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

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Author: Dr. V.P. Evangelou

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University of Kentucky Research Foundation
Office of Sponsored Programs
201 Kinkead Hall
Lexington, KY 40506-0057

OBJECTIVES

1. Overall Objective

To investigate the potential of fly ash to control acid mine drainage (AMD) production.

2. Broad Objectives

a. To evaluate the role of silica contained in fly ash to control acid mine drainage production.

b. To evaluate the role of silica contained in fly ash to inhibit pyrite oxidation.

SUMMARY OF TECHNICAL PROGRESS

1. Introduction

The results of pyrite oxidation in mining areas are very low pH and elevated concentrations of iron and sulfate in the groundwater. Pyrite oxidation is therefore the main cause for acid mine drainage production. One approach to prevent AMD production is microencapsulation of pyrite crystals with an iron-oxide/silica coating (Zhang and Evangelou, 1998). Coating prevents diffusion of oxygen and Fe^{3+} to the crystal's surface and they are no longer able to oxidize it. The objective of this portion of the study was to test the hypothesis that fly ash is able to provide the necessary silica for iron-oxide/silica coating formation on the pyrite surfaces thus, decreasing pyrite oxidation and diminishing acid mine drainage production.

2. Pyrite leaching column experiments by selected fly ashes

All experiments were designed as indoor column leaching studies. The columns were approximately 5 cm (2 inches) in diameter and of 20 cm (8 inches) in height and they were loaded with a mixture of about 90 % quartz sand and 10 % pyrite. The ratio sand-pyrite / fly ash was 7:3. Three fly ash samples were chosen for the pyrite leaching columns, with and without oxidant (Ca-hypochlorite), for silica-coating formation (Zhang and Evangelou, 1998):

- BP: High alkalinity (17.8 meq/100 g) with 140 mg/kg soluble Si at pH 7.
Surface: Fe: 0.53 %, Al: 7.58 %, Fe/Al: 0.07.
- GH2: Low alkalinity (3.5 meq/100 g) with 200 mg/kg soluble Si at pH 7.
Surface: Fe: 0.27 %, Al: 4.43 %, Fe/Al: 0.06.
- GH-IS: Low alkalinity (0.3 meq/100 g) 60 mg/kg soluble Si at pH 7.
Surface: Fe: 0.25 %, Al: 8.20 %, Fe/Al: 0.11.

It is expected, that samples BP and GH2 will be able to establish an iron-oxide/silica coating on the pyrite surface because of the high content of soluble silica. GH-IS should not be able to establish a coating because of the very low silica content. Alkalinity of all fly ash samples is not high enough to establish alkaline conditions in the columns and therefore lime was added to all columns. As oxidizer calcium-hypochlorite was used which was expected to oxidize Fe^{2+} and provide an iron-oxide base on the pyrite surface for condensation of silica (Zhang and Evangelou, 1996; Zhang and Evangelou, 1998; Vandiviere and Evangelou, 1998).

Figure 1. Schematic of the column leaching apparatus.

2. Evaluation of fly ash performance

Triplicates of three fly ashes for four treatments were loaded into columns: 1) Fly ash, sand, and pyrite; 2) fly ash, sand, pyrite, and lime; 3) fly ash, sand, and lime; 4) fly ash, sand, pyrite, lime, and hypochlorite. As a control, three additional columns were loaded with sand and pyrite only. A schematic of the pyrite leaching apparatus is shown in Fig. 1.

Treatments 1, 2, and 4 contained a combination of 30% fly ash, and 70% of a 10% pyrite/90% clean angular sand mixture. The pulverized pyrite used in these columns was only 80% pure. In order to obtain 10% total pyrite needed for the experiment, the quantity of pyrite mixture was increased proportionally. The amount of needed lime in treatments 2, 3, and 4 was calculated by the acidity produced by the oxidation of 20% of the pyrite. The addition of lime to the columns was necessary to establish precise alkaline conditions. In treatment 4, amounts of hypochlorite were based on the oxidation of 10% of the total pyrite in the mixture. Hypochlorite oxidized the pyrite and Fe^{+2} to supply an iron-oxide coating on the surface of the sample. This allowed the reaction with silica to take place. The overall calculations for the total weight of the mixture was based upon the density of the fly ashes.

The columns used were approximately 5 cm in diameter and 25 cm in height with a removable lower bed support. To prevent any clogging during oxidation due to precipitates, 105 g (approximately 4 cm) of clean angular sand was placed in the bottom of the column. To stop the loss of material out of the column, a 149 mm monofilament cloth-nylon mesh was placed at the base of the lower bed support (Small Parts, Inc., Miami Lakes, FL). Depending on treatment, 125 g fly ash, 261.9 g sand, 32.3 g pulverized pyrite (29.1 g total pyrite available), 20.46 g lime, and 13.81 g Ca-hypochlorite were placed in a bag, and mixed thoroughly in order to distribute each component evenly. Finally, 75 g more of clean sand was placed on top of the mixture contained in each column. The oxidative conditions were established by constantly flushing the column with humidified air. Periodically, sampling of two pore volumes are taken by pumping deionized water through the bottom of each of the columns.

All columns were saturated with deionized water ($\text{di-H}_2\text{O}$) on June 24, 1998. Leachates were collected for the first time on July 23, 1998. The columns were left dry until August thirteenth, 1998 when they were again saturated with $\text{di-H}_2\text{O}$. After one month of saturation, the second leachate sampling was collected as follows. All columns were drained, filled to saturation, drained again after four hours and both collections combined.

3. Leachate data from the GH2 fly ash column set

Data on chemical composition and leachate volume are presented in figures 2 - 7. All treatments have maintained a circumneutral pH to date (Fig. 3). The control has dropped to pH 3.9 and this drop is due to pyrite oxidation. The electrical conductivity (EC) of the fly ash + pyrite + lime + hypochlorite treatment was very high (53.2 mmhos cm^{-1}) at the first sampling, but by the second sampling had dropped significantly (Fig. 3). This was due to the flushing out of the calcium (Ca) coming from the calcium hypochlorite in these columns (see Fig. 5). There was little or no iron (Fe) concentration in the leachates collected from the treatments while the control had an increase in the amount of Fe released between the two samplings of 49 parts per million (ppm) (Fig. 6). Sulfate ($\text{SO}_4\text{-S}$), however, was released at approximately the same rate from all columns (Fig. 7). The fly ash + pyrite + limestone + hypochlorite treatment has released the least amount of $\text{SO}_4\text{-S}$ to date.

4. Leachate data from the GH1-S fly ash column set

Data on chemical composition and leachate volume are presented in figures 8 - 13. The pH of the leachates collected from the control and the fly ash + pyrite columns

Fig. 2. Cumulative leachate volume collected from the GH2 flyash columns through the second sampling.

Fig. 3. pH of leachate collected from the GH2 flyash columns through the second sampling.

Fig. 4. Electrical conductivity (EC) of leachate collected from the GH2 flyash columns through the second sampling.

Fig. 5. Cumulative calcium (Ca) concentration of leachate collected from the GH2 flyash columns through the second sampling.

Fig. 6. Cumulative iron (Fe) concentration of leachate collected from the GH2 flyash columns through the second sampling.

Fig. 7. Cumulative sulfate ($\text{SO}_4\text{-S}$) concentration of leachate collected from the GH2 flyash columns through the second sampling.

Fig. 8. Cumulative leachate volume collected from the GH-1S fly ash columns through the second sampling.

Fig. 9. pH of leachate collected from the GH-1S fly ash columns through the second sampling.

Fig. 10. Electrical conductivity (EC) of leachate collected from the GH-1S fly ash columns through the second sampling.

Fig. 11. Cumulative calcium (Ca) concentration of leachate collected from the GH-1S fly ash columns through the second sampling.

Fig. 12. Cumulative iron (Fe) concentration of leachate collected from the GH-1S fly ash columns through the second sampling.

Fig. 13. Cumulative sulfate ($\text{SO}_4\text{-S}$) concentration of leachate collected from the GH-1S fly ash columns through the second sampling.

Fig. 14. Cumulative leachate volume collected from the BP fly ash columns through the second sampling.

Fig. 15. pH of leachate collected from the BP fly ash columns through the second sampling.

Fig. 16. Electrical conductivity (EC) of leachate collected from the BP fly ash columns through the second sampling.

Fig. 17. Cumulative calcium (Ca) concentration of leachate collected from the BP fly ash columns through the second sampling.

Fig. 18. Cumulative iron (Fe) concentration of leachate collected from the BP fly ash columns through the second sampling.

Fig. 19. Cumulative sulfate ($\text{SO}_4\text{-S}$) concentration of leachate collected from the BP fly ash columns through the second sampling.

have dropped from about 6.2 to approximately 4.0. The leachate pH of these columns has dropped due to pyrite oxidation. All other treatments have maintained a circum - neutral pH to date (Fig. 9). As with the GH2 column set, the EC of the leachate collected from the fly ash + pyrite + limestone + hypochlorite treatments were extremely high due to the flushing out of the Ca (Figs. 10 and 11). The amount of Fe and $\text{SO}_4\text{-S}$ released into the leachate from the control and the fly ash + pyrite columns increased significantly from the first to second sampling (Fig. 12 and 13). This increase in Fe and $\text{SO}_4\text{-S}$ concentration in the leachates from the control and fly ash + pyrite columns is due to pyrite oxidation. The release of Fe from all other treatments was negligible. However, $\text{SO}_4\text{-S}$ concentration in the leachate from the fly ash + pyrite + limestone treatment also showed a significant increase. This increase has, as yet, not been accompanied with a drop in pH and increase in Fe release. To date the fly ash + limestone and fly ash + pyrite + limestone + hypochlorite columns have performed best with respect to pH and Fe and $\text{SO}_4\text{-S}$ released into their leachate.

5. Leachate data from the BP fly ash column set

Data on chemical composition and leachate volume are presented in figures 14 - 19. The pH of the leachates collected from the control columns have dropped from about 6.2 to approximately 4.0 due to pyrite oxidation. The fly ash + pyrite + limestone + hypochlorite column's leachate pH has remained steady at about 7. The leachate from all other columns started at very high pH values of approximately 11.5, but have now dropped to approximately pH 7 (Fig. 14). Again, as with the other two fly ash types, the EC of the leachate from the fly ash + pyrite + limestone + hypochlorite columns was initially very high at $106 \text{ mmhos cm}^{-1}$, but had dropped to $10.7 \text{ mmhos cm}^{-1}$ by the second sampling. This high EC is due to flushing out of the Ca (Fig. 16 and 17). Only the control released high amounts of both Fe and $\text{SO}_4\text{-S}$ into the leachate (Fig. 18 and 19). The leachate collected from the fly ash + limestone columns had a relatively small increase in the concentration of $\text{SO}_4\text{-S}$ (from 42 to 168 ppm). All other columns showed a significant increase in the amount of $\text{SO}_4\text{-S}$ released (Fig. 19). To date the fly ash + limestone columns have performed best with respect to pH, and the amount of Fe and $\text{SO}_4\text{-S}$ released into their leachate.

CITATIONS

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