PYRITE MICROENCAPSULATION:
POTENTIAL FOR ABATEMENT OF ACID MINE DRAINAGE[1]

by

A. K. Seta and V. P. (Bill) Evangelou[2]

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 controling AMD problems is through the mixing alkaline substances, such as limestone, with the AMD producing materials. However, the effectiveness of this method is still questionable. The main reason for this is that the surface of pyrite particles in mining waste are still exposed to the atmospheric O_2 after treatment. Experimental evidence on novel pyrite microencapsulation technologies currently under development in our laboratory are presented. It was demonstrated that these technologies, which include ferric hydroxide-phosphate-coatings and ferric-hydroxide-silica coatings, could effectively protect pyrite from oxidation.

Introduction

Pyrite is a mineral commonly associated with coal and most metal ores. When exposed to the atmosphere, pyrite initially reacts with oxygen producing H^+, SO_4, and Fe^{2+} (Nordstrom, 1982). The Fe^{2+} produced can be further oxidized by O_2 into Fe^{3+}, which in turn hydrolyses into amorphous iron hydroxide and releases additional amounts of acid into the environment (Nordstrom, 1982; Fornasiero et al., 1992). During the initial stage of pyrite oxidation, the process is relatively slow. However, as acid production continues and pH in the vicinity of the pyritic surfaces drop below 3.5, the formation of ferric hydroxide is hindered and activity of free Fe^{3+} in solution increases (Lindsay, 1979). Under these conditions, oxidation of pyrite by Fe^{3+} becomes the main mechanism for acid production in coal waste because Fe^{3+} can oxidize pyrite at a much faster rate than O_2 (Singer and Stumm, 1970). In addition, at low pH, an acidophilic, chemoautotropic, iron-oxidixing bacterium, *Thiobacillus ferrooxidans*, can catalyze and accelerate the oxidation of Fe^{2+} into Fe^{3+} by a factor larger than 10^6 (Singer and Stumm, 1970).

The approaches currently used to prevent pyrite oxidation in the field are mainly aimed at eliminating Fe from pore waters and/or blocking the access of the atmospheric O_2 to pyritic surfaces. These approaches include the use of limestone or rock phosphate to precipitate Fe in the insoluble form as iron hydroxide/oxyhydroxide or $FePO_4$, respectively (Skousen et al., 1987 and references therein; Renton et al., 1988; Brown and Jurinak, 1989), and the application of bactericides to inhibit the oxidation of Fe^{2+} into Fe^{3+} (Kleinmann, 1980). Both approaches have shown a certain degree of success in preventing pyrite oxidation and acid production in pyritic waste. However, they both have a weakness, i.e., they have a

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[2] Postdoctoral Research Scholar and Professor, respectively, in the Department of Agronomy, University of Kentucky, Lexington, Kentucky 40546. Address correspondence to V. P. Evangelou, Department of Agronomy, N-122 Ag. Sci. Center North, University of Kentucky, Lexington, KY 40546-0091. The work for this review was funded by the U.S. Bureau of Mines, U.S. Geological Survey and the Kentucky Agricultural Experimental Station and is published with the approval of the Director.

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short span of effectiveness. The main reason for this is that the surface of pyrite particles in mining waste are still exposed to the atmospheric O_2 after treatment. Consequently, as Fe^{2+} accumulates and *T. ferrooxidans* repopulates on pyritic surfaces, pyrite oxidation by Fe^{3+} and acid production initiates (Kleinmann and Crerar, 1979). In addition, recent findings suggest that limestone may actually accelerate, under certain conditions, the pyrite oxidation process (Evangelou and Huang, 1994a). Therefore, better understanding on the effects of environment on the pyrite oxidation mechanisms is needed to make sound recommendations on the use of appropriate technologies in controlling AMD. To completely prevent pyrite oxidation, it appears essential to block the access of the atmospheric O_2 to pyritic surfaces. Recently in our laboratory we developed a number of pyrite coating technologies to inhibit pyrite oxidation. These technologies include (a) iron-oxide coating, (b) iron-phosphate coating, and (c) iron-silica coating (Evangelou and Huang, 1994b; Evangelou, 1996). The objective of this study is to demonstrate the use of the novel pyrite microencapsulation technologies developed in our laboratory for abatement of acid mine drainage in field leaching columns.

Materials and Methods

Coating Technology Experiments

Three new microencapsulation (coating) methodologies for preventing pyrite oxidation and acid production in coal pyritic waste have been developed in our laboratory using small leaching columns. The first coating methodology is that of *iron-oxide-phosphate coating*. This was done by leaching coal waste with a solution composed of 0.01 *M* sodium acetate buffer (NaOAc) plus 0.106 *M* H_2O_2 and 0.001 *M* KH_2PO_4. During the leaching process, H_2O_2 oxidizes pyrite and produces Fe^{3+} so that iron phosphate precipitates as a coating on pyrite surfaces. The purpose of pH buffer (NaOAc) in the coating solution is to eliminate the inhibitory effect of the protons, produced during pyrite oxidation, on the precipitation of iron phosphate (Evangelou, 1995a,b).

The second coating methodology is that of an *iron-oxide coating*. This was done by leaching pyritic waste with a solution composed of 0.106 *M* H_2O_2 and 0.01 *M* NaOAc (Evangelou and Zhang, 1995).

The third coating methodology is that of an *iron-oxide-silica coating*. This was done by leaching pyritic waste with a solution composed of 0.145 *M* H_2O_2 and 50 mg L^{-1} of dissolved Si at pH 5 adjusted with 0.01 *M* NaOAc. In order to demonstrate that the coating on the surface of pyrite was acid resistant because it was composed of two distinct layers, an iron-oxide layer (acid sensitive) and a silicon oxide layer (silica) (acid resistant), an iron-oxide-silica coated pyrite sample was treated as follows: sample A was leached with water; sample B was oxidized with 0.145 *M* H_2O_2; sample C was leached with 50 ml of 4 *M* HCl and then it was oxidized with 0.145 M H_2O_2; sample D was treated with 50 ml of 4 *M* HF (remove the iron-oxyhydroxide coating as well as the silica coating) and then it was oxidized with 0.145 *M* H_2O_2. The purpose of these two treatments (HCl versus HF) was to demonstrate that silica coating on the surface of pyrite was produced and that this coating was resistant to acid attack.

Outdoor Leaching Column Experiments

In order to test the coating technology under natural environment for possible mass application in the field, an outdoor leaching column experiment was conducted. The set of leaching columns consisted of three treatments in duplicate: limestone, phosphate coating, and silica coating. The leaching columns were made from plexiglass tubing with a height of 18" and inside diameter of 6" equipped with a leachate collection system. All columns were fitted with drain tubes. Actual support for the columns were weighted 5 gallon plastic buckets, and collection vessels were one gallon polypropylene jugs.

The phosphate coating columns were constructed by filling the column with 0.5 kg mine tailing mixed with 9.5 kg sharp sand. Furthermore, 800 g of limestone covered with 107 g of $Ca(OCl)_2$ was added to the column to neutralize all of the potential acidity of the columns and 5 L of coating solution consisting of 0.1 *M* NaAC and 0.001 *M* KH_2PO_4 (P = 30 mg L^{-1}) at pH 5, was then leached down to the columns prior to setting up in the field. The same method was used for silica coating except that in this treatment 0.001 *M* Na_2SiO_3 (Si = 30 mg L^{-1}) was used instead of phosphate. The limestone treatment was constructed by filling the column with 0.5 kg mine tailing mixed with 9.5 kg sharp sand and 800 g limestone and were leached with deionized water only. After a 1-3 week incubation time the columns were set up in the field. Leachates were collected and analyzed periodically for pH, Fe, and SO_4-S concentration. Finally, after a 3 month period in the field, pyrite oxidixing bacteria were introduced to the columns to evaluate the pyrite coating technology in preventing microbial oxidation.

Results and Discussions

Coating Technologies Experiment

The phosphate coating process is shown schematically in Fig. 1. The dotted lines in Fig. 1. signify physical bonding between pyrite and $FePO_4$. When iron (Fe^{3+}) reacts with PO_4^{3-} it forms an acid resistant ferric phosphate ($FePO_4$) coating, which inhibits oxidation of pyrite as shown in Fig. 2A (see also Evangelou, 1995a,b). It is important to note that the technology of coating pyrite as described above, is not to be confused with field application of rock phosphate (Flynn, 1969). Rock phosphate complexes dissolved iron (Fe(II)), thus, reducing the potential of Fe(III) production, and reducing the potential for pyrite oxidation as well (Stumm and Morgan, 1970). Rock phosphate does not coat pyrite; rather, it complexes released Fe(II) from the oxidizing pyrite (Evangelou et al., 1992). Instead, a rock phosphate surface coating with Fe(II) forms, reducing rock phosphate dissolution. Therefore, the effectiveness of rock phosphate in controlling pyrite oxidation is short lived.

During the leaching process, H_2O_2 oxidizes pyrite and produces an iron oxide coating on the surface of pyrite (Fig. 2C). The purpose of a pH-buffer in this case is to buffer the solution during coating formation at a pH between 5 and 7 where iron oxide formation is promoted.

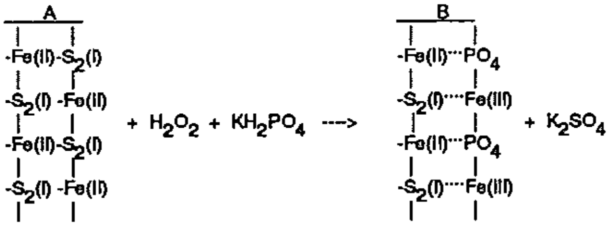

Figure 1. Schematic of H_2O_2 induced oxidation proof phosphate surface coating on iron sulfides (Evangelou and Huang, 1994b, U.S. Patent No. 5,286,522, Feb. 15, 1994).

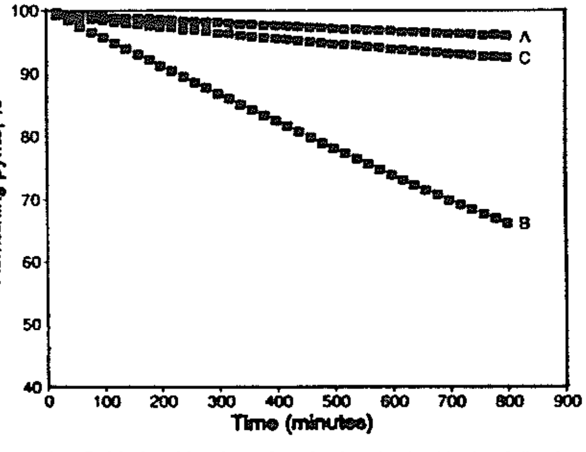

Figure 2. Oxidation kinetics of pyrite leached with the following three pH 6 solutions: A) 0.01 *M* sodium acetate (NaOAc) plus 0.106 *M* H_2O_2 and 0.001 *M* KH_2PO_4; B) 0.01 *M* NaOAc plus 0.106 *M* H_2O_2 and 0.013 *M* EDTA; C) 0.01 *M* NaOAc plus 0.106 *M* H_2O_2.

The data in Fig. 3 show the oxidation potential of framboidal pyrite by 0.145 *M* hydrogen peroxide (H_2O_2) in the presence and absence of 50 mg L^{-1} dissolved silica at pH 5 adjusted with 0.01 *M* sodium acetate. As can been seen, silica significantly suppressed the potential of H_2O_2 to oxidize pyrite. The explanation for this behavior is that oxidation of pyrite by H_2O_2 in the presence of Si and sodium acetate lead to the formation of an iron-oxide silica coating as shown schematically in Fig. 4. The resistance of silica coating to low pH or strong acid attack is demostrated in Fig. 5. The data from zero to 900 minutes represents the silica coating process of pyrite. After 900 minutes, the data labeled A represent leaching of iron-oxide-silica coated pyrite with oxygenated water alone. No pyrite oxidation was apparent. The data labeled B represent coated pyrite oxidation with 0.145 *M* H_2O_2, a strong pyrite oxidizer. These data show that the iron-oxide-silica coating protected pyrite from oxidizing by inhibiting H_2O_2 diffusion to the pyrite surface. The data in Fig. 5C (representing 4 *M* HCl treatment) show that oxidation of pyrite by 0.145 *M* H_2O_2 was greatly suppressed relative to that treated with 4 *M* HF (Fig. 5D). This strongly suggested that the silica part of the coating offers substantial protection to pyrite from H_2O_2 (a very strong oxidizer) attack due to the fact that silica is not soluble in acid.

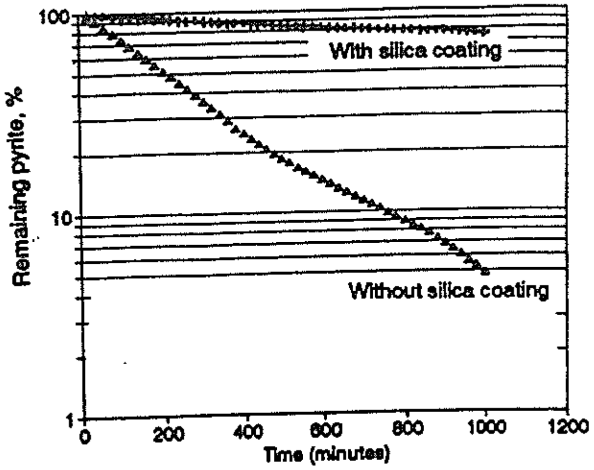

Figure 3. Pyrite leached with 0.145 *M* H_2O_2, with and without 50 mg L^{-1} silica (Si) (having as source sodium meta-silicate (Na_2SiO_3 $5H_2O$) at pH 5 buffered with 0.01 *M* sodium acetate at room temperature (Zhang and Evangelou, Unpublished data, 1994).

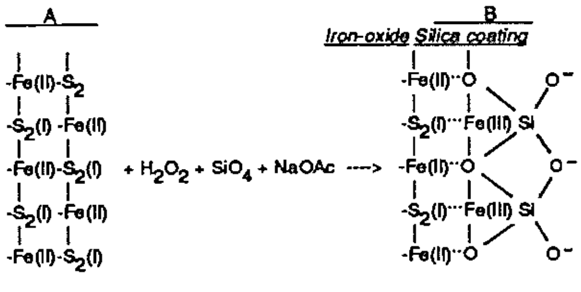

Figure 4. Schematic of H_2O_2 induced oxidation proof silica surface coating on iron sulfides (Evangelou, 1996, U.S. Patent No. 5,494,703, Feb. 27, 1996).

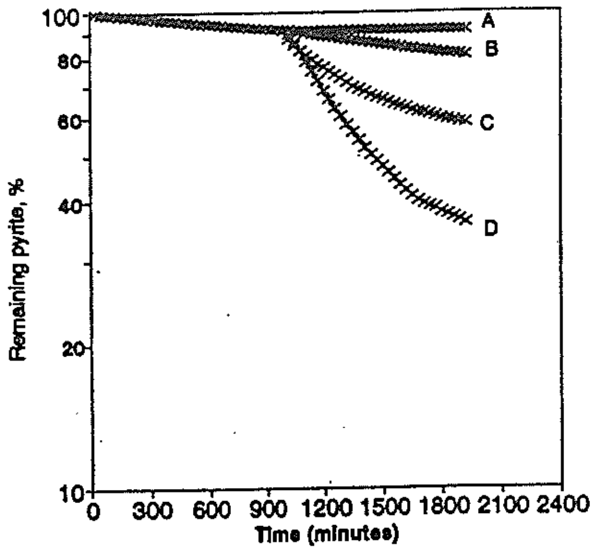

Figure 5. Various pyrite samples first (up to 900 min) leached with 0.145 *M* H_2O_2, 50 mg L^{-1} silica (Si) at pH 5 buffered with 0.01 *M* sodium acetate at room temperature. Each of the pyrite coated samples was treated as follows: Sample A was leached with water; sample B was leached with 0.145 *M* H_2O_2; sample C was first leached with 50 ml 4 *M* hydrochloric acid (HCl) and then leached with 0.145 *M* H_2O_2; sample D was first leached with 50 ml 4 *M* hydrofluoric acid (HF) and then leached with 0.145 *M* H_2O_2 (Zhang and Evangelou, Unpublished Data 1994).

Successful application of such coating methodologies in the field could mean long term solution (perhaps even permanent solution) to certain types of acid mine drainage problems. These coating methodologies are expected to be cost effective since they involve readily available materials and only cover the surface of pyrite particles. Furthermore, the coating solution could be applied to any permeable coal mine waste thus, little or no physical disturbance of coal mine waste during treatment would be necessary.

Outdoor Leaching Columns Experiments

To date, pH of the leachate samples collected from the limestone treatment is slightly lower than that from phosphate and silica treatments (Fig. 6). On the average, pH of the leachate samples from limestone, phosphate-coating, and silica-coating treatments are 6.75, 6.88, and 7.00, respectively. The lower pH of the limestone treatment may be due to higher pyrite oxidation from mine tailing as indicated by the higher Fe concentration of the leachate samples (Fig. 7). The average iron concentration of the leachate samples from limestone treatment is 148 while those from phosphate and silica-coating treatments are 11 and 8 mg L^{-1}, respectively. However, the sulfate concentration from all of the treatrment seems to be similar (Fig. 8). We expect that during long-term column exposure to atmospheric conditions, leachate composition will differ between limestone treated column and coated columns if indeed coating has taken effect by the procedures employed.

As expected, the introduction of pyrite oxidizing bacteria (*Thiobacillus ferrooxidans*) temporary increased the rate of Fe (Fig. 7) and SO_4-S (Fig. 8) production in all of the treatments. However, introduction of pyrite oxidixing bacteria has more significant affect on the Fe production from the limestone treatment than phosphate and silica-coating treatments suggesting that, up to now, pyrite coating is protecting microbial pyrite oxidation. The fluctuation of all chemical concentrations of the leachate samples from sampling to sampling apparently is affected by the rainfall pattern through flusing and/or dilution effects.

The results of these outdoor column leaching experiments show that application of the coating technology seems to give new promise in the abatement of acid mine drainage. However, long term meticulous monitoring and evaluation are still needed. We will be monitoring these columns for several years.

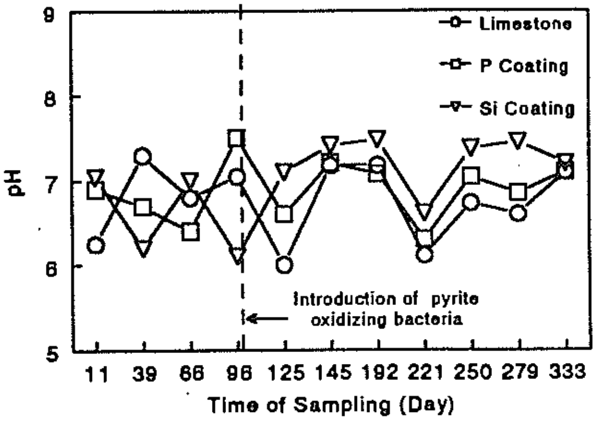

Figure 6. Leachate pH from outdoor columns taken at the ten sampling (unpublished data).

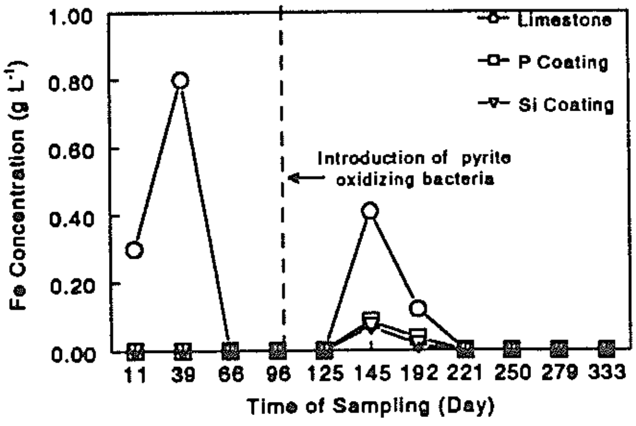

Figure 7. Iron (Fe) concentration of the leachate samples from outdoor columns taken at the ten sampling (unpublished data).

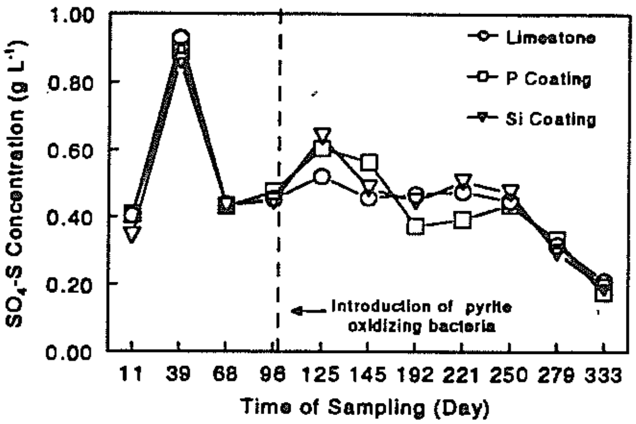

Figure 8. Sulfate (SO_4-S) concentration of the leachate samples from outdoor columns taken at the ten sampling (unpublished data).

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Disclaimer

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