PYRITE OXIDATION IN SATURATED AND UNSATURATED COAL WASTE[1]

by

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Abstract. Currently, the main strategy used to limit acid mine drainage (AMD) from pyritic coal waste materials (i.e. spoil and refuse) is to minimize the contact of these materials with water. An alternative approach, not generally practiced in the coal industry, is to keep the pyritic material inundated with water. Concerns with this latter technique include the potential detrimental effects of dissolved oxygen and ferric iron on pyrite oxidation, as well as the ability to maintain complete and continuous water saturation. Laboratory tests were conducted to determine the effects of dissolved oxygen and ferric iron on pyrite oxidation. These tests used small columns (5.1 cm diameter x 46 cm) filled with 590 g each of coal refuse (2.54 cm x 10 mesh) that contained 10.1% (by weight) pyritic sulfur. Triplicate columns of four different hydrologic scenarios were studied: leaching with deionized water under unsaturated and saturated conditions and leaching with a ferric-iron-laden AMD under unsaturated and saturated conditions. Results indicate that maintaining the pyritic material under water virtually stops pyrite oxidation. After 189 days, sulfate loads removed from the columns averaged ($\pm$ one standard deviation) 34.5 $\pm$ 4.9 g for the unsaturated columns leached with deionized water; 34.2 $\pm$ 5.8 g for the unsaturated columns leached with AMD; 0.15 $\pm$ 0.04 g for the saturated columns leached with deionized water: and -0.46 $\pm$ 0.06 g for the saturated columns leached with AMD. The negative sulfate load indicates that sulfate was retained in the columns. Results from this and other studies, theoretical calculations, and experience from the metal mining industry show that the disposal under saturated conditions can significantly reduce contaminant concentration from pyritic material.
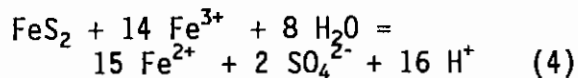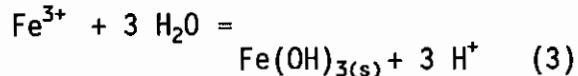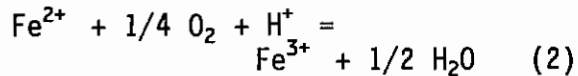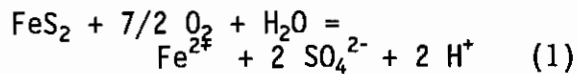
Additional Key Words: acid mine drainage, iron disulfide oxidation, coal refuse, coal spoil, coal mine wastes.

191

Introduction

According to Singer and Stumm (1970) the equations governing pyrite oxidation are:

$$FeS_2 + 7/2\ O_2 + H_2O = Fe^{2+} + 2\ SO_4^{2-} + 2\ H^+ \quad (1)$$

$$Fe^{2+} + 1/4\ O_2 + H^+ = Fe^{3+} + 1/2\ H_2O \quad (2)$$

$$Fe^{3+} + 3\ H_2O = Fe(OH)_{3(s)} + 3\ H^+ \quad (3)$$

$$FeS_2 + 14\ Fe^{3+} + 8\ H_2O = 15\ Fe^{2+} + 2\ SO_4^{2-} + 16\ H^+ \quad (4)$$

Equation 1 describes the oxidation of pyrite in the presence of oxygen and water, yielding ferrous iron, sulfate, and hydrogen ions. The oxidation rate of ferrous iron, described by Equation 2, is strongly dependent on pH. At a pH greater than 7.0, and in the presence of sufficient dissolved oxygen, ferrous iron will oxidize to ferric iron in a matter of minutes (Stumm and Morgan 1970). At near-neutral pH values, ferric iron is then removed from solution as precipitated ferric hydroxide (Equation 3). At lower pH values, ferrous iron oxidation is slow; at pH 3.0, the reaction has a half life of about 3 years. Iron-oxidizing bacteria, however, can greatly accelerate the rate of ferrous iron oxidation. The bacterium *Thiobacillus ferrooxidans* is ubiquitous to the coal mining environment and their presence has been shown to increase the rate of ferrous iron oxidation by a factor of 10^6 (Singer and Stumm 1970 and Dugan 1975). At low pH (< 3.0), the ferric iron produced from biological ferrous iron oxidation can oxidize pyrite as shown in Equation 4. After the pH of the water within a mine site is lowered by acid production (Equations 1 and 3), conditions are ideal for growth of iron-oxidizing bacteria and the system becomes bacterially-mediated. Pyrite oxidation can then be described by Equations 2 and 4 (Temple and Delchamps 1953 and Kleinmann et al. 1980).

Water plays a dual role in the generation of acid mine drainage (AMD), as a reactant and as a transport medium. Very small quantities of water are necessary as a reactant (equation 1). Studies have shown that sufficient water is normally available as humidity in the pore gas to not limit the rate of pyrite oxidation (Geidel 1980 and Watzlaf and Hammack 1989). In addition, Hammack (1988) found that the oxidation products that build up around pyrite are hygroscopic, supplying ample water for reaction.

To eliminate AMD generation, attempts are often made to limit water, thus limiting the transport of contaminants. At surface mines, selectively handled pyritic spoil and/or coal refuse hauled backed to the site are regularly placed "high and dry" in the backfill in hopes of minimizing acid generation. Coal refuse is disposed of in large piles or used to build impoundment dams for placement of refuse fines. Drains are built into the refuse to attempt to keep the refuse unsaturated in order to maintain physical stability.

Oxygen is the other reactant necessary for pyrite oxidation as shown in equation 1. To limit pyrite oxidation, oxygen levels must be reduced from an atmospheric level of 21% (0.21 atm) to extremely low levels. It has been shown that the biotic rate of pyrite oxidation is not limited unless pore gas oxygen is reduced to less than 1% (0.01 atm) (Carpenter 1977 and Hammack and Watzlaf 1990). With current reclamation practices, limiting oxygen to less than 1% is not feasible. At the current time, the only practical method to reduce oxygen to levels low enough to limit pyrite oxidation is by saturating the pyritic material with water.

Underwater disposal of pyritic materials may have some drawbacks. If

contaminants are present from previously oxidized pyrite, they will be released upon saturation. Therefore, it is important to saturate the material quickly and/or take measures to minimize pyrite oxidation prior to saturation.

Upon disposal under water, dissolved oxygen (DO) and ferric iron can continue to oxidize pyrite. In order to examine this potential situation in more detail, the quantity of pyrite that could oxidize (and the subsequent concentrations of iron, sulfate, and acidity) can be calculated. The saturation concentration of dissolved oxygen in water is dependent on temperature and the partial pressure of oxygen in the gas in contact with that water. Field measurements of oxygen in the pore gas within surface mine backfill have been shown to be significantly lower than atmospheric levels. A typical value at a depth of 6 meters in reclaimed surface mine would be about 5 percent oxygen (Lusardi and Erickson 1985, Jaynes, et al. 1985). At 13°C, this would result in a saturated DO concentration of 2.5 mg/L. If all of this dissolved oxygen is used to oxidize pyrite (equation 1), the resultant water would contain 1.2 mg/L ferrous iron, 4.3 mg/L sulfate, and 4.5 mg/L acidity as $CaCO_3$ equivalent. This assumes that all oxygen is used to oxidize pyrite and no additional oxygen transfer occurs. Even if atmospheric levels (21%) of oxygen are present in the backfill, the 10.5 mg/L of dissolved oxygen at saturation would only increase these contaminant concentrations by a factor of four. Additional pyrite oxidation would require oxygen diffusion through the backfill and through the zone of saturation. Diffusion of oxygen through water is about 10,000 times slower than diffusion through spoil atmosphere (Ohio State University 1971).

Another concern regarding subaqueous disposal of pyritic material is contact with soluble ferric iron originating in the unsaturated zone. The dissolved ferric iron in water that contacts pyritic material in the saturated zone can oxidize pyrite (equation 4). If the contacting water contains 25 mg/L ferric iron (and probably little dissolved oxygen since it would have been used to oxidize pyrite and ferrous iron), and if all of the ferric iron is used to oxidize pyrite, the concentrations of total iron, sulfate, and acidity (as $CaCO_3$) would increase by only 1.8 mg/L, 6.1 mg/L, and 6.4 mg/L , respectively (see table 1).

Table 1. Theoretical concentrations before and after contacting pyrite. 'After' values based on the stoichiometry of equation 4.

Parameter	Before	After
Ferrous Iron	0.02	6.8
Ferric Iron	25.0	0.0
Total Iron	25.0	26.8
Acidity	67.2	73.6
Sulfate	86.0	92.1

The most encouraging information concerning the disposal of pyritic coal wastes under water is the success that the metal mining industry has had with this method (Ritcey 1991, Balins et al. 1991, Rescan Environmental Services Limited 1990, and Bell 1987). The opinion of many people involved in metal mine waste disposal is summed up by Bell 1987, "at the current time, the only practical and proven long-term approach to controlling the formation of acid in sulphide tailings is to limit the availability of oxygen as a reactant by maintaining the waste in a saturated or submerged condition".

In this study, pyritic material was leached under saturated and unsaturated conditions. Six columns were leached under saturated conditions. Three of these six received deionized water as the leachant, simulating clean water recharge. The other three received an AMD solution that contained ferric iron as well as iron-oxidizing bacteria, simulating recharge with AMD that could be formed prior to contacting the disposed pyritic material. Another six columns were leached under unsaturated conditions. Three were leached with deionized water and three with an AMD solution. Comparisons of leachate water quality parameters were made to determine the effect of saturation on pyrite oxidation rates.

Methods

Description of Pyritic Material

The pyritic material used in this study was refuse from the cleaning of Pittsburgh-seam coal that had been mined about 20 miles east of Pittsburgh, Pennsylvania. Refuse material was collected from the disposal pile within one day of being generated. This material was a mixture of coarse and fine refuse (1.5 inches x 0). After collection, the refuse was further sized to 1 inch x 10 mesh. The material was extensively rinsed with tap water to remove fines that tended to cling to coarser material. The material (approximately 10 kg) was coned and quartered to obtain sixteen equal splits. Twelve splits were randomly loaded into columns, three used for sulfur analysis, and one reserved for reference purposes. Sulfur speciation was determined using standard test methods (American Society for Testing and Materials, 1983) (see table 2).

Leaching Procedures

The columns used in this study were constructed from translucent PVC pipe,

Table 2. Sulfur content of the coal refuse used in column leaching tests.

	Total	Pyritic	Organic	Sulfate
		Sulfur Percentage		
Sample #1	10.32	9.77	0.48	0.07
Sample #2	9.60	9.29	0.26	0.05
Sample #3	11.49	11.15	0.31	0.03
Mean	10.47	10.07	0.35	0.05

5.1 cm in diameter, and capped at the bottom. A stainless steel nipple was affixed in a hole drilled in the bottom cap. Tygon tubing was attached to this nipple to facilitate leachate collection. A glass microfiber filter (4.7 cm in diameter) was placed on the bottom cap followed by 0.14 kg acid-washed sand and 0.59 kg of refuse (figure 1).
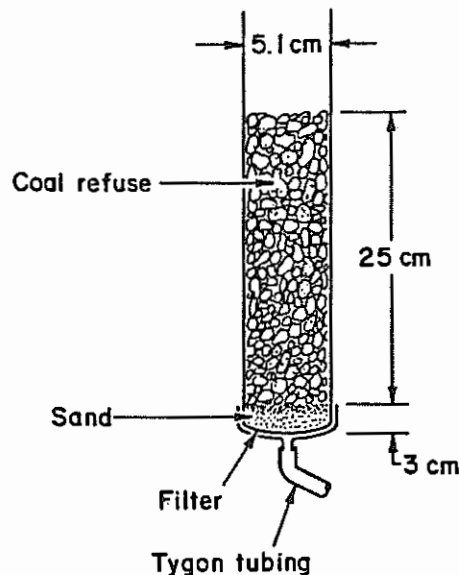

Figure 1. Schematic of a column used in leaching tests.

Four different leaching scenarios were carried out in triplicate: 1) unsaturated, leached with deionized water; 2) unsaturated, leached with previously collected leachate (recycled

AMD); 3) saturated, leached with deionized water; and 4) saturated, leached with previously collected leachate (recycled AMD). The unsaturated columns periodically received 250 mL of water, which was allowed to gravity drain. The saturated columns were always inundated with water to a depth 3 cm above the top of the refuse. Initially, six of the columns were flooded with 250 mL of deionized water that resulted in a water level about 3 cm above the refuse (approximately 1.2 pore volumes). For the first leach, 250 mL of deionized water was added to all 12 of the columns. The volume of leachate from each column was measured with a graduated cylinder to the nearest 5 mL. Approximately 70 mL were acidified with 1.0 mL of concentrated (12.1 N) hydrochloric acid. A separate 100 mL aliquot was collected in another sample bottle. These samples were used for the water quality analyses described below. The remaining leachate (about 80 mL) from each column was added to a loosely covered flask for use as the recycled AMD leachant in the next week of leaching. Approximately weekly, this procedure was repeated. In addition, during each leaching cycle, samples of the deionized water and the recycled-AMD leachant were collected for chemical analysis.

Water Analysis

Upon collection, water samples were refrigerated at 4°C until analyzed. The unacidified sample was used for pH, acidity, alkalinity, and sulfate determinations. Acidified samples were analyzed for ferrous iron, total iron, manganese, aluminum, calcium, magnesium and sodium.

For acidity determinations, 1.0 mL of a 30% hydrogen peroxide solution was added to 50.0 mL of sample and boiled on a hot plate for 10 minutes. The sample was allowed to cool to room temperature

and was titrated with 0.1 N sodium hydroxide to pH 8.3. The titration was performed with the Orion Model 960 autochemistry system[1] using 0.3 mL additions of titrant every 15 seconds. All acidity concentrations were converted to mg/L of calcium carbonate equivalence. Alkalinity was analyzed by titration with sulfuric acid to a pH endpoint of 4.8 and converted to calcium carbonate equivalent.

Sulfate was analyzed by a barium chloride titration. The sample was passed through a cation exchange resin (Amberlite, 1R-120H, C.P., medium porosity). The first 25 mL through the resin was discarded. Depending on expected sulfate concentration, 1.0 to 10.0 mL of sample was added to 40.0 mL propanol in a white porcelain disk and stirred with a magnetic stir bar. Two drops of thorin ((o-[2-hydroxy-3,6-disulfo-1-naphtyl)azo] benzenearsonic acid, disodium salt) was added as an indicator. A 1:99 solution of ammonium hydroxide was added until a pink color developed. The solution was then adjusted with a 1:99 solution of hydrochloric acid back to the original yellow color. This solution was then titrated with a 0.005 M solution of barium chloride to a pink endpoint. Periodically, sulfate concentrations were confirmed by liquid chromatography.

The acidified sample was used for metal analysis. Concentrations of all metals, except ferrous iron, were determined using inductively coupled argon plasma spectroscopy (ICAP). For ferrous iron analysis, 50.0 mL of sample was mixed with 9.0 mL of a solution containing 175.0 mL of concentrated sulfuric acid (36 N), 650.0 mL of distilled water, and 175.0 mL of

195

phosphoric acid (85%). Three drops of diphenylamine sulfonic acid was added to the sample as an indicator. The sample was titrated with a 5.6 g/L potassium dichromate solution using a redox platinum electrode attached to the Orion 960 autochemistry system. The Orion 960 was set in the first derivative mode and programmed to add 0.1 mL increments of the potassium dichromate titrant.

Iron-oxidizing bacteria were estimated using a multiple-tube serial-dilution method (American Public Health Association 1981 and Carpenter 1977). Three tubes with nine ten-fold serial dilutions were used with the media developed by Cobley and Haddock (1975).

Results

In this section, several figures are presented that show the cumulative contaminant load produced by the refuse material. In all cases, the contaminant load of the water added to the column (leachant) was subtracted from the contaminant load of water removed from the column (leachate).

Deionized Water Leaching

Except for a few days when the deionizing apparatus was not functioning properly, acidity, alkalinity, and sulfate never exceeded 4 mg/L and iron, manganese, aluminum, calcium, and magnesium never exceeded 1 mg/L in the deionized water leachant.

The pH of the leachate from the three saturated and three unsaturated columns and the pH of the distilled water leachant is presented in figure 2. Typically, the pH of the leachate from saturated columns was higher than the pH of the deionized water leachant. Conversely, the pH of the leachate from the unsaturated columns was consistently lower than the deionized water.
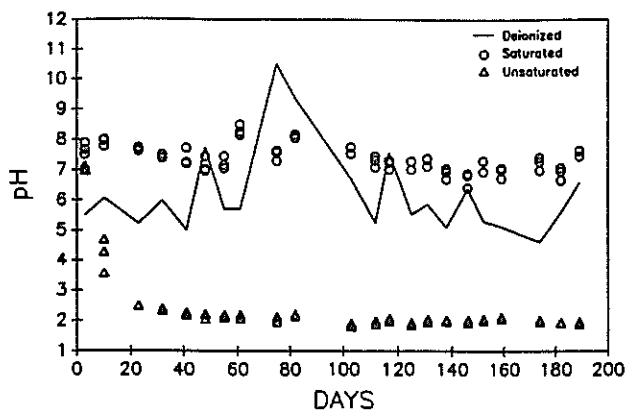

Figure 2. pH of the leachate from the three saturated and three unsaturated columns

Cumulative sulfate loads are shown in figure 3. After 189 days, cumulative sulfate loads were 34,900 mg, 40,400 mg, and 28,300 mg for the unsaturated columns and 202 mg, 117 mg, and 134 mg for the saturated columns. Cumulative loads of manganese, aluminum, calcium, and magnesium all followed the same basic trend as sulfate. Table 3 shows cumulative loads for each of these constituents after 189 days of leaching.
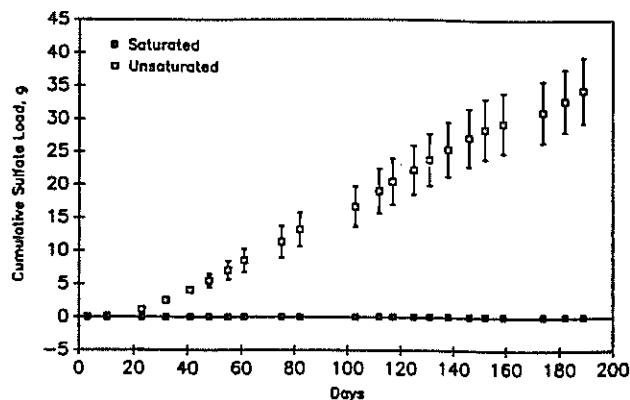

Figure 3. Mean cumulative sulfate load in the leachate from the saturated (n=3) and unsaturated (n=3) columns that were leached with deionized water. Error bars represent ± one standard deviation; where no error bars are shown, they are less than the size of the symbol.

196

Table 3. Cumulative loads after 189 days of leaching with distilled water.

Leaching Condition	Replicate Number	Cumulative Load, mg							
		Sulfate	Acidity*	Fe	Mn	Al	Ca	Mg	Na
Saturated	1	202	-152	<1	<1	<1	<1	<1	153
	2	117	-150	<1	<1	<1	<1	<1	145
	3	134	-188	<1	<1	<1	<1	<1	164
Unsaturated	1	34,900	32,800	10,700	37	486	563	246	147
	2	40,400	38,000	13,000	40	490	637	249	156
	3	28,300	26,800	8,800	25	373	470	195	155

*as $CaCO_3$ equivalent, negative values indicate alkalinity

Table 4. Cumulative loads after 189 days of leaching with recycled AMD.

Leaching Condition	Replicate Number	Cumulative Load, mg[a]							
		Sulfate	Acidity*	Fe	Mn	Al	Ca	Mg	Na
Saturated	1	-482	-3,820	-784	3.3	-29	714	85	209
	2	-517	-3,690	-770	4.1	-29	818	86	203
	3	-373	-3,330	-650	3.2	-12	586	90	242
Unsaturated	1	29,400	25,800	8,900	31.	442	457	237	169
	2	42,400	38,700	13,500	40.	510	644	248	132
	3	30,900	28,800	9,300	31.	391	460	207	140

[a]negative acidity values indicate acidity being neutralized, other negative numbers indicate retention within columns.
*as $CaCO_3$ equivalent.

Twice during the course of the experiment, selected leachate samples were analyzed for iron-oxidizing bacteria. No viable iron-oxidizing bacteria were detected in the leachates from the saturated columns (lowest detectable limit was 12 cells/100 mL). However, leachates from the unsaturated columns were found to contain between 3,700,000 and 8,000,000 cells/100 mL.

Recycled AMD Leaching

For the recycled-AMD leaching, the first leach used deionized water. For all subsequent leachings, a mixture of the previous weeks leachate from all of the columns was used. The water quality of this recycled leachate averaged 1370 mg/L sulfate, 1310 mg/l acidity (as $CaCO_3$), 405 mg/L total iron (5 mg/L ferric iron and 400 mg/L ferrous iron), 1.4 mg/L manganese, 18 mg/L aluminum, 37 mg/L calcium, and 12 mg/L magnesium.

Figure 4 shows the pH from the three saturated and three unsaturated columns and the pH of the recycled AMD. Except for the first day of leaching, when deionized water was used as the leachant, the pH of the leachate from saturated columns was higher and the pH of the leachate from the unsaturated columns was lower than the pH of the recycled AMD leachant.

Cumulative sulfate loads are presented in figure 5. The saturated refuse actually retained sulfate as well as acidity, iron, and aluminum (Table 4) Manganese, calcium, and magnesium were not retained in the saturated columns (Table 4).

Twice during the course of the experiment, selected leachate samples were analyzed for iron-oxidizing bacteria. For the saturated columns, leachate samples contained between 9,200 and 37,000 cells/100 mL. Samples of leachate from the unsaturated columns

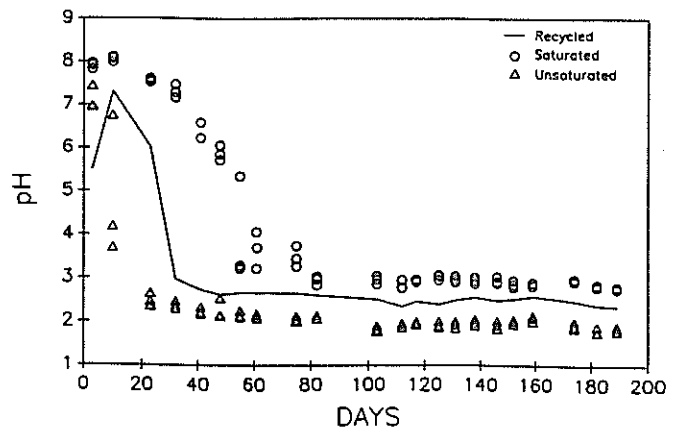were found to contain between 170,000 and 920,000 cells/100 mL.

Figure 4. pH of the leachate from the three saturated and three unsaturated columns that were leached with recycled AMD. Also shown is pH of the recycled AMD leachant.
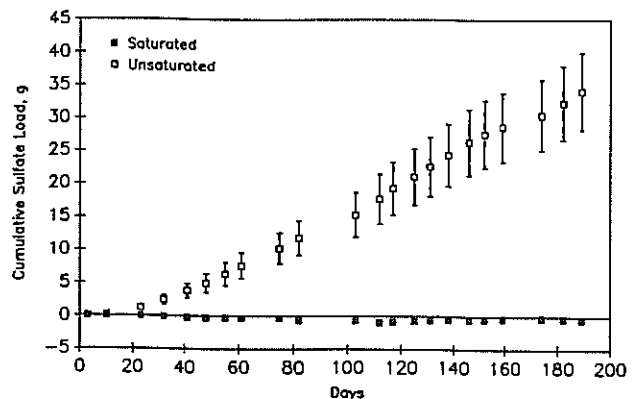

Figure 5. Mean cumulative sulfate load in the leachate from the saturated (n=3) and unsaturated (n=3) columns that were leached with recycled AMD. Error bars represent ± one standard deviation; where no error bars are shown, they are less than the size of the symbol.

Discussion

Deionized Water Leaching

The pH of the leachate from the unsaturated columns dropped to 2.5 after

198

about 20 days of leaching and stabilized around 2.0 through day 189 (figure 4). Sulfate in the leachate of the unsaturated columns indicates that pyrite oxidation was occurring at a much higher rate than in the saturated columns. To enable comparison of pyrite oxidation rates to other research studies, sulfate loads can be normalized by dividing by the amount of pyrite present. Others have expressed pyrite oxidation rates in terms of mg of sulfate per g of pyrite per hour. Pyrite oxidation rates for the unsaturated columns in this study rose to 0.05 (mg sulfate)(g pyrite)$^{-1}$(hr)$^{-1}$ after 30 days. Rates from day 30 to day 189 ranged from 0.05 to 0.14 (mg sulfate)(g pyrite)$^{-1}$(hr)$^{-1}$ (figure 6). These rates are consistent with values reported in the literature (table 5).

In the unsaturated columns, the pH fell to 2.5 within about 20 days. Significant levels of iron, as well as manganese, aluminum, calcium, and magnesium were leached (table 4). These metals followed the same basic trend as sulfate (see figure 5).
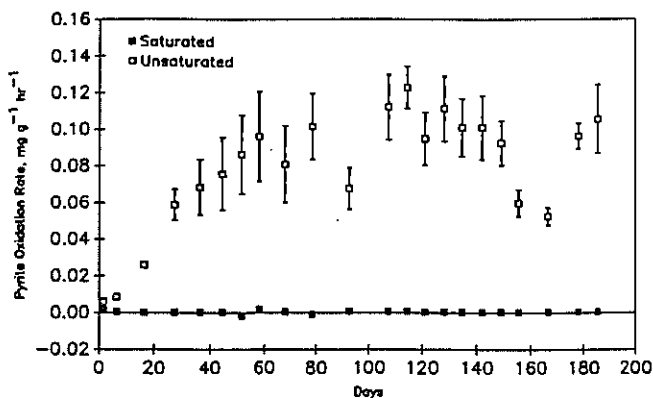

Figure 6. Mean pyrite oxidation rates for the saturated (n=3) and unsaturated (n=3) columns that were leached with deionized water. Error bars represent ± one standard deviation; where no error bars are shown, they are less than the size of the symbol.

Saturation had a highly significant effect on coal refuse leached with deionized water. Water chemistry was most strongly effected by carbonate dissolution processes. The cumulative sulfate loads in the leachates from the saturated columns (figure 3 and table 3) indicate extremely low rates of pyrite oxidation. The average sulfate loads after 189 days of leaching for the saturated columns averaged only 0.4 percent (151 mg) of the average sulfate load from the unsaturated columns (34,500 mg).

The pH of the leachate (pH out) was typically higher than the pH of the deionized water leachant (pH in) (figure 2). This increase in pH coupled with the fact that the columns produced alkalinity (table 3) indicate the dissolution of carbonates. However, loads of calcium and magnesium in the leachate from any of the saturated columns were near zero. In fact, the only cation released from these columns was sodium. A strong correlation between alkalinity and sodium exists for the water quality data (r = 0.82) indicating, as others have found, that calcium and magnesium can exchange with sodium that is present in clays (Oertel and Hood 1983 and Krothe 1980).

To achieve the observed sulfate loads in the saturated columns, approximately 44 mg of ferrous iron had to have been released, based on the stoichiometry of equation 1. However, as expected, no iron was found in any leachate since ferrous iron oxidation and subsequent ferric iron precipitation should occur readily at this pH (> 6.5). Neither manganese nor aluminum was detected in the leachate.

The two analyses for active populations of iron-oxidizing bacteria found no viable cells (< 12 cells/100 mL). This is evidence that pyrite was oxidized mainly by the dissolved oxygen in the water. Recently, Moses and Herman (1990) have postulated that at circumneutral pH, dissolved oxygen does

Table 5. Pyrite oxidation rates reported by other authors.

Investigator	Observed Rate[*] mg g^{-1} hr^{-1}	Pyrite Type	Particle Size	Temperature, °C
Braley 1960	0.13	sulfur ball	8-40 mesh	--
Clark 1965	0.11	sulfur ball	40-50 mesh	20
Morth and Smith 1966	0.06	sulfur ball	70-100 mesh	25
Rogowski and Pionke 1984	0.16	not specified	2-8 mm	·25
Nicholson et al. 1985	0.13	massive	76 microns	23
Hammack and Watzlaf 1990	0.13	coal pyrite	>60 mesh	20-25
This study[#]	0.08	coal pyrite	2.5cm-10 mesh	20-25

*rate in milligrams of sulfate per gram of pyrite per hour
#average of three unsaturated columns leached with deionized water

not directly attack pyrite, but oxidizes ferrous iron that is adsorbed onto the pyrite surface. The resulting ferric iron then rapidly oxidizes pyrite. The adsorbed iron is cyclically oxidized and reduced and acts as a conductor of electrons from pyrite to dissolved oxygen (i.e. pyrite oxidation). Regardless of whether dissolved oxygen or ferric iron is the specific oxidant, the amount of oxygen used will result in the same amount of pyrite oxidized. The deionized water was typically about 20°C, and based on a few random measurements, was nearly saturated with respect to dissolved oxygen (9 mg/L). Assuming that all dissolved oxygen was used to oxidize pyrite, and that there was no additional oxygen transfer into the water, the theoretical sulfate loads that would have been generated by this dissolved oxygen can be calculated using equation 1.   Figure 7 shows this theoretical sulfate load along with the
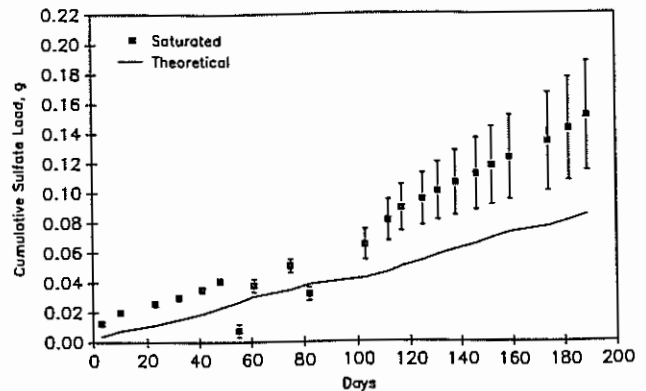

Figure 7. Mean cumulative sulfate load in the leachate from the saturated columns (n=3) that were leached with deionized water. Error bars represent ± one standard deviation; where no error bars are shown, they are less than the size of the symbol. Also shown is the theoretical maximum sulfate load produced by pyrite oxidation using dissolved oxygen in the water as its sole oxidant.

observed loads from the three saturated columns. Since the observed loads are somewhat higher than the theoretical load, some oxygen transfer between the atmosphere and top surface of the water must have occurred. Using the average difference between observed and theoretical sulfate loads, oxygen was transferred at a rate of at least 0.82 mg per day.

Recycled AMD Leaching

Water quality from the unsaturated columns receiving recycled-AMD leachate was very similar to the unsaturated columns leached with deionized water (Table 6). As can be seen from this table, no significant differences in water quality were observed between the unsaturated columns receiving recycled AMD or deionized water. This appears to indicate that there was no significant pyrite oxidation caused by ferric iron added in the recycled-AMD leachant. However, for the 189 days of the experiment, the oxidation of pyrite by ferric iron would only amount to an additional 500 mg and 150 mg of cumulative sulfate and iron load,

respectively. This minor increase would be indiscernible due to the inherent variability among columns. Apparently, the addition of iron-oxidizing bacteria in the recycled leachate was not significant either. In fact, bacterial analysis showed greater populations in the leachate from a column receiving deionized water than in the leachate from a column receiving the recycled AMD. No measurements of the iron-oxidizing bacteria were taken in the recycle-AMD leachant, but the nearly complete and rapid (within one week) oxidation of ferrous iron at pH 2.5 indicate the presence of the bacteria. However, at the end of the week (when the leachant was added), the bacterial populations may have been stressed due to the extremely low ferrous iron concentrations.

Figure 8 shows the results of the columns receiving recycled AMD in terms of mg of sulfate per g of pyrite per hour. Again, the values for the unsaturated columns were very similar to the unsaturated columns that received deionized water.

Table 6. Average cumulative loads ± one standard deviation for the unsaturated columns after 189 days of leaching.

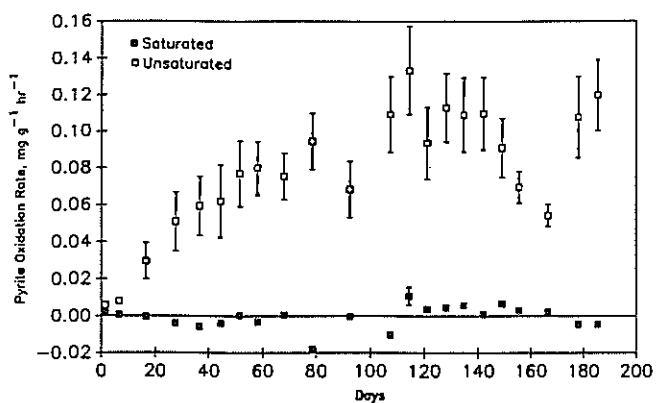| Leachant | Sulfate | Cumulative Load, mg | | | | | |
		Acidity*	Fe	Mn	Al	Ca	Mg
Recycled	34,200	31,100	10,600	34	448	520	231
AMD	±5,800	±5,500	±2,100	±4	±49	±87	±17
Deionized	34,000	32,500	10,800	34	450	557	230
water	±4,900	±4,600	±1,700	±6	±54	±68	±24

*as $CaCO_3$ equivalent

Figure 8. Mean pyrite oxidation rates in the saturated (n=3) and unsaturated (n=3) columns that were leached with recycled AMD. Error bars represent ± one standard deviation; where no error bars are shown, they are less than the size of the symbol.

Saturation with recycled AMD significantly affected pyrite oxidation. The pH in the leachate from the saturated columns remained above the pH of the recycled-AMD leachant but did fall to about 3.0 after 80 days (figure 4). Significant levels of acidity were neutralized by dissolution of carbonates with corresponding levels of calcium and magnesium found in the leachate. At this pH (3.0), manganese was also released indicating that manganese probably exists as, or is associated with, a carbonate. Iron, sulfate, and aluminum were all retained in the columns.

The iron in recycled-AMD leachant was 99% ferric iron. After passage through the column, the leachate typically contained less than 10% ferric iron. Using the mass of ferric iron chemically reduced during contact with the refuse, the theoretical amount of pyrite that could be oxidized and the corresponding mass of sulfate produced can be calculated using equation 4. The theoretical sulfate loads based on pyrite oxidation by ferric iron and by ferric iron plus dissolved oxygen

(assuming saturated levels of dissolved oxygen (9 mg/L) and no additional oxygen transfer), as well as the sulfate loads from the three saturated columns are shown on figure 9. This graph shows the limitation of using sulfate in the leachate as a measure of pyrite oxidation since sulfate may be stored within the column as a salt. This graph shows that sulfate was accumulated for the first 110 days and then began to be released. The release of sulfate corresponds to the time that pH stabilized around 3.0 (figure 4).
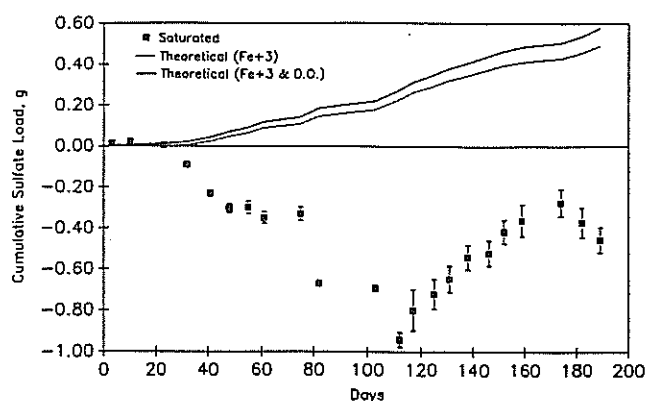

Figure 9. Mean cumulative sulfate load in the leachate from the saturated columns (n=3) that were leached with deionized water. Error bars represent ± one standard deviation; where no error bars are shown, they are less than the size of the symbol. Also shown is the theoretical maximum sulfate loads produced by pyrite oxidation using dissolved oxygen in the water as its sole oxidant and using both dissolved oxygen and ferric iron as oxidants.

The presence of bacteria in the saturated columns did not result in any observed pyrite oxidation. Bacterial populations from one of the three replicates ranged from 170,000 to 920,000 cells/100 mL. However, the low ferric iron concentrations in the leachate from these columns indicate these bacteria may not have been very

202

active within the columns, presumably due to the lack of oxygen. This illustrates one of the shortcomings of the MPN bacterial enumeration techniques as it measures active cells after the sample is placed in a media that is ideal for bacterial growth. It does not measure how active the bacteria are in-situ.

Summary and Conclusions

Saturation of the pyritic coal refuse significantly reduced the rate of pyrite oxidation. The sulfate load produced by the unsaturated columns after 189 days would take 118 years to be generated under saturated conditions in the columns receiving the deionized water leachant.

In an unsaturated system, pyrite oxidation has been found to be independent of oxygen levels down to about 1% (Myerson 1981 and Hammack and Watzlaf 1990). Pore gas oxygen levels in surface mine spoil or in coal refuse piles are almost always above 1% (Watzlaf and Erickson 1986, Lusardi and Erickson 1985, and Jaynes et al. 1983). Disposal methods to avoid contact with water will not slow pyrite oxidation. Pyrite will continue to oxidize and soluble salts (containing sulfate, iron and hydrogen ions) will be formed. Any water contacting these salts will become saturated with high concentrations of sulfate, iron, acidity, and any other contaminants that are dissolved under acidic conditions.

In a saturated system, pyrite would oxidize at a very low rate that is dependent on the amount of dissolved oxygen and ferric iron in the contacting water. Once dissolved oxygen is consumed, the rate of diffusion of pore gas oxygen through water becomes limiting. Additionally, any ferric iron in solution would be reduced to ferrous iron upon oxidation of pyrite. This study indicated that this ferrous iron

would then remain in the reduced state. As can be seen in equation 4, it takes 14 moles of ferric iron to oxidize one mole of pyrite. The lower rate of pyrite oxidation under saturated conditions should result in very low contaminant concentrations, quite possibly below effluent limits. Even if effluent limits were exceeded, significant reductions in chemical treatment cost would be realized.

To help neutralize the small levels of acidity that may be produced under saturated conditions, limestone could be codisposed with the pyritic material. Under saturated conditions, ferric iron should not be present and limestone armoring should not be a problem. The problem of codisposing limestone with pyritic material under unsaturated conditions is armoring of the limestone and the relatively low solubility of limestone (alkalinity generation) compared to the rapid and highly soluble acid salts from pyrite oxidation (i.e. acidity is generated faster than alkalinity) (Caruccio and Geidel 1987).

Theoretical calculations, column leaching, and experience from the metal mining industry show the disposal under saturated conditions can significantly reduce contaminant concentration from pyritic material. A field scale study is needed to demonstrate the utility of this approach.

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205