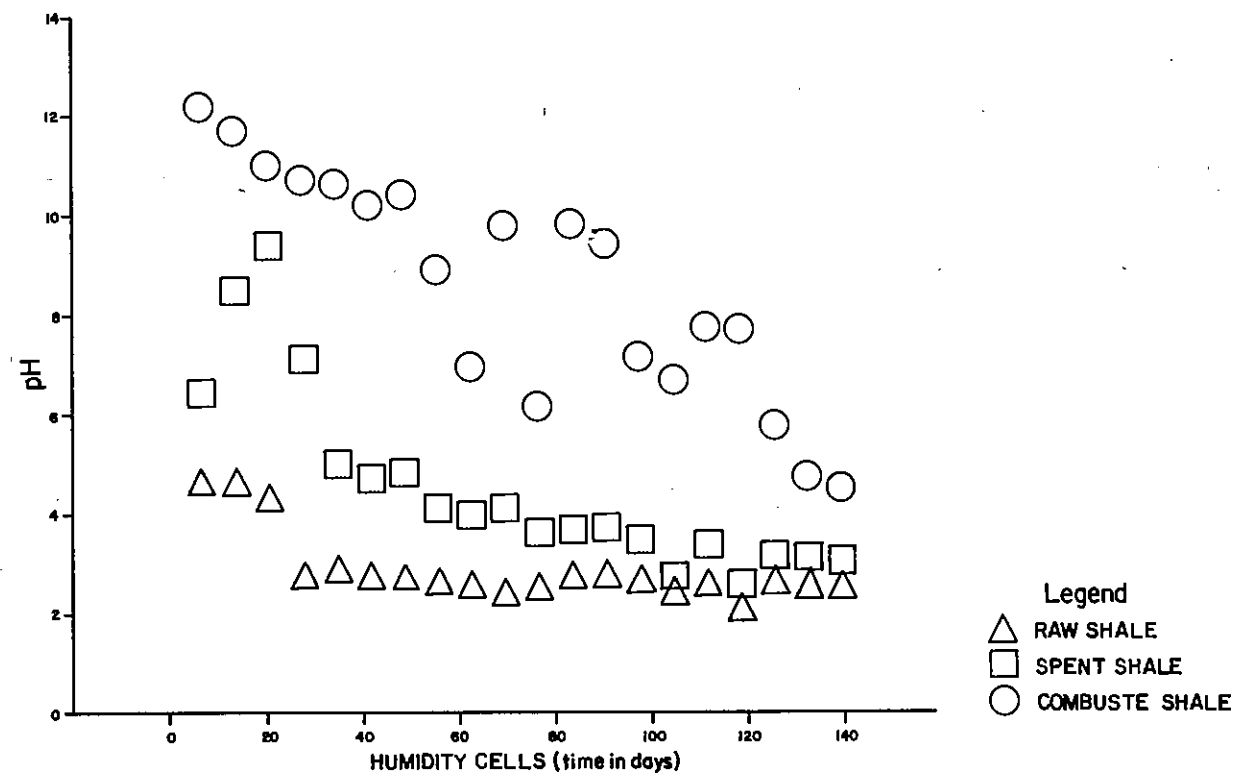


Figure 2.--pH data for the Chattanooga Shale humidity cell extracts.

NEW ALBANY SHALE

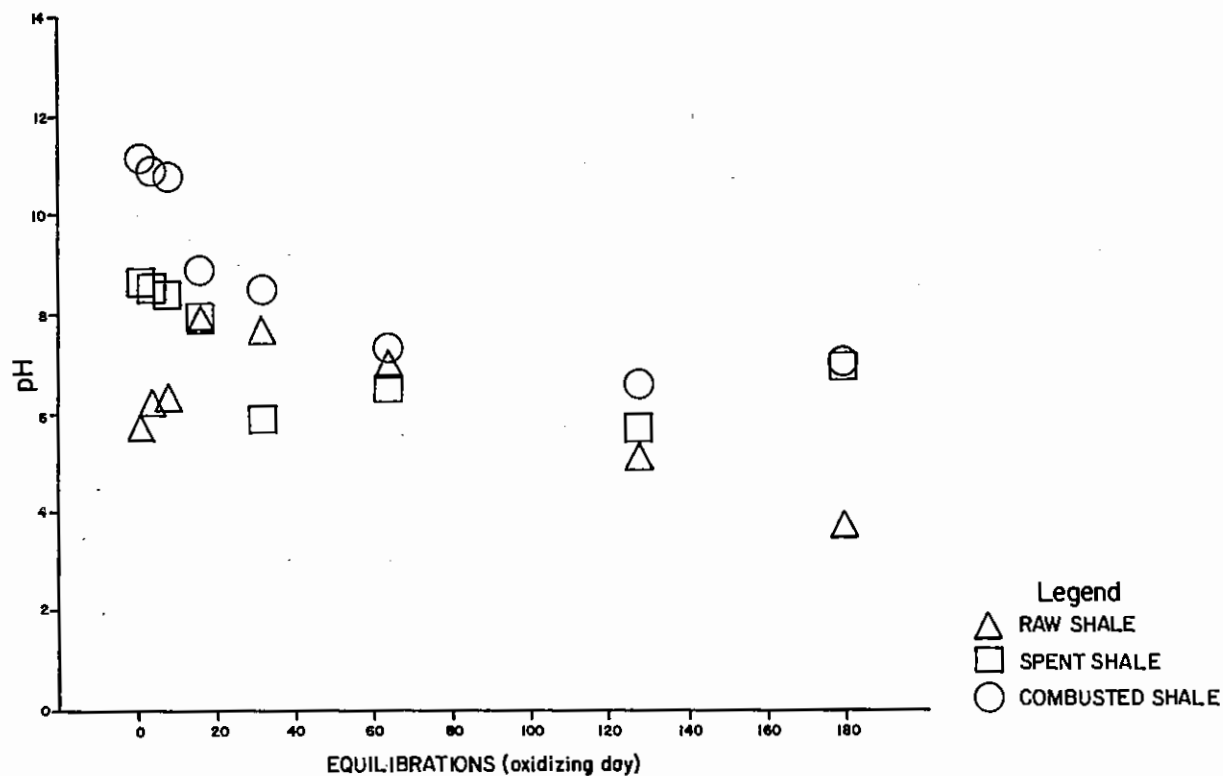


Figure 3.--pH data for the New Albany Shale oxidizing equilibrium extracts

CHATTANOOGA SHALE

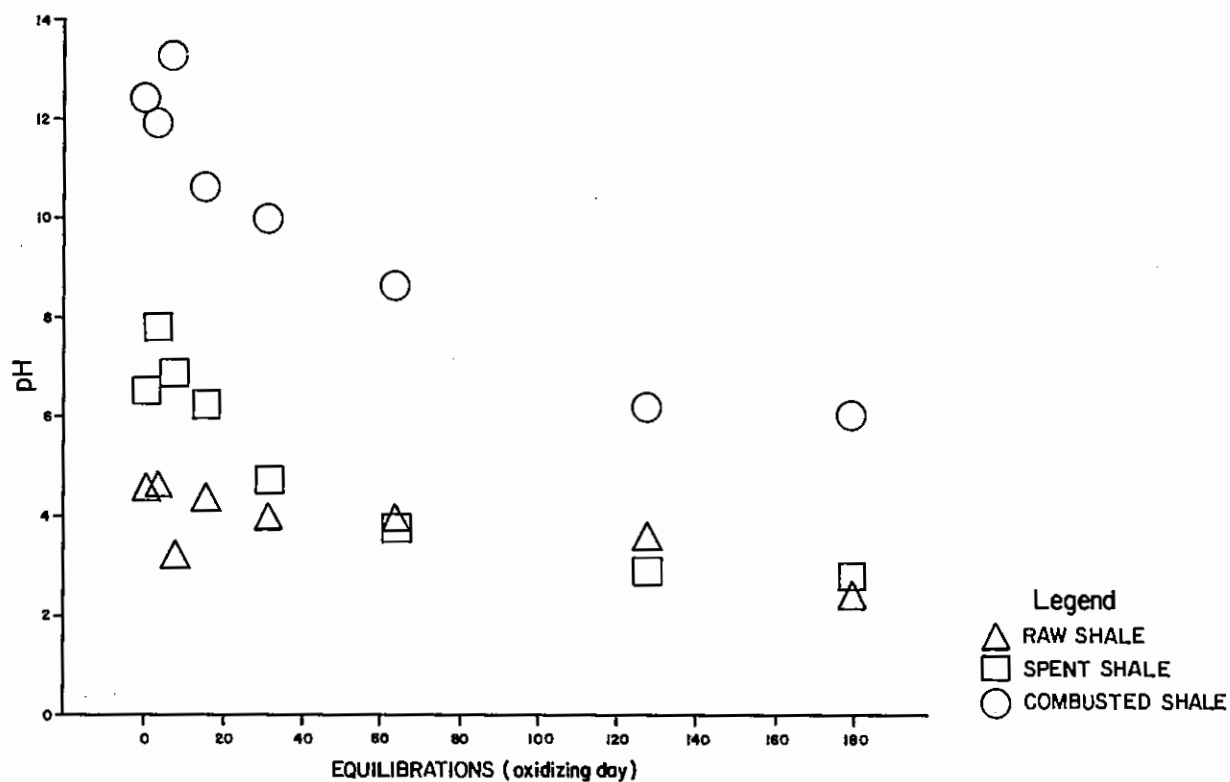


Figure 4.--pH data for the Chattanooga Shale oxidizing equilibrium extracts.

This once again demonstrates the influence of mineral weathering prior to disposal (and not the concentration of pyrite). Both final pH values are still very low but not to the same degree as the humidity cell leachates. However, these data still support the fact that these raw shales will produce acid mine drainage if they occur in a similar groundwater environment.

The retorted Chattanooga Shale also exhibits a pH trend that will eventually produce acid mine drainage; however, the New Albany Shale does not exhibit the same trend. Unlike the humidity cell, there is more time for neutralization reactions to occur. Since the retorted New Albany Shale has a greater neutralization potential than the retorted Chattanooga Shale, this trend is not unexpected. These data correspond more closely to the predicted acid potential as indicated by the acid-base account.

The pH of all combusted shale solutions remains fairly alkaline to 180 days. Even with potential iron sulfide oxidation and recarbonation, the pH tends to remain high due to a greater concentration of alkaline materials (note: the combusted New Albany Shale has a higher neutralization potential than the combusted Chattanooga shale).

In this simulated environment, the acid-base account method more accurately predicts acid-producing potential. However, it still does not

indicate the hazard of mineral weathering and soluble acidity.

Reducing Equilibrium

In the simulated reducing ground water environment, it is assumed that 1) the flow rate of groundwater in contact with a specific waste material will be slow enough to establish chemical equilibrium and 2) atmospheric oxygen will not influence solution chemistry. Like the oxidizing equilibrium studies, leaching does not occur in this system, so pH will be controlled by secondary mineral formation and hydrolysis and not iron sulfide oxidation. The reducing equilibrium pH as a function of time for the New Albany Shale is given in figure 5 and for Chattanooga Shale in figure 6.

The data for the raw shales show that the pH of the New Albany Shale extracts remains just slightly acidic, while the Chattanooga Shale extracts are very acidic. This trend, once again, shows how soluble acidity can influence solution chemistry without pyrite oxidation. In the absence of 1) an atmospheric influence on solution chemistry and 2) leaching, retorted and combusted shale solutions does not generate acid mine drainage.

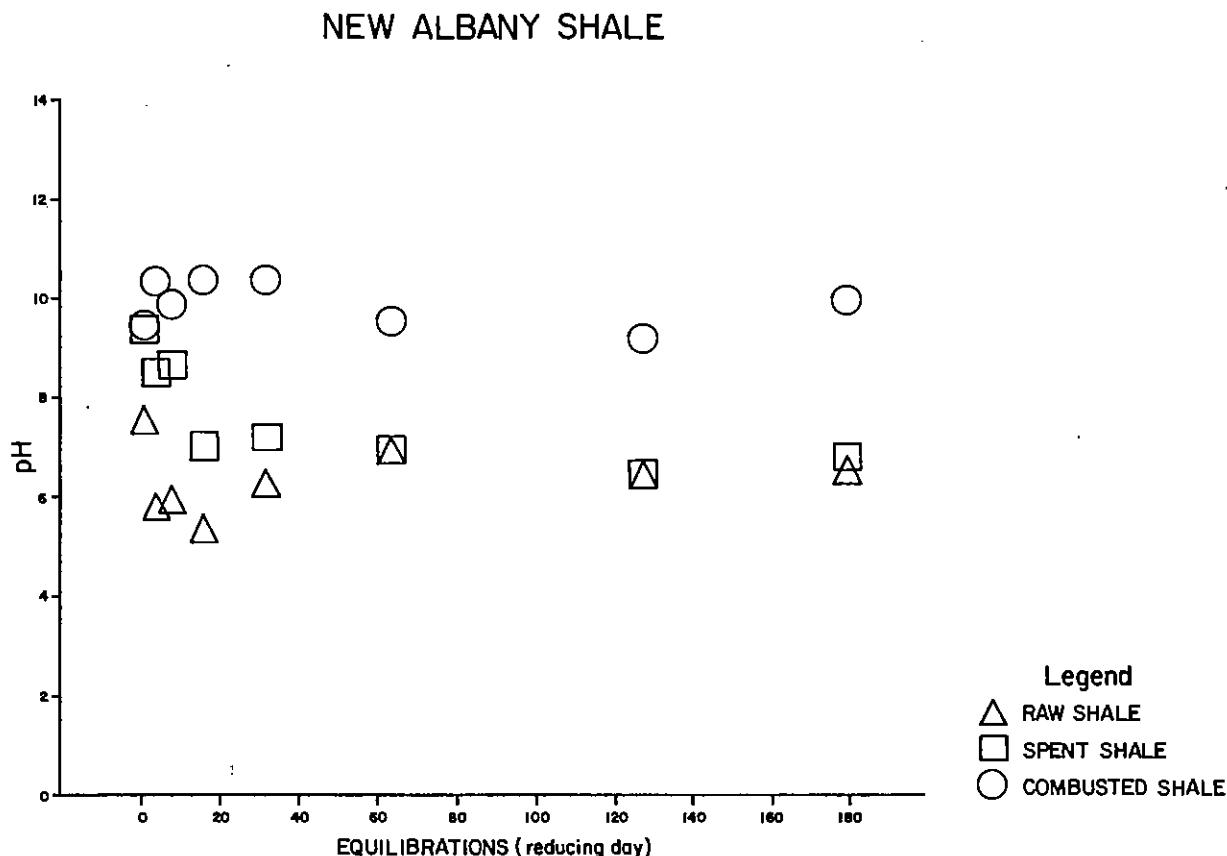


Figure 5.--pH data for the New Albany Shale reducing equilibrium extracts.

CHATTANOOGA SHALE

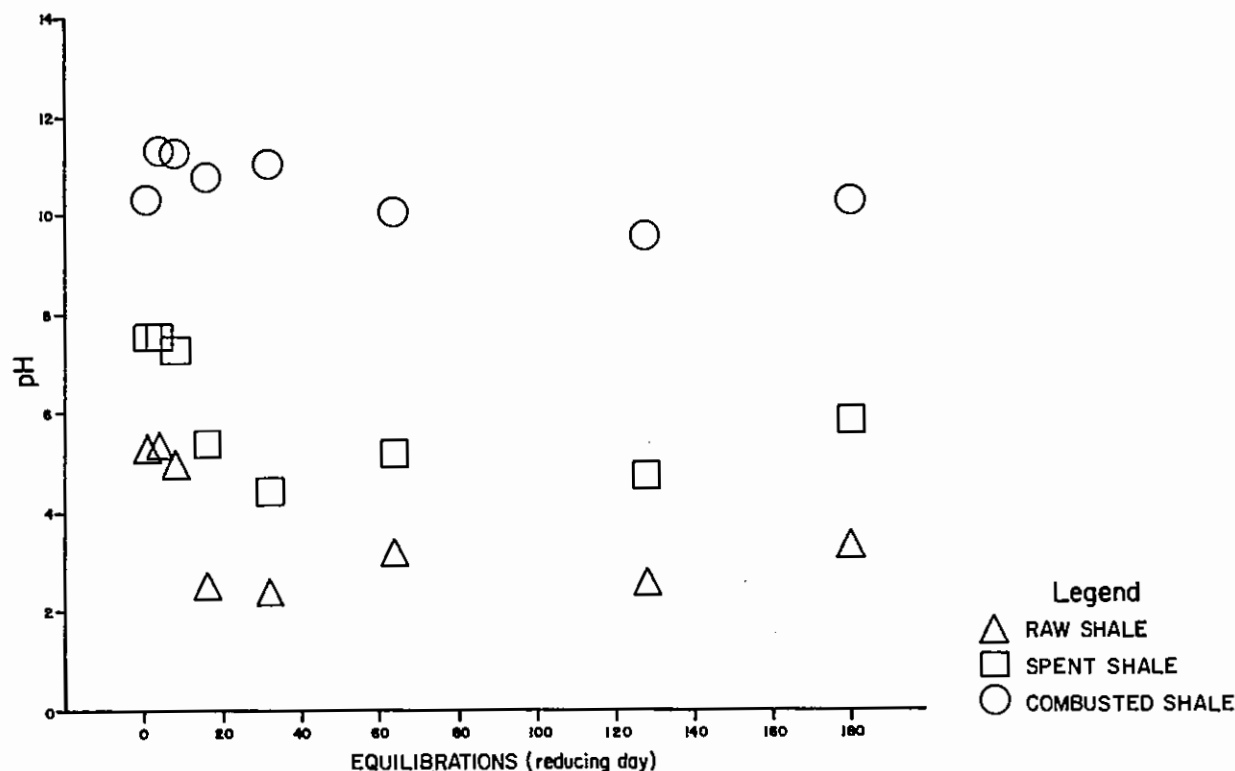


Figure 6.--pH data for the Chattanooga Shale reducing equilibrium extracts.

Generation of Acidity

All total chemical analyses from each study were coded and speciated with the WATEQFC geochemical code (Runnells and Lindberg 1981) to calculate ion activities. Based on this speciation, the minerals that control iron and aluminum solubility in acid mine drainage solutions were determined. The results of this analysis are given in Sullivan, et al. (1988). The equations that control iron and aluminum solubility are given in figure 7 (Sullivan et al. 1988). The results of this study demonstrate that below a pH of 6.00, the activities of Fe^{3+} and Al^{3+} are controlled by basic sulfate solid phases. This shows that equations 3 is not valid below a pH of 6.00.

In addition, there is a significant interaction between Al^{3+} and SO_4^{2-} influencing acid generation. Thus, the equations describing acid production associated with pyrite oxidation below a pH of 6.00 (most acid mine drainage is well below pH 6.00) should include the following reactions: In aqueous solutions below pH 6.00, AlOH^{2+} , $\text{Al}(\text{OH})_2^+$, $\text{Al}_2(\text{OH})_2^{4+}$, FeOH^{2+} , $\text{Fe}(\text{OH})_2^+$, and $\text{Fe}_2(\text{OH})_2^{4+}$ are the predominant ionic species. This suggests that at chemical equilibrium, pH will be a function of Al^{3+} and Fe^{3+} hydrolysis.

Predicting Aqueous Chemistry

In a disposal environment, the rate of infiltration or ground water flow will influence the aqueous chemistry. If waterflow is slow enough

to allow contact times necessary to establish equilibrium (i.e., rate of reaction faster than the flow rate through the system), the water quality characteristics will reflect the influence of secondary mineral formation. With increased leaching rates and rapid removal of reaction products, the kinetics of mineral dissolution-precipitation and adsorption will determine water quality characteristics. This may result in a nonequilibrium or metastable equilibrium condition influencing the aqueous chemistry.

If the waste/water system is at chemical equilibrium and the aqueous chemistry can be defined by secondary mineral reactions, then any leachate that leaves the disposal environment can be predicted using fundamental thermodynamic constants. With these fundamental relationships established, waste-specific/site-specific test methods can be used to predict water quality as a function of disposal site design (i.e., design which influences waste composition and flow rate).

If water quality predictions are not acceptable, then treatment options can be included in the test procedure.

Manage Acid Mine Drainage

It is clear from the weathering study data that the acid-base account should be used as the first step in determining acid potential.

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