

A SILICA/FLY ASH-BASED TECHNOLOGY FOR CONTROLLING PYRITE OXIDATION

SEMI-ANNUAL TECHNICAL REPORT

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OBJECTIVES

1. Overall Objective:

To develop methodologies by which sodium metasilicate or fly ash may produce an effective coating on pyrite surfaces for inhibiting pyrite oxidation.

2. Broad Objective:

a. To evaluate the mechanisms by which a stable silica coating can be produced on the surface of pyrite/pyritic coal waste using reagent grade sodium silicate.

b. To evaluate alternative oxidants (Na - hypochlorite or Ca - hypochlorite vs. hydrogen peroxide) and pH buffers (acetate vs. bicarbonate) for the most cost effective silica coating process.

c. To evaluate the most effective method (based on results from "objective a and b") in establishing silica coatings employing fly ash as silica source.

d. To evaluate durability of coating produced a) by sodium metasilicate, and b) by fly ash; compare coating performance results with results obtained from control treatments and traditional limestone treatments.

3. Milestones:

First six-month: Characterize pyrite surface reactions for understanding pyrite coating establishment. Start a preliminary outdoor leaching - column experiment using 10 kg mine pyritic spoil treated with silicates to evaluate potential application of coatings on a large scale.

Second six-month: Characterize silicate - iron reactions in solution and on pyrite surface for understanding pyrite silica - coating formation.

Third six-month: Evaluate pyrite surface deposition of silicate having Na - silicate or fly ash as source.

Fourth six-month: Evaluate silicate coating durability in large outdoor columns.

Introduction

Pyrite in coal waste is initially oxidized by atmospheric O_2 , releasing acidity and Fe^{2+} and is the main source of acid mine drainage (AMD). At pH around 3, Fe^{2+} is rapidly oxidized by *T. ferrooxidans* to Fe^{3+} which oxidize pyrite at a much faster rate than O_2 (Singer and Strumm, 1970). Commonly, the approach used to control AMD in the field involves the use of limestone. This approach, however, has a short span of effectiveness (Evangelou, 1995 and references therein). The objective of a study carried out in our laboratory was to demonstrate that pyrite oxidation could be controlled or inhibited through the formulation of an iron - oxide - silicate coating on the surface of pyrite which would prevent either O_2 or Fe^{3+} from further oxidizing pyrite. Silica solubility is relatively constant for a wide pH range while relatively strong short-range interactions between silicate ions and Fe^{3+} may make the latter (Fe^{3+}) unavailable to electron transfer processes (U. S. Gov., 1969). Ferric hydroxide-silica coating formation involved leaching pyrite at room temperature with a solution containing H_2O_2 , NaOAc, and soluble silicate at a flow rate of 0.43 ml min^{-1} (Zang and Evangelou, 1998). It was postulated (based on the results of our previous studies and on reported solubility behavior of silica in the presence of Fe^{3+} (Iler, 1979)) that when H_2O_2 would reach the pyrite, its outermost layer would oxidize and release Fe^{3+} which in the pH range of 4-6 would form an ferric hydroxide coating with some form of polymerized silica. The ferric hydroxide-silica coating would be expected to significantly

reduce the rate of pyrite oxidation most likely because of the coating's ability to serve as a sink for Fe^{3+} , and/or the coating's ability to act as a barrier to H_2O_2 and other oxidants. The bench-scale study showed that formation of a ferric hydroxide-silicate coating on the surface of pyrite was induced and inhibited pyrite oxidation (Zang and Evangelou, 1998).

The objective of this study was to test the durability of the silica pyrite coatings under natural environmental conditions in large leaching columns for possible application in the field.

Materials and Methods

Two types of pyritic waste material were used for this field - leaching column study. One type represented a fresh, salt free pyritic waste obtained from a metal ore processing plant located in Dester, Canada, which contained approximately 80% pyrite. Prior to use, this material was stored under water saturated conditions to create a reduced environment. The pyritic waste was mixed with sharp sand at a waste to sand ratio of 1:20, giving 4.0% pyrite based on weight. The second type of pyritic waste represented a highly weathered Western Kentucky coal spoil with 21.4% pyrite content, which was obtained from a site close to Central City in Muhlenberg County, Kentucky. This spoil was mixed with sharp sand at a 10:1 waste to sand ratio, giving a 19% pyrite content on a weight bases. The percent pyrite present in both of these waste materials was determined by oxidizing the pyrite in the presence of excess 30% hydrogen peroxide (H_2O_2) and measuring the acidity produced from the pyrite by titrating with NaOH, under nitrogen gas, to pH 7 (O'Shay et al., 1990). We used the Canadian mine tailings because it was free of salts that may have interfered with the coating process. The Muhlenberg spoil, in contrast, had a high salt content (see results and discussion) and was selected as a good representation of what may be encountered at a reclamation site. The total soluble salt concentration was determined by carrying out water saturated paste extracts on the spoil and using the extracts for chemical analyses (U.S. Salinity Lab. Staff, 1954). In addition, successive extractions by water and 1M KCl were carried out and these extracts used to determine solution and exchangeable acidity, water extractable chemical species, and cation exchange capacity (CEC) of the spoil (Thomas, 1982).

The field - leaching study consisted of three groups of leaching columns. One group included enough agricultural limestone to neutralize approximately 113.5% of the potential acidity in the pyritic material while the other two groups used only enough limestone to neutralize approximately 9% of the potential pyritic acidity. Under field conditions, enough limestone is used to neutralize one hundred percent of the potential pyritic acidity; therefore, we used close to this amount in one group of our field columns to approximate those conditions. Only enough limestone to neutralize 9% of the potential pyritic acidity was used in the other two column groups so that we could quickly distinguish a coating effect from a limestone neutralization effect on pyrite oxidation. The 113.5% neutralization group and one of the 9% groups used the Canadian mine tailings as their pyritic material while the other 9% group used the Western Kentucky mine spoil as the pyritic material source. Each of these field - leaching column groups consisted of a control, silica coating treatments, and limestone treatment. In addition, columns that combined limestone with each individual component of the coating process (calcium hypochlorite ($\text{Ca}(\text{OCl})_2$), sodium acetate (NaOAc), and silica (Na_2SiO_3)) were included so that these components could be evaluated separately. All of these columns were in duplicates. Calcium hypochlorite was substituted for the H_2O_2 used in earlier studies because it was considered to be a more stable oxidizer in the open environment than H_2O_2 .

The leaching columns were placed in a field located close to our laboratory at the University of Kentucky in Lexington, Kentucky. The leaching columns were constructed from polyvinyl chloride pipe with a height of 46 cm and inside diameter of 15 cm. All columns were fitted with drain tubes and one gallon polypropylene jugs to collect the leachate and supported in the field by wood benches (Fig. 1).

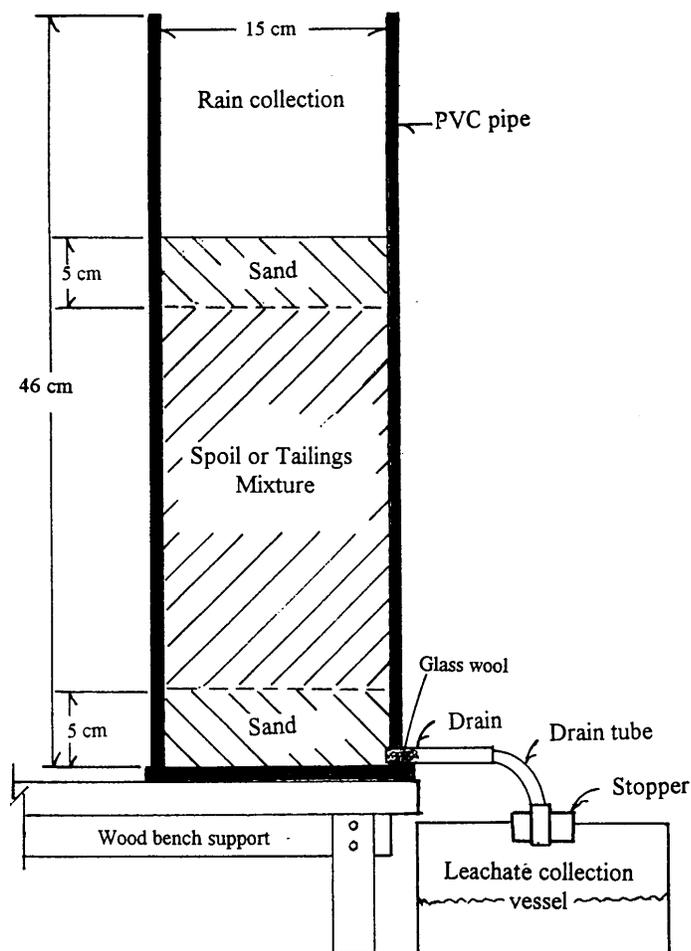


Figure 1. Diagram of an outdoor leaching - column.

All of the columns were filled with a 50 mm layer of sharp sand on the bottom, followed by either the spoil or tailings mixture described below, and a 50 mm layer of sharp sand on top. For the 113.5% potential acid neutralization column group using the Canadian tailings, control columns were filled with a uniform mixture of 0.5 kg Canadian mine tailings and 9.5 kg of sharp sand. All other columns in this group used a uniform mixture of 0.5 kg tailings, 9.5 kg sharp sand, and 0.8 kg agricultural limestone. The purpose of the sand was to improve hydraulic flow through the columns and the limestone was the amount required to neutralize 113.5% of the potential pyritic acidity.

Control columns in the 9% potential acid neutralization group using Canadian tailings were filled with a uniform mixture of 0.5 kg Canadian mine tailings and 9.5 kg sharp sand. All other columns in this group used a uniform mixture of 0.5 kg tailings, 9.5 kg sharp sand, and 0.067 kg agricultural limestone. This amount of limestone was required to neutralize 9% of the potential pyritic acidity.

For the 9% potential acid neutralization column group utilizing Western Kentucky mine spoil, control columns were filled with a uniform mixture of 5.52 kg Western Kentucky mine spoil and 0.552 kg sharp sand. Two sets of the limestone treatment columns were made for this group. One set included enough limestone to neutralize 88% of the potential pyritic acidity and all of the solution and exchangeable acidity and a second set used enough limestone to neutralize only 9% of the potential pyritic acidity and all of the solution and exchangeable acidity. The 88% limestone treatment columns were filled with 5.52 kg of mine spoil mixed well with 0.552 kg of sharp sand plus 2.17 kg of agricultural limestone to neutralize the required amount of acidity. All other columns in this group were filled with a uniform mixture of 5.52 kg Western Kentucky mine spoil, 0.552 kg sharp sand, and 0.515 kg agricultural limestone. This amount of limestone was required to neutralize 9% of the potential pyritic acidity plus all of the already existing solution and exchangeable acidity.

The columns were leached with either a coating solution or deionized (di) H₂O prior to setting them up in the field. These initial leaching processes were identical for the controls and the various treatments within each of the column groups. The leaching procedure for the silica coating columns involved placing 107 g of Ca(OCl)₂ on top of the pyritic waste - sand - limestone mixture contained in all of these coating columns. The purpose of the Ca(OCl)₂ was to oxidize the pyrite during leaching events (natural rainfall) and produce Fe³⁺ which would then form a ferric hydroxide coating with polymerized silica on the surfaces of pyrite. For the 113.5% and 9% Canadian tailings groups, three sets of silica coating columns were fabricated and leached with 5 L of coating solutions, adjusted to pH 5 with HCl, having the following concentrations of Na₂SiO₃ and NaOAc: one set with 0.001 M Na₂SiO₃ (Si=30 mg L⁻¹) and 0.1 M NaOAc; a second set with 0.005 M Na₂SiO₃ (Si=150 mg L⁻¹) and 0.1 M NaOAc; and a third set with 0.01 M Na₂SiO₃ (Si=300 mg L⁻¹) and 0.1 M NaOAc. The 9% Western Kentucky spoil group used only two sets of silica columns: one set leached with the above Si=150 mg L⁻¹ solution; and a second set leached with the above Si=300 mg L⁻¹ solution. The purpose of the pH buffer (NaOAc) in the coating solution was to eliminate the inhibitor effect of the protons, produced during pyrite oxidation, on the precipitation of ferric hydroxide.

The silica + limestone columns in all of the column groups were leached with a 0.005 M Na₂SiO₃ solution adjusted to pH 5 with HCl. All of the NaOAc + limestone columns were leached with a solution of 0.1 M NaOAc adjusted to pH 5 with HCl. The pyritic waste - sand - limestone mixture in all of the Ca(OCl)₂ + limestone columns were covered with 107 g of Ca(OCl)₂ and then leached with 5 L of di-H₂O. All limestone treatment and control columns were leached with 5 L of di-H₂O.

Twenty four hours prior to leaching through the columns the di-H₂O or solutions described above, each was leached with 1 L of di-H₂O. Both leaching procedures were carried out indoors at 25° C. The first leaching was done to remove the excess salts in the Western Kentucky spoil. Although the Canadian mine tailings did not have the high amount of salts, they too were leached with the 1 L of di-H₂O to maintain consistency in the handling of all columns. The 5 L of either coating solutions or di-H₂O were pumped at a rate of 1 L hr⁻¹ into the top of each column with

a Technicon Swords proportioning pump. Seven 2.4 ml min^{-1} flow rated pump tubes (either FisherBrand from Fisher Scientific Inc., Pittsburgh, Pa. or Technicon SMA, Tarrytown, New York) were used in order to evenly distribute the solution or di- H_2O over the surface of each column. The final leaching was followed by a 1-3 week incubation time to allow for coatings to form, after which the columns were set up in the field. Leachates were collected and analyzed periodically for pH, Fe, and $\text{SO}_4\text{-S}$ concentration. Sulfate concentration in all leachates were measured turbidmetrically with BaCl_2 (Massoumi and Cornfield, 1963). Iron concentrations in all leachates were determined by atomic absorption spectrophotometry and pH was measured using a Markson Model 4603 solution analyzer. Samples were analyzed in duplicate and tested against samples of known concentration. The detection limit was 3 mg L^{-1} for $\text{SO}_4\text{-S}$ analysis and 0.5 mg L^{-1} for Fe analysis.

After a four to seven month period in the field, pyrite oxidizing bacteria (*Thiobacillus ferrooxidans*) were added to the columns to evaluate the pyrite coating technology's effectiveness at preventing microbial oxidation of pyrite. The 4 to 7 month waiting period was considered necessary to leach, through rainfall events, all NaOAc, which was verified by acetate analysis. The oxidizing bacteria used for inoculating the columns were obtained from field AMD and cultured in a Thiobacillus nutrient medium solution described by Gerhardt (1994). The medium consisted of two solutions. First, 16,000 ml of a solution of $10^{-2.12} \text{ M}$ $(\text{NH}_4)_2\text{SO}_4$, $10^{-2.42} \text{ M}$ KH_2PO_4 and $10^{-2.82} \text{ M}$ $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ was prepared. Next, 4,000 ml of a solution of $10^{-0.44} \text{ M}$ $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and 1N H_2SO_4 was prepared. Both of these solutions were combined and adjusted to pH 2.8. Five hundred ml of AMD was then added to this medium and allowed to incubate for two weeks. Following the incubation period, the clear solution was decanted, leaving a concentrated slurry of bacteria. Finally, 50 ml of this slurry was poured into each of the columns, immediately followed by 500 ml of di- H_2O to wash the bacteria further into the mine tailings / spoil mixture.

Results and Discussion

113.5 % Potential Acid Neutralization Group with Canadian Mine Tailings.

After twenty eight months of monitoring this column group, all of the treatments continue to significantly inhibit pyrite oxidation when compared to the control. This inhibiting effect is indicated by the much lower total Fe and $\text{SO}_4\text{-S}$ released from the treatment columns as opposed to the control (Figs. 2a and 3a). Furthermore, a pH value of approximately 7 has been maintained by all of the treatments while the control has remained steady at pH 2 (Fig. 4). The lower pH of the control is due to the higher pyrite oxidation rate as indicated by the overall higher total Fe and $\text{SO}_4\text{-S}$ released into the leachates from these columns. As expected, the addition of pyrite oxidizing bacteria to the columns temporarily increased the Fe and $\text{SO}_4\text{-S}$ production from the control columns, but did not have an effect on the treated mine tailings (Figs. 2a and 3a). The limestone treatment, however, has been releasing iron at a greater rate than any of the other treatments for the last six months (Fig. 2b). This increased rate of Fe release may be an indication that the limestone treatment is losing its effectiveness at controlling pyrite oxidation. Figure 5 shows the amount of leachate collected at each sampling.

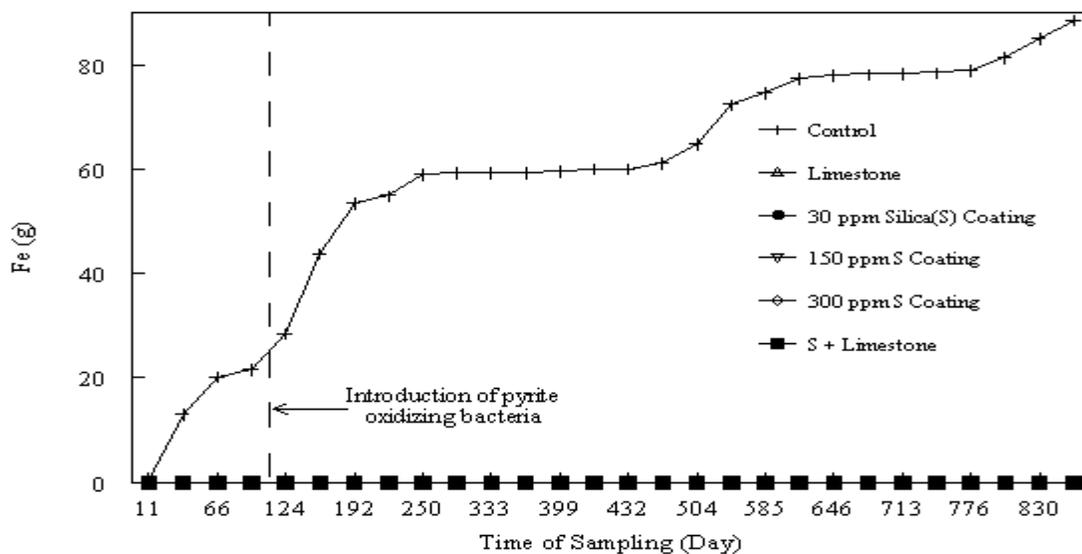


Figure 2a. Cumulative Iron (Fe) from field columns (113.5% pyrite neutralization of Canadian mine tailings) through the twenty eighth sampling.

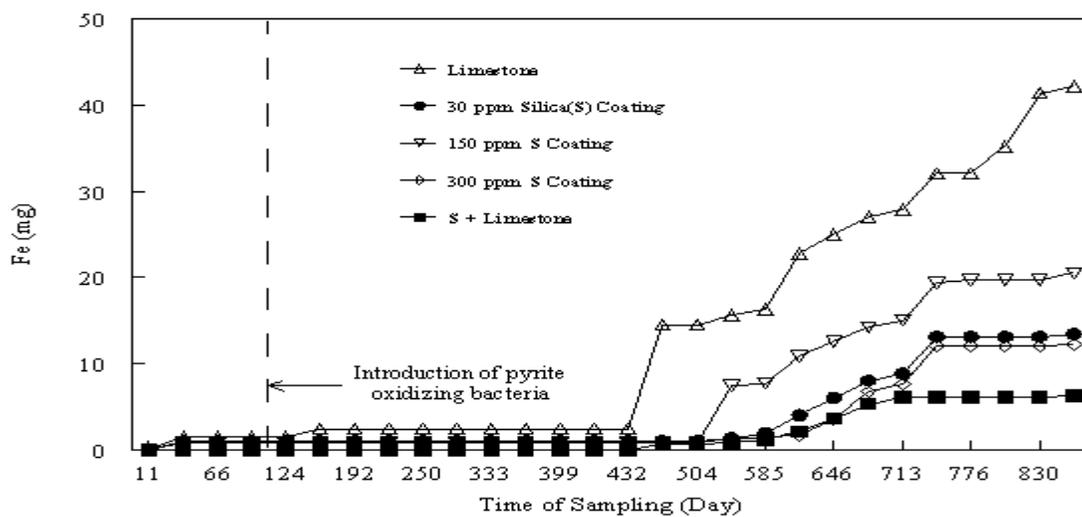


Figure 2b. Cumulative Iron (Fe) from field columns (113.5% pyrite neutralization of Canadian mine tailings) through the twenty eighth sampling.

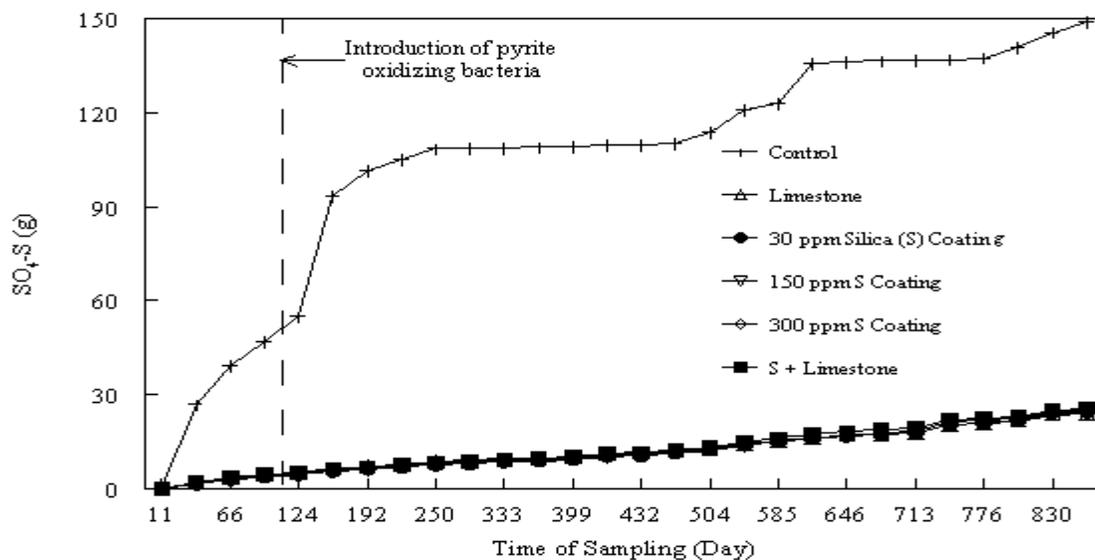


Figure 3a. Cumulative Sulfate (SO_4-S) from field columns (113.5% pyrite neutralization of Canadian mine tailings) through the twenty eighth sampling.

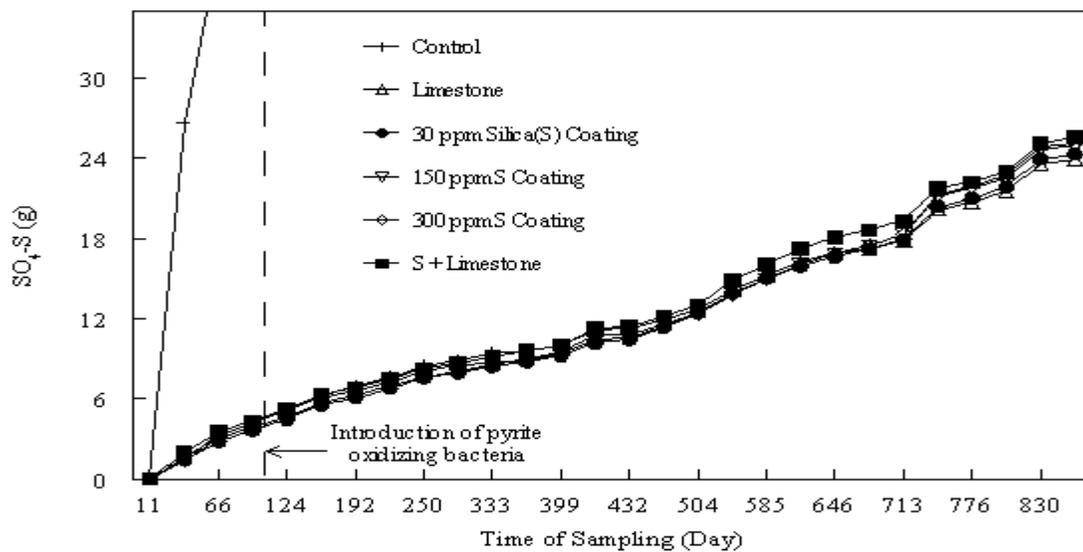


Figure 3b. Cumulative Sulfate (SO_4-S) from field columns (113.5% pyrite neutralization of Canadian mine tailings) through the twenty eighth sampling.

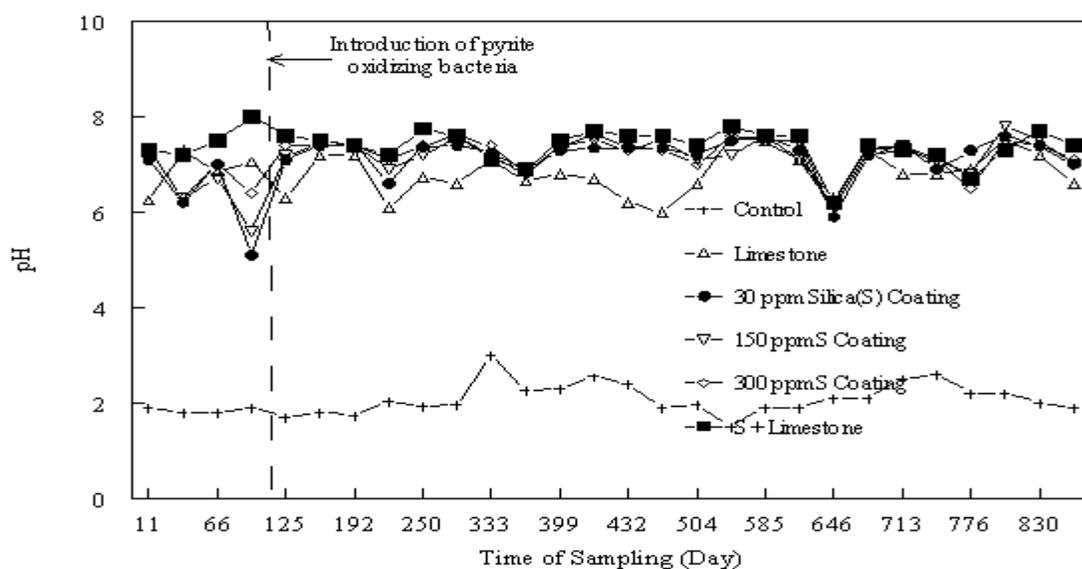


Figure 4. Leachate pH from field columns (113.5% pyrite neutralization of Canadian mine tailings) through the twenty eighth sampling.

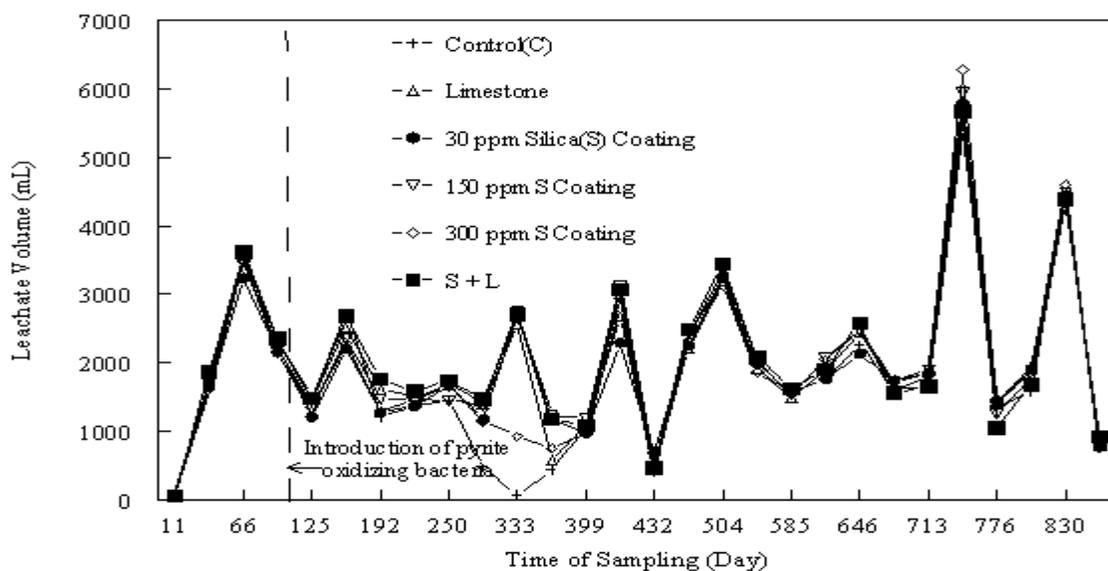


Figure 5. Leachate volume collected from field columns (113.5% pyrite neutralization of Canadian mine tailings) through the twenty eighth sampling.

Table 1 shows pH and cumulative data to date for all of the columns and indicates that, except for the control and limestone + acetate columns, all column sets in this group behaved as duplicates. The control is only represented by one column due to the fact that early into the study one of the control columns broke and had to be replaced. This delay resulted in a five month time differential between the two columns; therefore, they were no longer synchronized and could not be used as true duplicates. All treatments have released a total of 25.4 ± 2.72 g $\text{SO}_4\text{-S}$ into their leachate to date. Figure 2a indicates that the rate of $\text{SO}_4\text{-S}$ production from all of the treated columns was unaffected by the pyrite oxidizing bacteria that were introduced on the 97th day; however, the control column was significantly affected and continues to produce $\text{SO}_4\text{-S}$ at a faster rate than any of the treatments.

If a coating has taken place in the treated columns, then after long exposure to the atmosphere, we should begin to see differences between the Fe and $\text{SO}_4\text{-S}$ concentrations coming from the limestone treated columns and the coating columns. This is so because the limestone only treats the symptoms of pyrite oxidation, by creating an alkaline environment that lowers both the solubility of Fe^{3+} and bacterial activity, but does not prevent it (Evangelou, 1995). In fact, limestone may actually accelerate the pyrite oxidation process by forming Fe-HCO_3^- complexes on the surface of pyrite (Evangelou, 1995 and references therein). In addition, the limestone may eventually become coated with iron oxides and no longer be an effective neutralizer (Evangelou, 1995). For these reasons the limestone treatment should begin to release Fe and $\text{SO}_4\text{-S}$ at a faster rate.

Table 1. Summary of cumulative data from the Canadian mine tailings column group (113.5% potential pyritic acidity neutralization) through the twenty eighth sampling. (Mean of duplicates; \pm deviation from the mean).

Treatment	pH	Fe (mg)	$\text{SO}_4\text{-S}$ (mg)	Leachate volume (ml)
Control	1.9	88,605.6	149,054.0	53,570
Limestone (L)	6.6 (± 0.09)	42.2 (± 4.1)	23,935.6 ($\pm 2,305.0$)	55,420 ($\pm 4,410.0$)
L + Hypochlorite	7.1 (± 0.16)	36.9 (± 14.4)	22,630.7 ($\pm 2,219.5$)	52,795 ($\pm 4,125.0$)
L + Acetate	7.1 (± 0.00)	13.5 (± 4.7)	31,161.4 ($\pm 5,913.7$)	56,890 ($\pm 3,860.0$)
L + Silica (Si)	7.4 (± 0.05)	6.3 (± 0.1)	25,637.0 (± 413.4)	58,060 (± 350.0)
30 mg L^{-1} Si Coating	7.5 (± 0.00)	13.4 (± 1.3)	24,336.2 (± 557.9)	55,217 ($\pm 1,392.5$)
150 mg L^{-1} Si Coating	7.1 (± 0.05)	20.5 (± 7.4)	24,991.3 (± 193.8)	57,300 (± 630.0)
300 mg L^{-1} Si Coating	7.1 (± 0.05)	12.2 (± 1.0)	25,111.9 (± 341.5)	54,019 (± 449.0)

9% Acid Neutralization Column Group with Canadian Mine Tailings.

The data in Figures 6 and 7 show that there has been an overall increase in the rate of Fe and $\text{SO}_4\text{-S}$ release from the 9% limestone treatment, the silica + limestone treatment and the control since the introduction of the *Thiobacillus ferrooxidans* bacteria at 189 days. Only the silica coating treatments remained unaffected by the oxidizing bacteria. There was, however, a sharp increase in the rate of Fe and $\text{SO}_4\text{-S}$ release from all the silica coating columns over the last couple of months of monitoring. Figure 8 reveals that the pH of the leachate from the control as well as the 9% limestone treatment have remained stable at approximately 2 throughout the study. However, the silica coating treatments maintained a circum - neutral pH through 272 days before they too fell to approximately pH 2. The drop in the pH of leachates from the silica coating columns was followed by a gradual increase to around pH 5, probably as a result of a re-establishment of the silica coatings, but have recently fallen back to the pH 2 range. The recent drop in the pH of the leachates from these silica coating columns, together with the increased rate of Fe and $\text{SO}_4\text{-S}$ production over the last two months, suggests that the silica coatings are no longer effective. Figure 9 shows the leachate volume collected at each sampling.

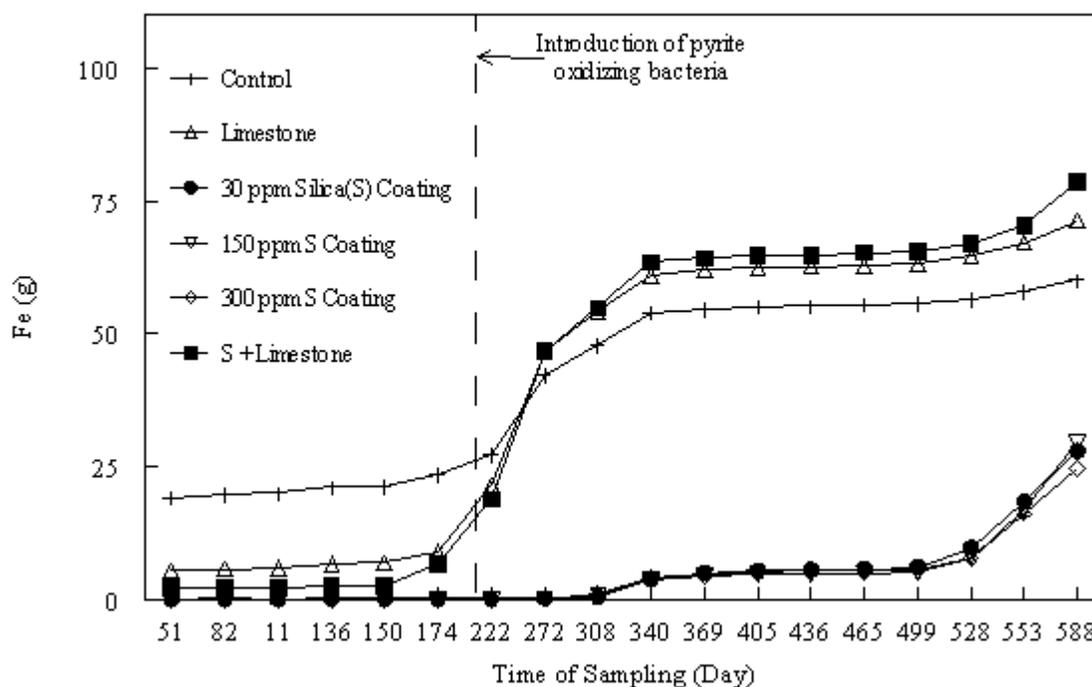


Figure 6. Cumulative Iron (Fe) from field columns (9% pyrite neutralization of Canadian mine tailings) through the eighteenth sampling.

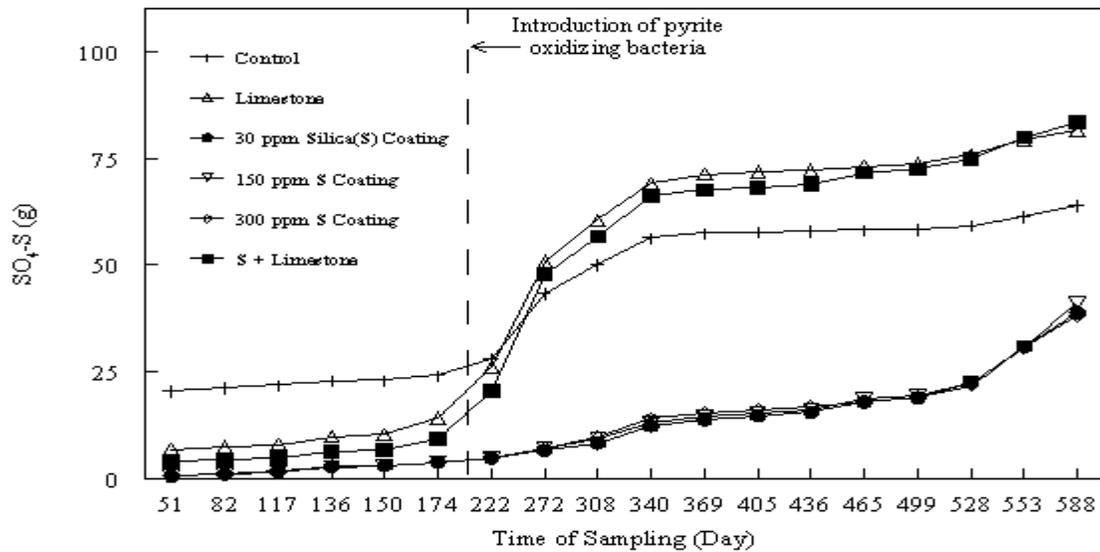


Figure 7. Cumulative Sulfate ($\text{SO}_4\text{-S}$) from field columns (9% pyrite neutralization of Canadian mine tailings) through the eighteenth sampling.

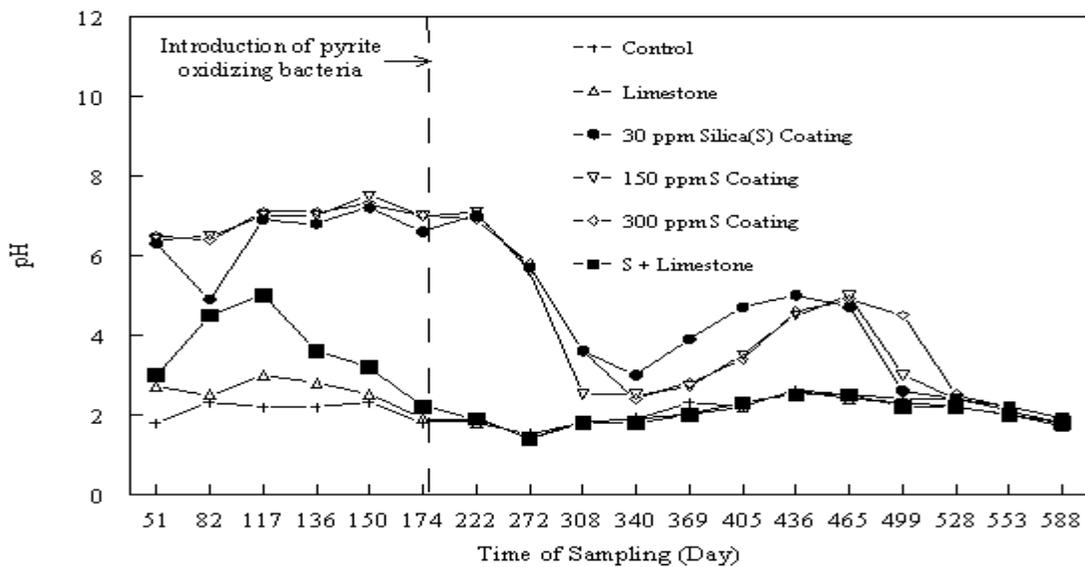


Figure 8. Leachate pH from field columns (9% pyrite neutralization of Canadian mine tailings) through the eighteenth sampling.

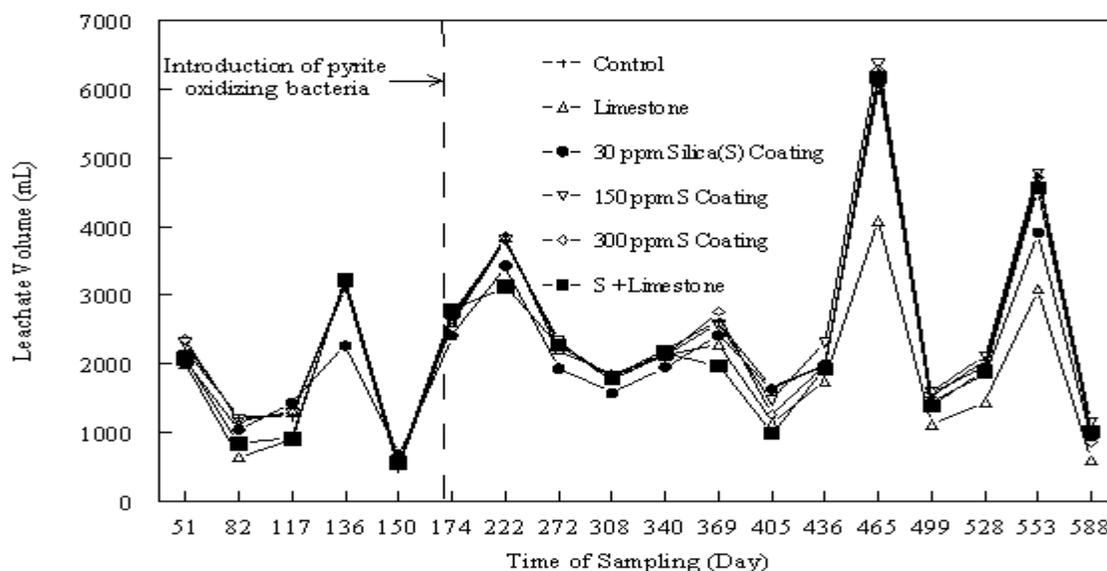


Figure 9 Leachate volume collected from field columns (9% neutralization of Canadian mine tailings) through the eighteenth sampling.

The data in Table 2 shows the pH and cumulative data values for this column group through 588 days. This data reveals that, unlike the 113.5% Canadian column group, not all of these treatments behaved as duplicates. The cumulative Fe and $\text{SO}_4\text{-S}$ released from the duplicates of the 30 mg L^{-1} and 300 mg L^{-1} silica coating treatments had very large deviation from the mean values. The fact that these coating columns did not behave as duplicates may be due to differences in the amount of pyrite successfully coated in each column. Factors that may have affected pyrite coating are: gypsum precipitation, which would channel water / solutions flowing down through the column thereby preventing a uniform flow; and/or a buildup of salts within the columns, which would provide surfaces other than pyrite for the silica coatings to bind to. That we got greater variation in these coating columns than in the previous column group may be due to a masking effect caused by the large amount of limestone used in the 113.5% Canadian tailings group. Once the limestone in the 113.5% group becomes ineffective at controlling pyrite oxidation, these columns may also show greater variability between the duplicates.

The data in Figure 7 and Table 2 also reveals that there may be an acceleration of pyrite oxidation effect caused by the presence of limestone. Of the eight column sets in this group, three have released significantly more $\text{SO}_4\text{-S}$ than the control. These three columns are the limestone, silica + limestone, and hypochlorite + limestone (data not plotted in Fig. 7) treatment columns. We believe that the reason for the increase may be the result of a higher rate of pyrite oxidation due to Fe-HCO_3^- complexation on the surface of pyrite (Evangelou, 1995). All of the coating treatments have released less $\text{SO}_4\text{-S}$, suggesting that these treatments may have successively encapsulated a significant portion of the pyrite.

Table 2. Summary of cumulative data from the Canadian mine tailings column group (9% potential pyritic acidity neutralization) through the eighteenth sampling. (Mean of duplicates; \pm deviation from the mean).

Treatment	pH	Fe (mg)	SO ₄ -S (mg)	Leachate volume (ml)
Control	1.8 (\pm 0.04)	60,077.1 (\pm 1,409.3)	63,872.7 (\pm 1,158.5)	42,880 (\pm 480.0)
Limestone (L)	1.7 (\pm 0.03)	71,208.7 (\pm 3,453.7)	81,649.5 (\pm 3,409.1)	35,400 (\pm 860.0)
L + Hypochlorite	1.8 (\pm 0.02)	66,520.5 (\pm 3,775.0)	72,324.0 (\pm 2,997.0)	41,735 (\pm 185.0)
L + Acetate	1.9 (\pm 0.07)	35,198.4 (\pm 9,714.0)	44,704.0 (\pm 7,473.0)	41,745 (\pm 415.0)
L + Silica (Si)	1.8 (\pm 0.02)	78,591.4 (\pm 1,354.6)	83,387.6 (\pm 2,497.1)	40,840 (\pm 140.0)
30 mg L ⁻¹ Si Coating	1.9 (\pm 0.08)	27,919.3 (\pm 16,510.1)	38,798.3 (\pm 13,972.2)	38,980 (\pm 480.0)
150 mg L ⁻¹ Si Coating	1.9 (\pm 0.01)	29,424.2 (\pm 5,044.8)	41,016.6 (\pm 3,394.1)	43,455 (\pm 25.0)
300 mg L ⁻¹ Si Coating	1.9 (\pm 0.05)	24,531.0 (\pm 12,067.8)	37,986.1 (\pm 9,400.8)	42,370 (\pm 170.0)

By adding only enough limestone to neutralize 9.0 % of the potential acidity, we were able to quickly discern whether a coating effect had occurred. The data shows an overall lower rate of Fe and SO₄-S release from all of the silica coating columns in this group. However, Table 2 reveals that the 30 mg L⁻¹ and 300 mg L⁻¹ silica coating, and acetate + limestone treatments did not behave as true duplicates. Therefore, only the overall lower rate of Fe and SO₄-S released from 150 mg L⁻¹ silica coating treatment when compared to all treatments except the acetate + limestone treatment and the 30 mg L⁻¹ silica and 300 mg L⁻¹ silica coating treatments is significant and can be considered an indication that this coating treatment established pyrite coatings, which prevented or slowed the oxidation process for approximately 16 months.

9% Acid Neutralization Column Group with Western Kentucky Mine Spoil.

Figures 10 and 11 reveal that all of the treatments significantly inhibited pyrite oxidation. This inhibiting effect is suggested by the much lower total Fe and SO₄-S released from the treatment columns compared to the control. The 150 mg L⁻¹ silica coating, silica + limestone, and 88% limestone treatments, however, have performed best with respect to total SO₄-S and Fe released. The 300 mg L⁻¹ silica coating column and 9% limestone treatments have also performed well, but their rate of SO₄-S release was influenced by the pyrite oxidizing bacteria introduced after 216 days while the 150 mg L⁻¹ silica, silica + limestone, and 88% limestone treatments were not significantly affected (Fig 11). Figure 12 shows that the silica + limestone and the 88% limestone treatments have performed best with respect to pH. Both of these treatments

maintained a pH of approximately 7 throughout the study. After the bacteria were added, the 150 mg L⁻¹ silica coating treatment dropped from approximately pH 7 to pH 5 where it has since remained. All other treatments dropped to approximately pH 2 after the introduction of the oxidizing bacteria and subsequently maintained this pH while the control maintained a pH of 2 throughout the study. Only the 150 mg L⁻¹ silica coating, silica + limestone, and 88% limestone treatments have maintained both a circum-neutral pH and low release rates of SO₄-S and Fe after the bacteria were introduced, suggesting that, up to now, these treatments are protecting against microbial pyrite oxidation. Figure 13 shows the leachate volume collected at each sampling for this column group.

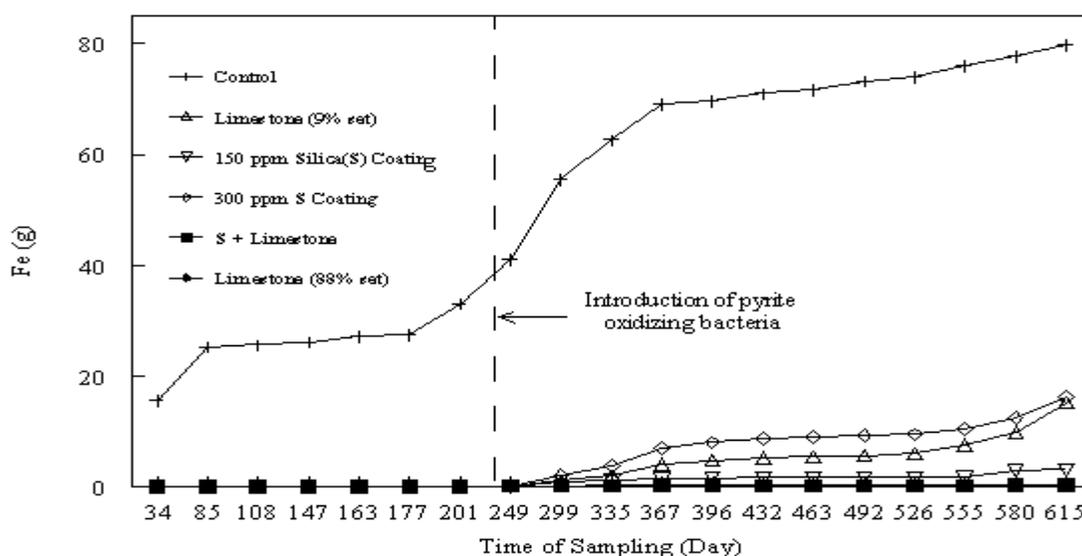


Figure 10. Cumulative Iron (Fe) from the field columns (9% pyrite neutralization of Western Kentucky mine spoil) through the nineteenth sampling.

The silica + limestone treatment in this leaching column group has performed very well, but this treatment did quite poorly in the 9% neutralization Canadian tailings group. The difference in performance between the two groups is likely due to the fact that the Kentucky spoil was a highly weathered material that therefore had large amounts of iron - oxides present. These iron - oxides provided the necessary ferric hydroxide coating on the pyrite surfaces to which the silica could adsorb. The Canadian tailings surfaces, however, had less iron - oxides and therefore the silica could not form a coating without the oxidizer (Ca(OCl)₂) present. This is so because, prior to use in the leaching columns, the Canadian tailings were kept under water saturated conditions, a reduced environment, which did not promote iron - oxide formation.

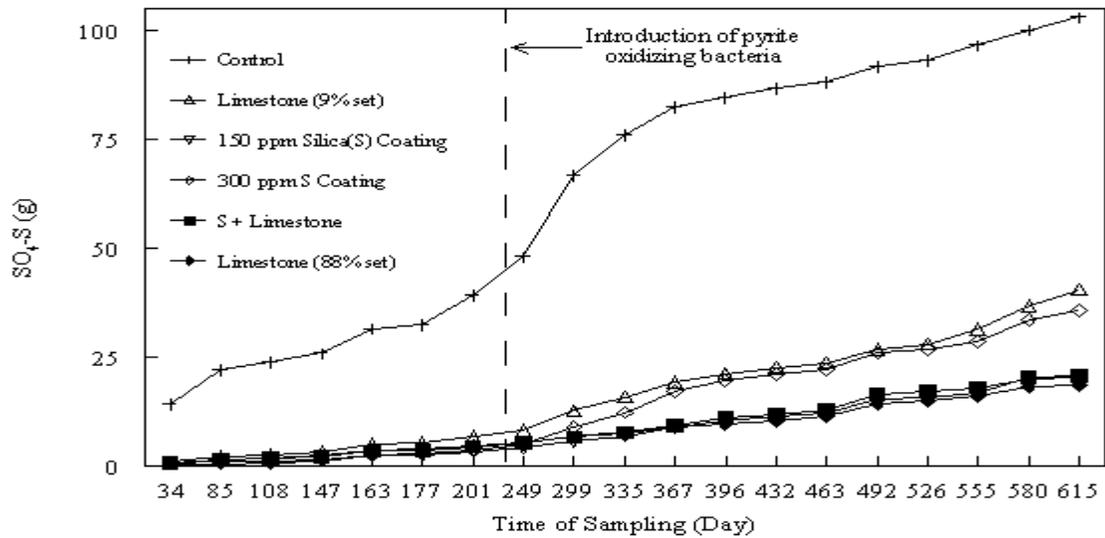


Figure 11. Cumulative Sulfate ($\text{SO}_4\text{-S}$) from the field columns (9% pyrite neutralization of Western Kentucky mine spoil) through the nineteenth sampling.

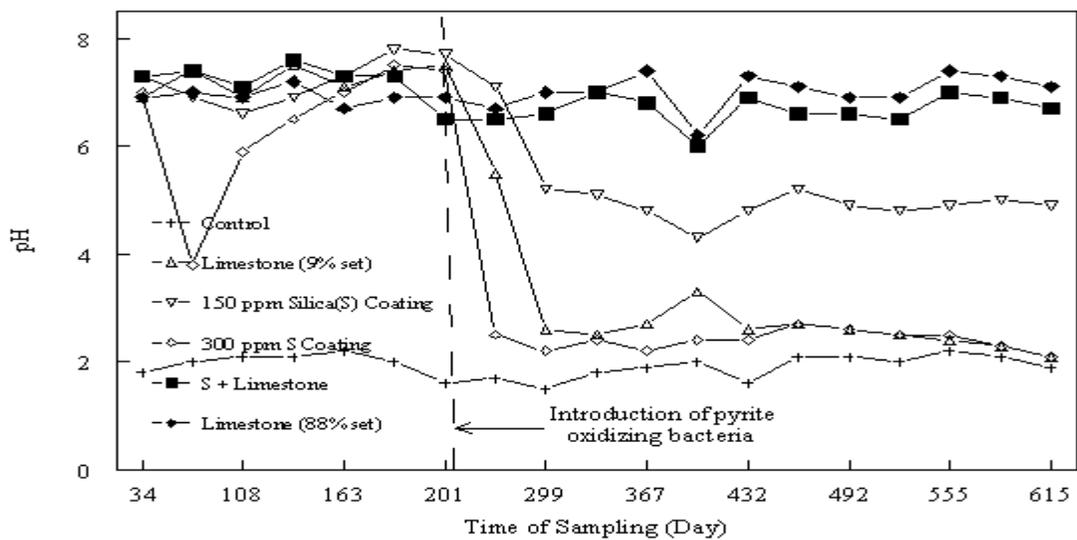


Figure 12. Leachate pH from field columns (9% pyrite neutralization of Western Kentucky mine spoil) through the nineteenth sampling.

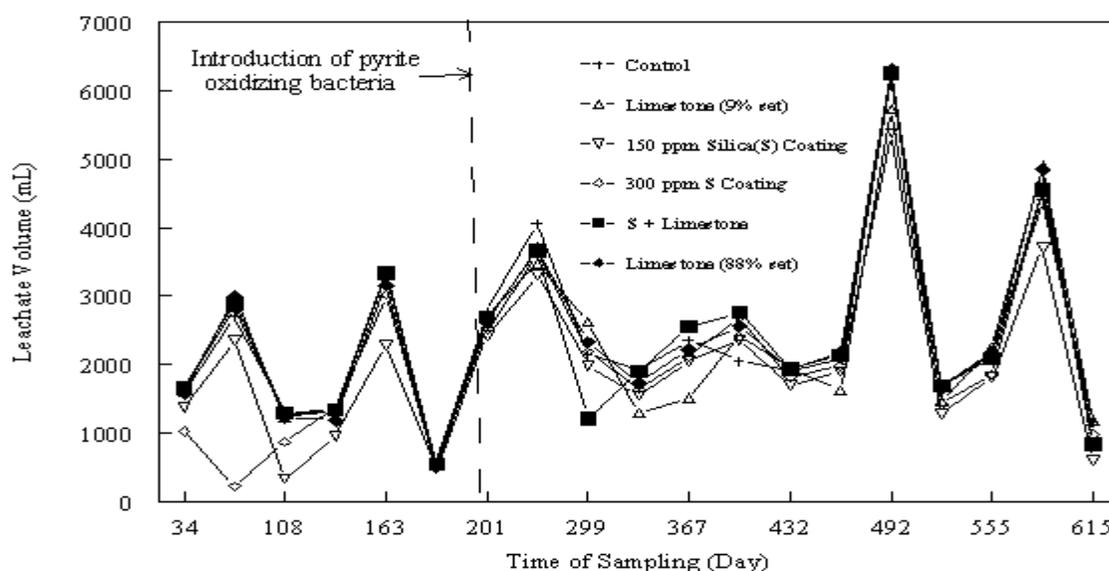


Figure 13. Leachate volume collected from field columns (9% pyrite neutralization of Western Kentucky mine spoil) through the nineteenth sampling.

In contrast to the Canadian tailings utilized in the two previous column groups, Table 3 shows that the Kentucky mine spoil used here had a very high salt content as well as high concentrations of metals and acidity. These salts, metal, and acidity would be readily released into solution. The Western Kentucky spoil material used for this column group released higher Fe and $\text{SO}_4\text{-S}$ concentrations into the water saturated extracts, and had lower pH, than do the majority of spoils in North America (Evangelou, 1995). Also, with a calcium (Ca) concentration of 495 mg L^{-1} combined with the very high $\text{SO}_4\text{-S}$ concentration, gypsum precipitation is likely. The presence of excess salts in these columns may have inhibited coating formation by providing too many binding sites other than pyrite surfaces for the silica.

Table 3. Chemical properties of extracts from water saturated paste by vacuum extraction for the Western Kentucky mine spoil (Mean of duplicates; \pm deviation from mean).

Saturation	pHw	EC	Ca	Mg	K	Na	Al	Fe	Mn	$\text{SO}_4\text{-S}$
Percentage		(mmhos/cm)	←			mg L^{-1}	→			
41.54	1.69	44.05	495	121	40.0	85.5	2028	26625	16.25	18118
(± 0.00)	(± 0.01)	(± 1.75)	(± 15)	(± 2)	(\pm)	(± 33.5)	(± 25)	(± 750)	(± 1.25)	(± 1008)

Table 4 shows the pH and cumulative data for this column group through 615 days. The data reveals that we got poorer repeatability between duplicates than with either of the previous two groups. That many of the duplicate treatments in this group had large deviation from the mean values may be due in part to the excess salts in one column providing too many binding sites for the silica and thereby inhibiting coating formation in that column but not its duplicate. Secondly, coating establishment in one but not the duplicate may be a result of the water channeling effect of gypsum precipitation within the non-coated columns. A third possibility for a failure in one column but not its duplicate is that the Kentucky spoil aggregates were large and irregular in size. Placement of the spoil-sand mixture in the columns may have created pockets that prevented a uniform flow of the rain water / solutions down through the column. This third consideration was not a factor in the Canadian tailings groups because all of the tailings in the sand-tailings mixture used in these two groups had a similar size to the sand particles and therefore promoted a uniform flow.

Table 4. Summary of cumulative data from the Western Kentucky mine spoil column group (9% potential pyritic acidity neutralization) through the nineteenth sampling. (Mean of duplicates; \pm deviation from the mean).

Treatment	pH	Fe (mg)	SO ₄ -S (mg)	Leachate volume (ml)
Control	1.9 (± 0.00)	79,791.4 ($\pm 8,918.6$)	103,106.0 ($\pm 8,730.0$)	45,905 (± 135.0)
Limestone (L) (88% acid neutralization)	7.1 (± 0.10)	108.1 (± 30.6)	18,354.1 ($\pm 1,189.8$)	45,515.0 (± 0.0)
L (9% acid neutralization)	2.1 (± 0.00)	15,112.3 ($\pm 8,488.8$)	40,491.8 ($\pm 8,229.8$)	43,640 ($\pm 2,160.0$)
L + Hypochlorite	2.5 (± 0.25)	9,159.5 ($\pm 8,789$)	31,521.1 ($\pm 12,733.0$)	44,490 ($\pm 1,690.0$)
L + Acetate	2.2 (± 0.05)	17,242.3 ($\pm 6,863$)	43,108.2 ($\pm 3,343$)	46,620 (± 90.0)
L + Silica (Si)	6.8 (± 0.25)	137.8 (± 37.1)	20,473.3 (± 964.7)	45,685 ($\pm 1,075.0$)
150 mg L ⁻¹ Si Coating	4.9 (± 2.70)	3,017.9 ($\pm 2,984.3$)	20,798.6 ($\pm 3,106.6$)	38,715.0 ($\pm 1,865.0$)
300 mg L ⁻¹ Si Coating	2.1 (± 0.00)	16,206.9 ($\pm 4,537.6$)	35,737.7 ($\pm 3,029.0$)	40,860 ($\pm 2,400.0$)

The data in Figures 10 and 11 shows that the 150 mg L⁻¹ silica coating, the silica + limestone, and the 88% limestone treatments may have prevented or slowed pyrite oxidation for the duration of this study. However, Table 4 reveals that only the control and the 88% limestone, and silica + limestone treatments behaved as duplicates. Therefore, only the low total amount of Fe and SO₄-S released from the silica + limestone and the 88% limestone treatments compared to the control can be considered significant and an indication that these treatments prevented or

slowed pyrite oxidation. The 150 mg L⁻¹ silica coating treatments may have also successfully coated and prevented or slowed pyrite oxidation in one column, but not its duplicate.

Conclusion

This experiment is limited by only having duplicates of each control / treatment. The deviation from the mean, given in tables 1, 2, and 4 show that many of these columns did not behave as duplicates and therefore exhibit poor repeatability. As already discussed, this may be due to factors such as gypsum precipitation, the presence of excess salts, or, in the case of the mine spoil, due to pockets in the columns that interrupted the uniform flow of rain water / solutions through the column. Another limitation is that by only analyzing the leachate, we know how water quality was affected by the various treatments; however, we do not know anything regarding the activities within the columns such as gypsum precipitation, the amount of pyrite consumed, or the percent of pyrite actually coated.

However, there is evidence that some of the coating treatments were successful. The silica + limestone treatment in the Western Kentucky spoil group performed quite well throughout the study showing little, if any, increase in the oxidation rate after the pyrite oxidizing bacteria were introduced. As for the 9% Canadian tailings group, the 150 mg L⁻¹ silica coating treatment appeared to prevent an increase in the pyrite oxidation rate for approximately 1.5 years before it failed. The 113.5% Canadian tailings group should begin to show some differentiation between the limestone treatment and the various other treatments in the near future. We plan to continue monitoring the 113.5% Canadian group as well as the Western Kentucky group for several years to assess the long term durability of the coating treatments. Although we are still early into this long term field-column experiment, these results show promise for the utilization of the microencapsulation technique to abate acid mine drainage.

Work Planned

The evaluation of fly ash to understand the fundamental differences between different fly ashes and to determine which fly ash is best suited to form coatings.

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**COMPARATIVE TESTING BETWEEN CONVENTIONAL AND
MICROENCAPSULATION APPROACHES IN CONTROLLING PYRITE OXIDATION**

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Abstract. Oxidation of pyrite in mining waste or overburden is the main source of acid mine drainage (AMD) production, which causes major environmental pollution. Presently, the most common method of controlling AMD is through the mixing of alkaline substances, such as limestone, with the AMD producing materials. However, the effectiveness of this method is still questionable due to the potential for iron armoring. Pyrite microencapsulation, utilizing silica coatings, is a novel approach for controlling AMD that is under development in our laboratory. Although under laboratory conditions this approach has been shown very effective in controlling pyrite oxidation, testing under natural conditions for possible field application is necessary. We are monitoring an outdoor leaching column experiment to evaluate the performance of both conventional and microencapsulation approaches for controlling AMD. The experiment consists of control, limestone, and silica treatments on mine spoil and tailing samples contained in leaching columns and set up in the field. Preliminary results indicate that, among the columns containing mine spoil, application of the silica microencapsulation approach significantly reduced pyrite oxidation. The average leachate sample pH were 1.9 from the control, 2.1 from the limestone, and 5.9 from the silica coatings. The results of these outdoor leaching experiments have shown that the application of silica coating could offer an improved solution for the abatement of AMD. However, long term monitoring and evaluation are still needed.

Key Words: Metal disulfides, kinetics of oxidation, reaction rates, ameliorates, surface catalysis, leaching