THE EFFECT OF OXYGEN, IRON-OXIDIZING BACTERIA, AND LEACHING FREQUENCY ON PYRITE OXIDATION

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ABSTRACT

Acid mine drainage (AMD) contaminates thousands of miles of streams and rivers in the Appalachian coal region. AMD results from the oxidation of pyrite, which is exposed to air and water by surface mining activities. The major objective of this study was to examine the rate of pyrite oxidation in column leaching tests and to relate these results to commonly used field abatement techniques. Specific objectives included determining the effect of oxygen, leaching frequency, and weathering on the biotic oxidation rate as well as the effect of oxygen on the abiotic rate. Pyrite oxidation was studied under various conditions using small (40 cm long by 2.54 cm I.D.) and large (1.92 m x 0.29 m I.D.) column leaching tests. The small columns contained 5 g of pyrite mixed with 100 g of inert silica sand. The large columns were filled with 175 kg of unweathered pyritic shale containing 3.5 pct sulfur. In the small column experiments, biotic oxidation of pyrite was faster than abiotic oxidation at all levels of oxygen tested with the largest difference occurring at the lowest oxygen level tested (0.5 pct). Biotic oxidation of pyrite at applied oxygen levels of 0.5, 1.0, 5.0, and 10.0 pct measured 12.9, 15.2, 13.2, and 16.0 mg SO_4^{2-}/day respectively. Abiotic oxidation rates of 1.9, 8.3, 11.0, and 14.8 mg SO_4^{2-}/day were observed for columns exposed to 0.5, 5.0, 9.6, and 14.5 pct oxygen. This suggests that unless the bacteria are inhibited, pyrite oxidation proceeds at approximately the same rate at any oxygen level above 0.5 pct. In the large column experiment s, pyrite oxidation, based on sulfate release, was calculated at 18.2 9 SO_4^{2-}/day for unsaturated leaching. After the material was saturated with water, the rate of pyrite oxidation resulting from biweekly flushings with oxygenated (8 mg 02/L) water was reduced to 0.7 g SO_4^{2-}/day. In another test, comparison of water quality of leachates from fresh material to weathered (26 pct less sulfur) material showed no differences in release

rates of sulfate (14.4-13.1 g/day), iron (4.26-4.20 g/day), or aluminum (0.29-0.27 g/day). Release rates for manganese, calcium, magnesium, and sodium were reduced by weathering to values 12.6, 23.2, 4.3 and 56.2 pct of the values from the fresh leaching tests, respectively. Partial pressures of carbon dioxide were reduced from between 0.8 and 3.2 to 0.01 and 0.4. Weathering caused oxygen to penetrate deeper into the material inferring the downward movement of the active pyrite oxidation zone with time. Additionally, four different leaching schedules were tested: 1 L every day, 7 L every 7 days, 14 L every 14 days, and 21 L every 21 days. The results indicated that leaching frequency did not have a significant effect on any water quality parameter or on pore gas composition.

INTRODUCTION

Acid mine drainage (AMD) is a water pollution problem associated with the mining of coal and sulfide minerals. These mining activities expose pyrite to oxygen and water with the ensuing oxidation of pyrite resulting in AMD. AMD is characterized by low pH and may contain high concentrations of acidity, sulfate, iron, and other metals. Acid mine drainage contaminates thousands of miles of streams and rivers, threatens aquatic life and vegetation, degrades natural water supplies, and contributes to the corrosion of contacted structures.

Previous research has defined the system of AMD formation and has identified several possible points of intervention. However, the results of many field studies are inconsistent. To better understand the reason for these inconsistencies, a series of experiments were conducted in two different sizes of leaching columns. Small columns were used to determine the effect of the partial pressure of oxygen on pyrite oxidation under both biotic and abiotic conditions. Larger columns were used to determine the effects of water saturation, leaching frequency, and extent of weathering on biotic oxidation under hydrologic conditions that simulated mine backfills.

BACKGROUND

The major chemical reactions involved in pyrite oxidation are as follows (1,2):

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

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

$$Fe^{3+} + 3H_2O = Fe(OH)_3 + 3H^+ \qquad (3)$$

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

Pyrite)(FeS_2) is oxidized (equation 1) to produce ferrous iron (Fe^{2+}), sulfate ($SO_4{}^{2-}$and hydrogen ion (H^+). At an interstitial pH above 3.5, the oxidation of ferrous iron can result in a ferric hydroxide precipitate (equations 2 & 3). At a lower pH, ferric iron will remain in solution (equation 2) and can oxidize pyrite producing more ferrous iron, sulfate and H^+ (equation 4). At this low pH, the oxidation of ferrous to ferric iron (equation 2) proceeds very slowly and, in fact, becomes rate-limiting under abiotic conditions (1,2).

In biotic systems, iron-oxidizing bacteria (namely Thiobacillus ferrooxidans) can catalyze ferrous iron oxidation, significantly increasing overall pyrite oxidation rates (1). T.

ferrooxidans accelerates pyrite oxidation via direct oxidation of pyrite or oxidation of Fe^{2+} to Fe^{3+}. Direct oxidation is probably most significant during initial acidification, as F^{3+} precipitates as $Fe(OH)_3$ and therefore, is unavailable for pyrite oxidation (1). As pH decreases, the abiotic oxidation of Fe^{2+} to Fe^{3+} slows according to the rate law:

$$\frac{-d(Fe^{2+})}{dt} = k\frac{(O_2(aq)(Fe^{2+}))}{(H^+)^2}$$

where (Fe^{2+}), (O_2(aq)), and (H^+) are activities, k is the rate constant, and t is time (4). As the abiotic rate of F^{2+} oxidation slows, T. ferrooxidans assumes its primary role of oxidizing Fe^{2+} to Fe^{3+}. Fe^{3+} then oxidizes pyrite resulting in a biologically-mediated cycle of equations 2 and 4 (5,6). It has been reported that T. ferrooxidans can increase the rate Fe^{2+} to Fe^{3+} oxidation by a factor of up to 1×10^6 (1,7).

AMD abatement techniques as applied in the field are usually targeted at one or more of the following: inhibiting iron-oxidizing bacteria, reducing pore gas oxygen levels, reducing water infiltration, increasing pH, or removing soluble ferric iron from the system.

T. ferrooxidans can be inhibited by some surfactants and certain food preservatives (a). Laboratory and field studies have shown that application of these chemicals can significantly reduce pyrite oxidation (8 - 15). To extend the longevity of these chemicals, Kleinmann (6) developed a slow-release formulation of rubber pellets impregnated with sodium lauryl sulfate (SLS). Current field studies with similar formulations have effectively reduced the pyrite oxidation rate for up to five years (16).

Pyrite oxidation can also be controlled by reducing the availability of oxygen, which affects direct oxidation of pyrite, oxidation of ferrous iron, and aerobic requirements of the iron-oxidizing bacteria. Standard reclamation, clay capping, and use of plastic liners are current methods thought to reduce pore gas levels in spoil and refuse. Pore gas oxygen levels measured in the field suggest an active pyrite oxidation zone delineated by oxygen consumption (17). These measurements, coupled with results of a study designed to assess the ability of topical treatments to reduce oxygen levels, show that while oxygen levels may be reduced to less than 10 or even 5 pct, this reduction does not seem to significantly slow the overall pyrite oxidation rate (17,18). Another method to reduce the availability of oxygen is to totally inundate the pyritic material with water. The maximum amount of oxygen that water can contain is 14.7 mg/L (at $O^{O}C$ and 0 ft elevation). This is equivalent to 0.00147 pct oxygen, which is much lower than the lowest levels observed in unsaturated spoil. It is common practice to totally inundate metal mine wastes, such as tailings. However, most highly pyritic material at surface coal mines is placed high in the backfill above the water table. In view of the recently discovered pseudo-karst hydrology found at some sites (19), complete inundation may not be as straightforward as once thought. Nevertheless, complete inundation of selectively placed pyritic material should not be difficult to achieve.

Another method thought to control AMD formation and transport of contaminants is to limit water infiltration. Current practices include standard reclamation (water loss by evapotranspiration), clay capping, and use of plastic liners. Using a mixture of fresh pyritic and alkaline materials, Geidel (20) showed that a decrease of water infiltration does not significantly affect cumulative acid loads, due to the limited solubility of limestone in water. This research led to the alkaline trench concept which promotes water infiltration through shallow pits filled with soda ash (highly soluble) and limestone (sparingly soluble) to offset these alkalinity limitations (19). More typically, alkaline addition has been in the form of topical spreading, mixed with backfill, and pit floor liming. An increased pH can inhibit bacterial activity, reduce the dissolution of other contaminants, and may remove ferric iron from solution. However, the limited alkaline solubility is a major drawback to these practices. While effective at neutralizing acidity at the surface, which enables plant establishment, the ability of these methods to significantly reduce pyrite oxidation within the spoil has not been demonstrated. For example, at one field site, high-quality limestone added at the surface at 327 metric tons per hectare yielded lush vegetation but no substantial improvement in water quality in the seeps or wells (17).

Another approach is to cause the precipitation of soluble ferrous and ferric iron. Phosphate is one chemical that can combine with soluble iron species to form iron-phosphate precipitates, thereby reducing oxidation of pyrite by limiting ferric iron in solution. Experiments with rock phosphate have resulted in reductions of total acid loads by up to 90 pct (2l).

METHODS

Small Columns

The pyrite was hand picked from a sample of Pittsburgh coal collected in Barbour County, WV. The pyritic material was crushed to <60 mesh and subjected to a density separation using tetrabromoethane (2.96 g/cc). The sink portion was then washed in boiling 6N HC1 to remove sulfate and iron oxides and to kill bacteria. Evolved gas analysis (22) indicated that virtually no organic or sulfate sulfur remained after this procedure. The material contained greater than 96 pct iron disulfide based on total sulfur measurements by combustion furnace (all sulfur was in pyritic form).

Four 40 cm by 2.54 cm I.D. columns were filled with 5 g of pyrite dispersed in 100 g of 30 - 60 mesh acid-washed silica sand. A porous glass frit at the base of each column prevented the packing material from washing out of the column. The columns were designed to allow pyrite to weather under unsaturated conditions in controlled oxygen atmospheres. Certified gas mixtures containing 0.5, 1.0, 5.0, 10.0, or 15.0 pct oxygen, 5.0 pct carbon dioxide, and balance nitrogen were obtained in compressed gas cylinders. Gas mixtures were bubbled through water to humidify the gas stream, passed through a rotometer, and then introduced into the base of each column (fig. 1). The gases flowed up through the pyritic material and were exhausted to the atmosphere through a gas trap. A flow rate of 20 mL/min was maintained through each column. Analysis of gases exiting the columns showed that this flow rate was sufficient to maintain a constant oxygen content throughout the column. The columns were leached weekly with 200 mL of 16 megohm deionized water (reduced oxygen atmospheres were maintained during leaching periods). Leachates were analyzed for sulfate. Periodically, a three-tube, most probable number (MPN) bacterial enumeration (23) using the media described by Cobley and Haddock (24) was performed to estimate the number of iron-oxidizing bacteria.

Large Columns

The large columns were constructed using 1.92-m lengths of 0.29-m diameter cast acrylic. To enable measurements of temperature and sampling of pore gas and water, sampling ports were installed at 0.25 m intervals of depth as shown in figure 2.

A slabby dark gray shale, overlying the Clarion coal seam, was collected at an active surface mine in Clearfield County, Pennsylvania. The material was crushed to <3.8 cm and placed into eighteen **0.53 m x 0.53** m x 0.30 m deep pans. A shovel was used to transfer the shale from each pan to five 20-L buckets. A shovel load was distributed from pan #1 to the five buckets. Then a shovel load from pan #2 was distributed to the buckets. This continued until all buckets were filled. The material in four of the buckets was transferred to the four columns. A sample was taken from the fifth bucket and the material remaining in this bucket was saved for other tests. This continued until all four columns were filled with 0.10 m^3 of shale (approximately 175 kg). The shale was analyzed using the combustion furnace method and found to contain 3.5 percent sulfur.

Deionized water was added through the top of the columns for all leaching and flushing tests. During all leaching tests, the valve on the leachate collection system remained open with the end of the tube kept underwater to avoid oxygen inflow. During flushing tests, the columns remained inundated with water to a level 0.15 m above the surface of the shale. Twenty liters of water were added and withdrawn simultaneously to maintain this water level. All water samples were analyzed for pH, acidity, sulfur, ferrous iron, total iron, calcium, magnesium, aluminum, sodium, and manganese.

The columns were constructed to allow contact of atmospheric gases to occur at the top surface of the shale only. Two evacuated tubes were used to sample pore gas within the columns. The first tube was used to purge the sample rod and tubing. Gas in the second tube was analyzed for oxygen, carbon dioxide, nitrogen, argon, carbon monoxide, and methane.

Analytical

For analysis of pH, sulfate, and acidity, an unacidified sample was used. For ferrous iron, total iron, calcium, magnesium, aluminum, sodium, and manganese determinations, the water sample was acidified with hydrochloric acid to pH less than 1.0. Ferrous iron was measured by potassium dichromate titration using the sodium salt of diphenylaminesulfonic acid as an indicator. Concentrations of total iron, calcium, magnesium, aluminum, sodium, and manganese were determined by inductively coupled argon plasma (ICAP) spectroscopy. After passing the sample through a cation-exchange resin, sulfate was analyzed by barium chloride titration using thorin as an indicator. Acidity analysis consisted of a fixed endpoint titration to pH 8.3 using a 1$\underline{N}$ sodium hydroxide solution and expressed as mg/L as $CaCO_3$.

Gas chromatography was used to determine volumetric, water-free concentrations of oxygen plus argon, carbon dioxide, nitrogen, carbon monoxide, and methane. Oxygen and argon values were calculated from the relative abundance of argon and nitrogen in standard air and the molecular weight of the gas molecules:

$$\text{Argon, vol-pct} = \frac{0.933}{78.1} \times \text{Nitrogen}$$

$$\text{Oxygen, vol-pct} = (\text{Oxygen plus Argon}) - (\text{Argon} \times 1.14)$$

RESULTS AND DISCUSSION

Small Columns

Abiotic oxidation experiments were carried out on HC1-washed pyrite under unsaturated conditions at oxygen contents of 0.5, 5.0, 9.6, and 14.5 pct. MPN bacterial counts performed on the leachates indicated that the columns were sterile throughout the experiment. Plots of cumulative sulfate in the leachates versus weathering time (fig. 3) are linear and show that abiotic pyrite oxidation is highly dependent on the oxygen content of the column atmosphere.

The biotic oxidation of pyrite was carried out under unsaturated conditions and at oxygen contents of 0.5, 1.0, 5.0, and 10 pct. Each column was inoculated with 30 mL of acid drainage from a coal mine in Westmoreland County, Pa. MPN's were performed after 7 and 42 days of weathering to determine the number of bacteria cells present in each column. After 7 days of weathering, the number of bacterial cells was significantly lower (95 pct confidence interval) in the column containing 0.5 pct oxygen than in columns with higher oxygen contents. This suggests that more time is required for bacterial growth at 0.5 pct oxygen. However, after 42 days of weathering, there was no significant difference in number of bacteria cells indicating that stable cell populations are independent of oxygen content between 0.5 and 10 pct.

Cumulative sulfate versus weathering time plots for biotic oxidation (fig. 4) reflect bacterial activity during the lag, log growth, and stationary phases of a bacteria-mediated process. Unlike abiotic oxidation, biotic oxidation is not significantly inhibited by reduced oxygen contents (fig. 4). In fact, plots representing 0.5 and 5.0 pct oxygen are virtually identical. All plots except the one representing 1.0 pct oxygen are coincident throughout the lag and log growth phase. The plot representing 1.0 pct oxygen is unusual because the logarithmic growth phase started earlier and resulted in the production of more sulfate than the other oxygen contents, including 5.0 and 10.0 pct.

Figure 5 shows the rates of sulfate production for abiotic and biotic pyrite oxidation at oxygen contents between 0.5 and 14.5 pct. Sulfate production rates from abiotic oxidation were calculated from the slope of the least squares regression line that best describes cumulative sulfate data (fig. 3). The highest rates of biotic oxidation occurred during the log growth phase. However, the constant activity of stable bacterial populations during the stationary phase is more relevant to sustained pyrite oxidation. Therefore, rates for biotic oxidation were based on the slope of regression lines for cumulative sulfate data during the stationary phase (fig. 4). As indicated in figure 5, the biotic oxidation of pyrite is more rapid than abiotic oxidation at all oxygen contents. However, the greatest difference between abiotic and biotic oxidation occurs at low oxygen contents (less than 5 pct oxygen) where abiotic oxidation is slow, but biotic oxidation occurs at rates only slightly lower than at 10 pct oxygen. These results signify that efforts to limit pyrite oxidation by reducing oxygen content will be successful only when bacteria are inhibited.

Large Columns

Bacterial analysis of leachates from the large columns showed that inoculation was not necessary. Healthy populations of iron-oxidizing bacteria were present in the shale. Therefore, all of the large column tests represent biotic oxidation of pyrite. Rates of pyrite oxidation were reported as mg SO_4^{2-}/day for the small columns and as g SO_4^{2-}/day for the large columns due to differences in scale. These rates can be presented on a similar basis if they are converted to weight SO_4^{2-}/weight FeS_2/day. However, a problem arises due to the variable oxygen levels in the large columns (see figure 11). Therefore, assumptions would have to be made to decide the amount of the shale exposed to various oxygen levels. For simplicity, all pyrite oxidation rates are presented as weight SO_4^{2-}/day.

However, if logical assumptions are made, the oxidation rates in the small and large columns are very similar. For example, the biotic oxidation rate of the 10 pct applied oxygen in the small columns can be converted from 16.0 mg SO_4^{2-}/day to 3.33 g SO_4^{2-}/kg FeS_2/day. In the large columns, figure 11 shows that for fresh shale, oxygen levels dropped from atmospheric (20.8 pct) to 0.8 pct in the top 0.75 m of the material. If the assumption is made that this upper 0.75 m is exposed to an average of 10 pct oxygen, the pyrite oxidation rate of 14.1 g SO_4^{2-}/day (see Table 2) can be converted to 2.93 g SO_4^{2-}/kg FeS_2/day. Changing the assumption that the weight of material exposed to a 10 pct oxygen level is the upper 0.5 m changes the calculated pyrite oxidation rate to 4 39 g SO_4^{2-}/kg FeS_2/day. It is reassuring to note that the oxidation rates in the small and large columns are of the same order of magnitude when they are converted to a similar basis.

Figure 6 compares cumulative sulfate loads for water saturated and unsaturated conditions. Sulfate was released at a rate of 18.2 g/day in unsaturated columns and only at a rate of 0.7 g/day when the shale remained inundated and flushed biweekly with 20 L of oxygen-saturated water (D.O. = 8 mg/L). Stoichiometrically, the amount of oxygen added through these flushes with oxygen-saturated water can account for 0.1 g/day of sulfate from the oxidation of pyrite. The remaining 0.6 g/day of sulfate released could be due to additional pyrite oxidation from dissolved oxygen transferred from the atmosphere and/or from continued solubilization of previously weathered sulfate compounds. Additional tests using oxygen-depleted water for the 20-L flushes resulted in a sulfate release rate of 0.5 g/day.

The importance of maintaining complete water inundation was clearly illustrated during these tests when a leak developed in one column and lowered the level of the water to 0.5 m below the surface of the shale. It was not known exactly how long this upper 0.5 m of shale was exposed, but it was not more than 32 days. Upon re-inundation, the minimum sulfate release rate into solution was 6.9 g/day, 10 times the rate of permanently saturated columns.

The effects of weathering on the release of sulfate, iron, aluminum, manganese, and calcium are shown in figures 7 - 9. The plots labeled 'fresh' represent results of weekly leaching tests that began 7 days after the material was crushed and loaded into the columns. At the start of the 'weathered' tests, the shale contained 26 pct less sulfur than it had at the beginning of 'fresh' tests. Before the weathered tests were begun, the columns were inundated and flushed with approximately 50 L of water to remove any oxidation products present as a result of previous tests. The different initial load values can be explained by how these two tests began. Rates of release of these contaminants were calculated by least squares regression and are given in Table 2. Sulfate, iron, and aluminum were released at the same rate and were not affected by previous weathering (significance tested at the 0.05 level using two-tailed Student's t-test). The sulfate and iron release rates indicate that the overall pyrite oxidation rate did not change even after 26 pct of the pyrite had been oxidized. Aluminum release rates suggest a direct relationship between pyrite oxidation processes and solubilization of this element. Manganese release rates were reduced by weathering and followed the same trend as calcium (figure 9). Both sodium and magnesium release rates also diminished with weathering.

Profiles of partial pressure of carbon dioxide and oxygen from the 'fresh' and 'weathered' tests were very different. At each depth increment (0.25 m), the partial pressure of carbon dioxide was much less after the shale had weathered (fig. 10). This can be directly attributed to the leaching of carbonates from the shale and is further supported by the calcium and magnesium data. Figure 11 shows the effect of weathering on oxygen profile. For the 'fresh' material, the active zone of pyrite oxidation extended from the surface to a depth of 0.75 m. In the 'weathered' test, the lower end of this zone had moved to a depth of between 1.00 m to 1.25 m. The lower oxygen levels in the 'weathered' test was probably due to the degradation in particle size and some compaction of the material which would decrease the diffusion of air through the column.

Leaching frequency has little effect on release rates of sulfate and manganese (figure 12). Columns 1-4 were leached as follows: column #1, 1L every day, column #2, 7L every 7 days; column #3, 14L every 14 days; and column #4, 21L every 21 days. The results of this experiment indicate that the build up of weathered products does not retard pyrite oxidation by surface passivation. No significant differences in any water quality parameter or pore gas composition was noted between columns.

CONCLUSIONS

These results have several important implications for field practices, particularly for sites that selectively handle highly pyritic material. Trying to place the pyritic material in the unsaturated zone at oxygen levels low enough to reduce the biotic oxidation of pyrite (<0.5%) may be pointless. If the bacteria are inhibited, however, placing the material in a reduced oxygen environment may help limit pyrite oxidation. Similarly, unless the material can be totally isolated from water, contaminant loads will not be significantly reduced. Water vapor within the spoil is sufficient for pyrite oxidation, and over time, may solubilize these hygroscopic oxidation products and eventually help transport these contaminants (very slowly -- inches/year) through the spoil. The results of this research indicate that the best method to control pyrite oxidation is to keep the pyritic material inundated with water. It is important to note that any exposure to air prior to inundation will allow pyrite to oxidize, causing an accumulation of contaminants that will be released upon inundation. Therefore, the storage of the material before inundation should be minimized with perhaps some type of interim treatment (i.e. bacterial inhibitors) to control pyrite oxidation. More importantly, the site must be designed to ensure complete and continual inundation. Any period of time that the material is not completely saturated, pyrite oxidation will occur at rates orders of magnitude higher than while inundated.

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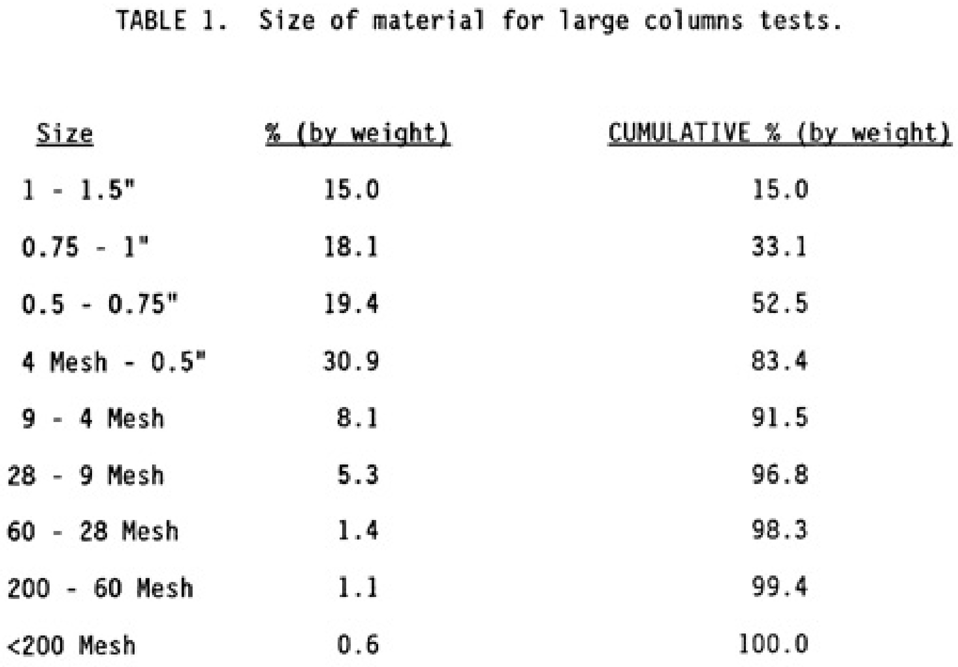

TABLE 1. Size of material for large columns tests.

Size	% (by weight)	CUMULATIVE % (by weight)
1 - 1.5"	15.0	15.0
0.75 - 1"	18.1	33.1
0.5 - 0.75"	19.4	52.5
4 Mesh - 0.5"	30.9	83.4
9 - 4 Mesh	8.1	91.5
28 - 9 Mesh	5.3	96.8
60 - 28 Mesh	1.4	98.3
200 - 60 Mesh	1.1	99.4
<200 Mesh	0.6	100.0

TABLE 2. Release rates of contaminants from fresh and weathered leaching tests in large columns.*

	FRESH		WEATHERED	
	RATE	S.E.	RATE	S.E.
Sulfate, g/day	14.37	0.45	13.13	0.75
Iron, g/day	4.26	0.16	4.20	0.25
Aluminum, mg/day	299.2	9.4	268.4	14.5
Manganese, mg/day	232.2	11.0	28.6	1.3
Calcium, mg/day	193.8	7.1	43.9	1.5
Magnesium, mg/day	468.3	24.9	19.7	0.6
Sodium, mg/day	16.3	0.6	8.9	0.6

* RATE = coefficient of linear regression
S.E. = standard error of the coefficient

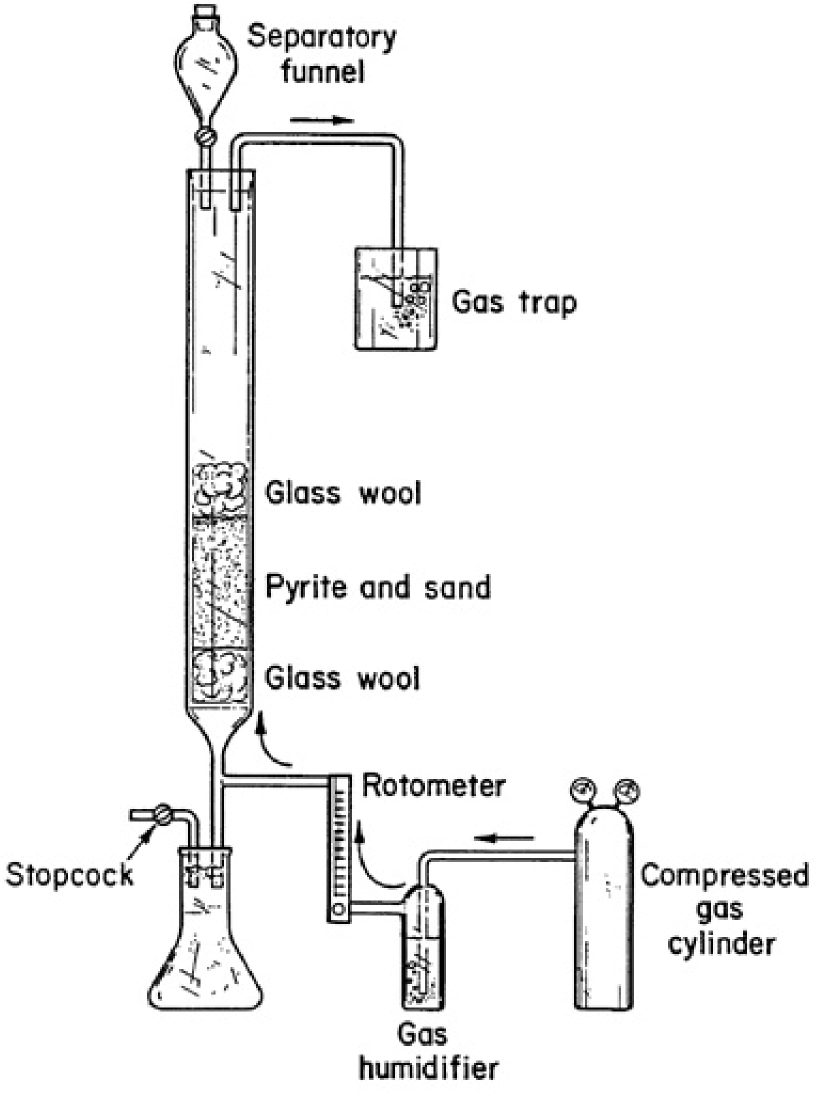

Figure 1. - Schematic of small column set-up.

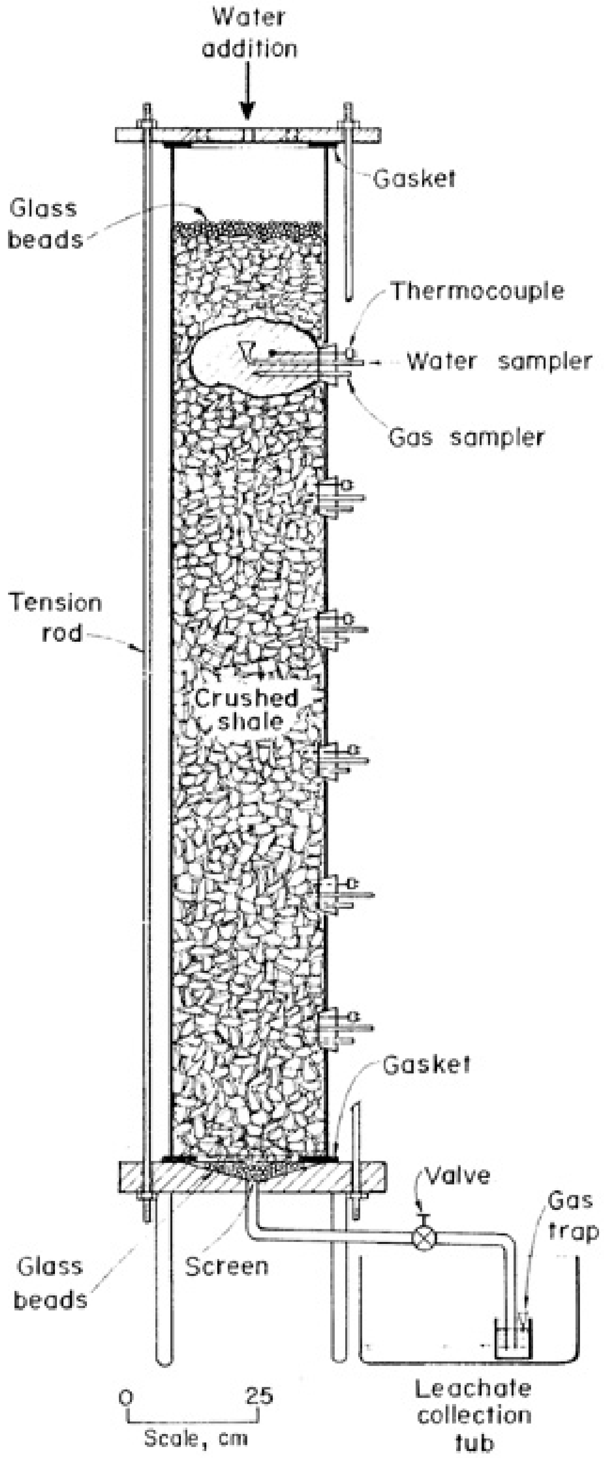

Figure 2. - Schematic of large column set-up.

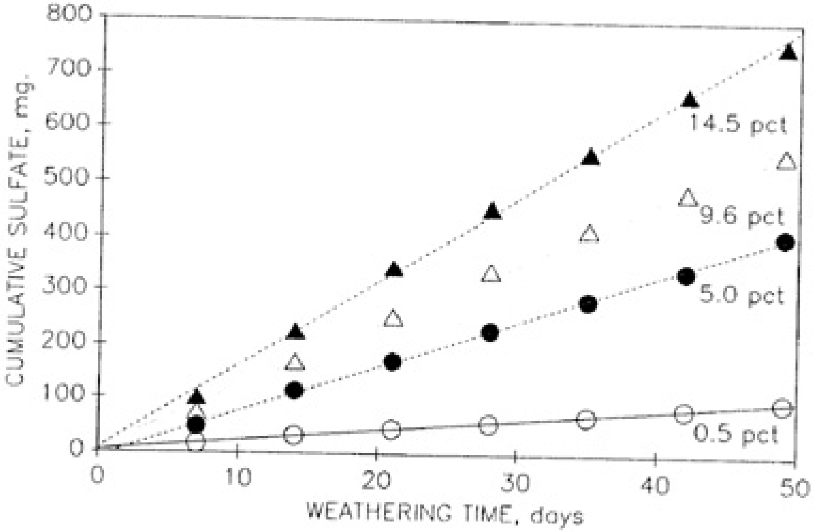

Figure 3. - Cumulative sulfate loads from small columns for four oxygen levels under abiotic conditions. Lines fitted by least squares regression.

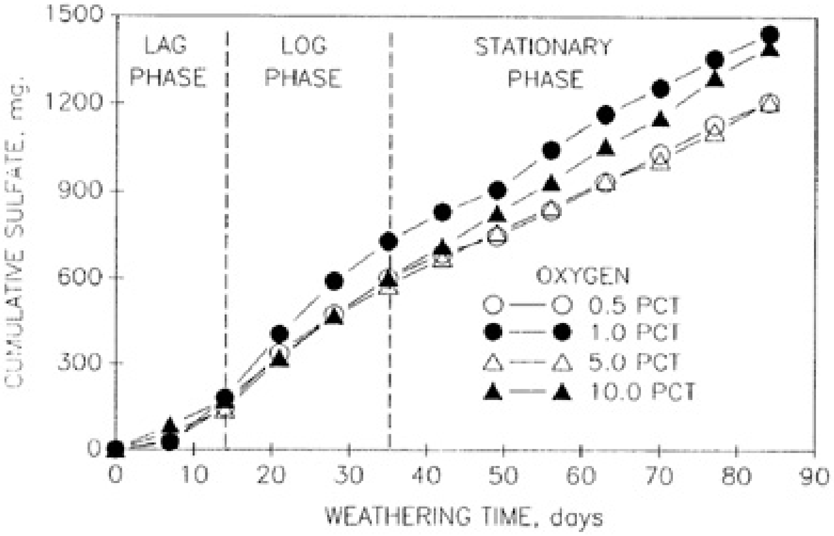

Figure 4. - Cumulative sulfate loads from small columns for four oxygen levels under biotic conditions.

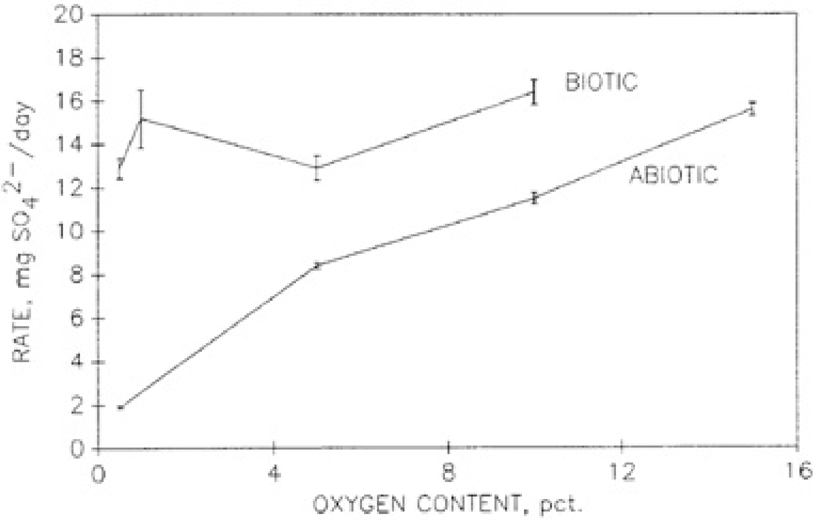

Figure 5. - Comparison of abiotic and biotic oxidation rates for the small column leaching tests. Each point represents the coefficient of least squares regression ± two standard errors. For aboitic rates, n=7 and for biotic rates n=6.

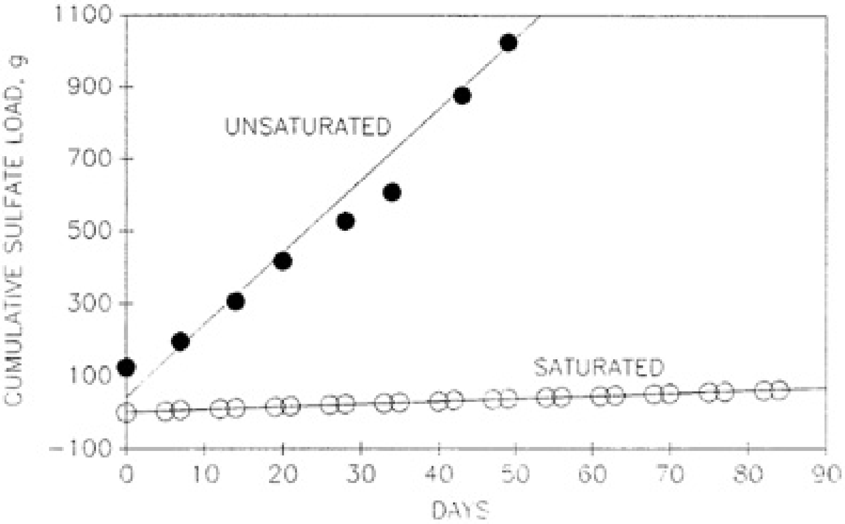

Figure 6. - Cumulative sulfate load released from large columns for water saturated and unsaturated conditions. Lines fitted by least squares regression.

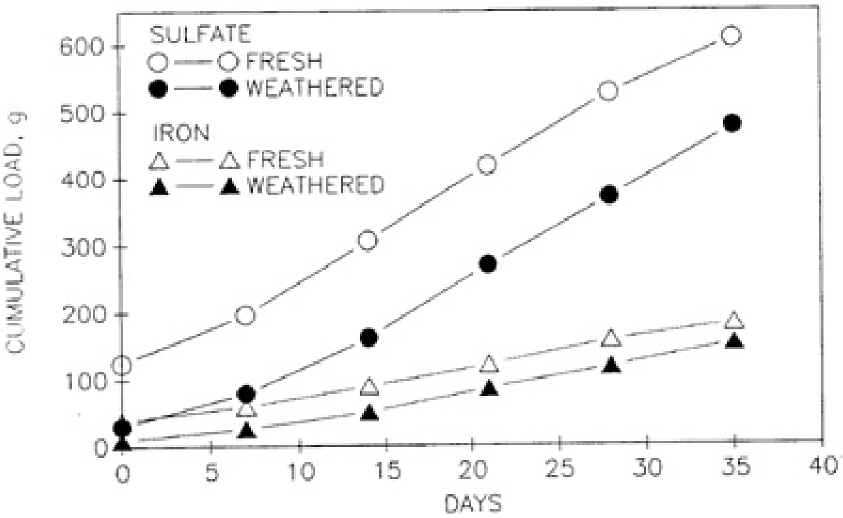

Figure 7. - Cumulative sulfate and iron loads released from large column leaching of fresh and weathered shale.

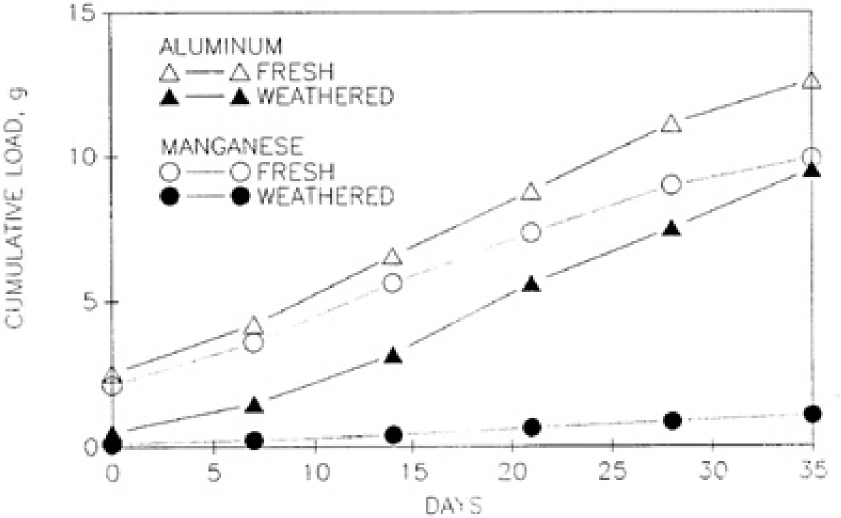

Figure 8. - Cumulative aluminum and manganese loads released from large column leaching of fresh and weathered shale.

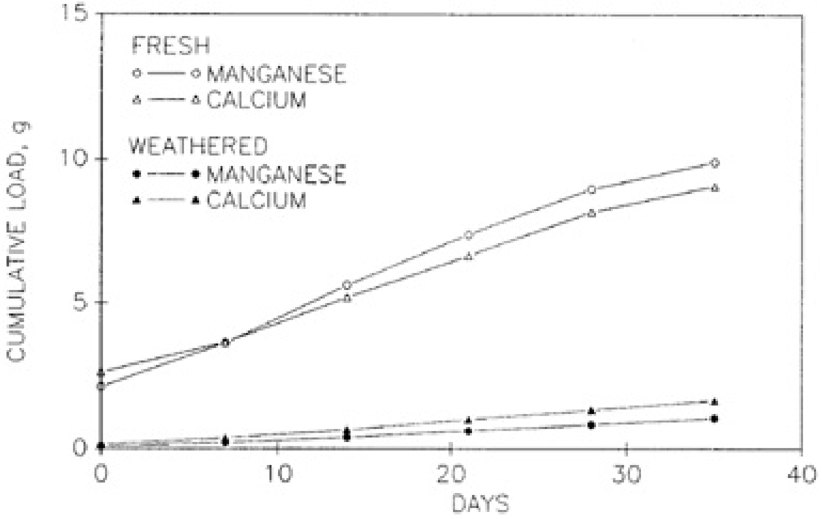

Figure 9. - Cumulative manganese and calcium loads released from large column leaching of fresh and weathered shale.

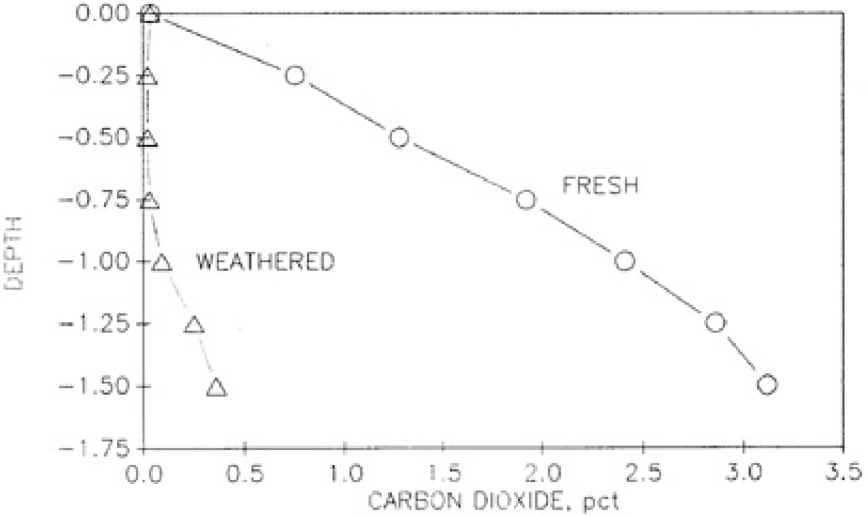

Figure 10. - Partial pressures of carbon dioxide versus depth in large column leaching tests for fresh and weathered shale.

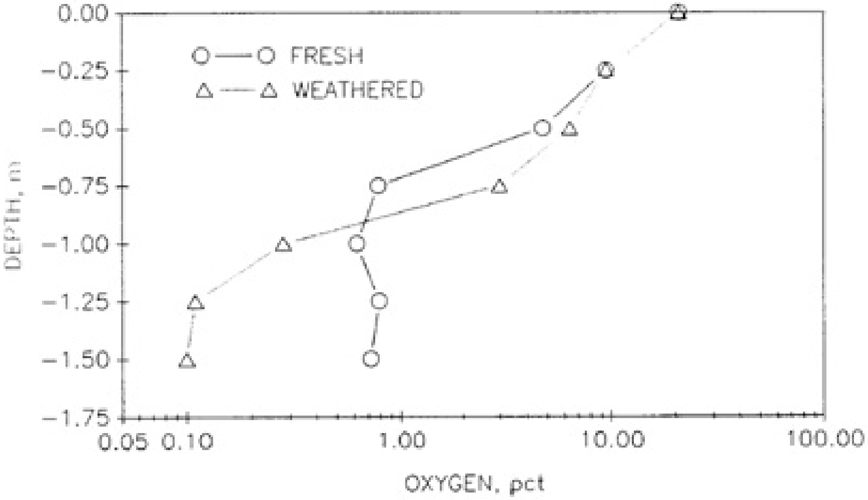

Figure 11. - Partial pressures of oxygen versus depth in large column leaching tests for fresh and weathered shale.

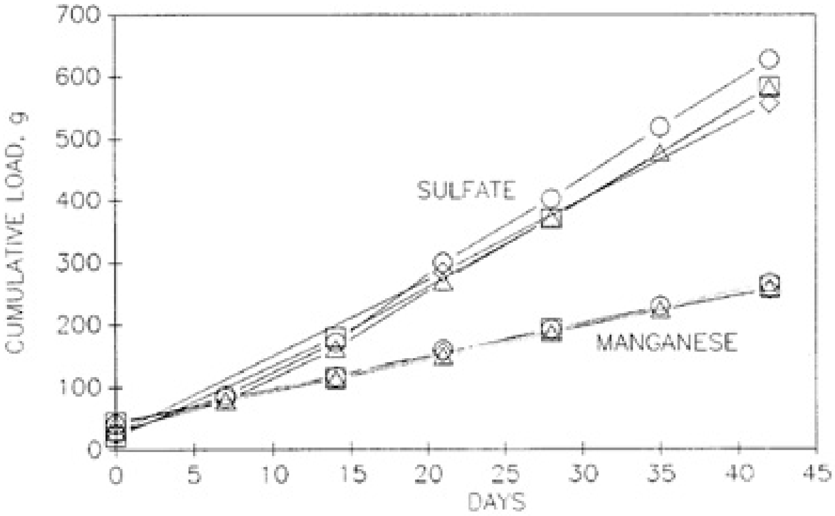

Figure 12. - Cumulative sulfate and manganese loads from large column with four different leaching frequencies (leached every day - circle, every 7 days - triangle, every 14 days - square, every 21 days - diamond).