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SILICA/FLY ASH BASED TECHNOLOGY
FOR CONTROLLING PYRITE OXIDATION

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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 Objectives:

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 small laboratory and large outdoor columns.

SUMMARY OF TECHNICAL PROGRESS

1. Pyrite Surface Reactivity

In the previous report (semi annual technical progress report on "Silica/fly ash-based technology for controlling pyrite oxidation", reporting period 09/01/95 to 02/29/96, by Evangelou (1996)) we demonstrated, using FT-IR spectroscopy, that CO_2 reacts with the surface of pyrite and forms a pyrite- HCO_3 complex. We further postulated that this complex, because of its unstable electron configuration, promotes abiotic pyrite oxidation. During the past six months we produced wet chemistry evidence demonstrating that pyrite- HCO_3 complexes promote pyrite oxidation. This is an important finding for our over all strategy in controlling pyrite oxidation because it suggests that pyrite microencapsulation is important in order to control oxidation in near circumneutral pH environments produced by addition of alkaline material, e.g., fly ash.

Wet chemistry evidence on promoting pyrite oxidation through formation of pyrite- HCO_3 complexes were produced using a pyrite sample obtained from the Western Kentucky coal fields, coalseam number 9. The pyrite sample was ground and passed through a 47 and a 75 μm sieve. The sample which remained on top of the 47 μm sieve was used for the study after it was washed with 4 mol L^{-1} hydrofluoric acid and repeatedly rinsed with nitrogen gas (N)-purged distilled water and acetone. Physical characterization showed that the pyrite sample had a spongy-like appearance with a surface area of 10 $\text{m}^2 \text{g}^{-1}$, a desirable physical property for this study.

Kinetics of pyrite oxidation were studied employing a bed-reactor, which was a nuclepore swin-lok filter holder (25 mm inside diameter) similar to that described by Jardine and Sparks (1984). For each test run, about 50 mg of the separated pyrite was placed in a nuclepore filter-

holder between two Whatman No. 42 ashless filters. The column was first rinsed with 5 ml of 1 N HCl and then 5 ml of 5 mmol L⁻¹ NaCl to remove any surface oxidation products prior to initiating leaching. The leaching solutions were passed through the pyrite nucleopore filter column at a constant flow rate of 0.50 mL min⁻¹. Aliquots of the effluent solution were collected every 2 minutes for the first 16 minutes and then at 10 min intervals for a total of 1 hour using an Eldex Universal fraction collector. Five duplicate tests were run: 1) 10 mmol L⁻¹ NaHCO₃ with 20 mmol L⁻¹ H₂O₂; 2) 100 mmol L⁻¹ NaHCO₃ with 20 mmol L⁻¹ H₂O₂; 3) 10 mmol L⁻¹ NaHCO₃ with 2 mmol L⁻¹ H₂O₂; 4) 100 mmol L⁻¹ NaHCO₃ with 2 mmol L⁻¹ H₂O₂; 5) 10 mmol L⁻¹ NaHCO₃, 20 mmol L⁻¹ H₂O₂ and 100 mmol L⁻¹ NaNO₃. The ranges of NaHCO₃ and NaNO₃ concentration were chosen based on the results reported by Millero and Izaquire (1989). They reported that Fe²⁺ oxidation rate was not affected when in the presence of 10 mmol L⁻¹ NaHCO₃ or NaNO₃. Additionally, Fe²⁺ oxidation rate remained unaffected when in the presence of 100 mmol L⁻¹ NaNO₃ but increased approximately 10-fold when in the presence of 100 mmol L⁻¹ NaHCO₃. Nitrate (NO₃⁻) was chosen because it does not complex appreciably with Fe³⁺. Sulfate concentration in all leachates was measured using turbidimetry with BaCl₂ (Massoumi and Cornfield, 1963).

The data in Figures 1 and 2 and Table 1 show that pyrite oxidation was greatly enhanced by HCO₃⁻ concentration. At H₂O₂ concentration of 20 mmol L⁻¹, increasing HCO₃⁻ concentration from 10 to 100 mmol L⁻¹ increased the oxidation rate by about 280% (calculated from the difference between slopes). Similarly, when H₂O₂ concentration was set at 2 mmol L⁻¹, the oxidation rate was about 230% higher at the 100 mmol L⁻¹ HCO₃⁻ concentration than at the 10 mmol L⁻¹ HCO₃⁻ concentration. This phenomenon was supported by FT-IR analyses of the pyrite sample before and after oxidation. The emergence of absorption bands at 1600 and 1356 cm⁻¹ on the oxidized pyrite clearly indicated the presence of Fe-HCO₃ on the pyrite surface (Figure 3). The formation of Fe-HCO₃ complexes on the pyrite surface enhanced pyrite

Figure 1. Influence of sodium bicarbonate concentration on the oxidation of pyrite using 20 mmol L⁻¹ H₂O₂. The two slopes are significantly different at the 95% confidence interval according to the t-test.

oxidation, leading to thiosulfate formation and thus, SO_4 production (Evangelou, 1995). This finding was consistent with frontier molecular orbital theory proposed by Luther et al. (1992) and our FT-IR data we reported previously (semi annual technical progress report on "Silica/fly ash-based technology for controlling pyrite oxidation", reporting period 09/01/95 to 02/29/96, by Evangelou (1996)).

Figure 2. Influence of sodium bicarbonate concentration on the oxidation of pyrite using $2 \text{ mmol L}^{-1} \text{H}_2\text{O}_2$. The two slopes are significantly different at the 95% confidence level according to the t-test.

Table 1. Summary of reaction rates of the various systems tested.

Oxidizing Systems	Slope	R^2
$20 \text{ mmol L}^{-1} \text{H}_2\text{O}_2$ plus $10 \text{ mmol L}^{-1} \text{HCO}_3^-$	0.042	0.999
$20 \text{ mmol L}^{-1} \text{H}_2\text{O}_2$ plus $100 \text{ mmol L}^{-1} \text{HCO}_3^-$	0.115	0.995
$2 \text{ mmol L}^{-1} \text{H}_2\text{O}_2$ plus $10 \text{ mmol L}^{-1} \text{HCO}_3^-$	0.024	0.999
$2 \text{ mmol L}^{-1} \text{H}_2\text{O}_2$ plus $100 \text{ mmol L}^{-1} \text{HCO}_3^-$	0.054	0.996
$20 \text{ mmol L}^{-1} \text{H}_2\text{O}_2$ plus $100 \text{ mmol L}^{-1} \text{NaNO}_3$	0.034	0.996

Figure 3. FT-IR diffuse reflectance spectra of pyrite (A) before and (B) after leaching with 100 mmol L⁻¹ HCO₃⁻ plus 20 mmol L⁻¹ H₂O₂.

Although the concentration of H₂O₂ also influenced the rate of pyrite oxidation, its effect was found to be smaller than that of HCO₃⁻. On the average, pyrite oxidation increased by about 250% by increasing HCO₃⁻ concentration 10-fold and only 190% by increasing H₂O₂ concentration also 10-fold. Furthermore, the role of H₂O₂ became less prominent at the higher HCO₃⁻ concentration. When HCO₃⁻ concentration was set at 10 mmol L⁻¹, increasing H₂O₂ concentration from 2 to 20 mmol L⁻¹ increased pyrite oxidation by 175% (Figures 1 and 2 and Table 1). However, when the concentration of HCO₃⁻ was set at 100 mmol L⁻¹, increasing H₂O₂ concentration from 2 to 20 mmol L⁻¹ increased pyrite oxidation by 215% (Figures 1 and 2 and Table 1). This implied that at the higher HCO₃⁻ concentration the oxidation rate was controlled mainly by the more rapid regeneration of Fe³⁺ due to HCO₃⁻. It appears that Fe³⁺ is a more effective pyrite oxidant because of its small ionic radius (steric effect) and its potential to form inner-sphere complexes (transition state intermediate) with the surface of pyrite while H₂O₂ is a molecule with a relatively large radius, thus limiting its potential to form pyrite surface complexes with all reactive sites potentially available to Fe³⁺ (Luther, 1987).

The data in Figure 4 show that the increase in pyrite oxidation could not be, in any way, contributed to ionic strength when HCO₃⁻ concentration was increased from 10 to 100 mmol L⁻¹. This can be deduced from the fact that addition of NaNO₃ (100 mmol L⁻¹) in the 10 mmol L⁻¹ HCO₃⁻ solution with 20 mmol L⁻¹ H₂O₂ did not in any way affect the oxidation of pyrite significantly. Apparently, the rate of Fe(II)-pyrite complex formation is not the rate limiting reaction, rather the electron transfer reaction from Fe(II) to O₂ or H₂O₂ is the rate controlling reaction.

Figure 4. Influence of 100 mmol L⁻¹ NaNO₃ on the oxidation of pyrite by 20 mmol L⁻¹ H₂O₂ and 10 mmol L⁻¹ sodium bicarbonate. The two slopes are not significantly different at the 95% confidence level according to the t-test.

2. Adsorption of Silica on Iron Oxides

In our previous studies (semi annual technical progress report on "Silica/fly ash-based technology for controlling pyrite oxidation", reporting period 09/01/95 to 02/29/96, by Evangelou (1996)) we reported that pyrite microencapsulation could be carried out by reacting pyrite with a pH buffered solution (using sodium acetate, NaOAc, in the pH range of 4 to 6) and in the presence of metasilicate (in the range of 10⁻³ molar). The coating forming on the surface of pyrite appeared to be an amorphous iron-oxide-silicate material. We also demonstrated that this iron-oxide-silicate coating inhibited pyrite oxidation. The purpose of our current studies was to evaluate the chemical stability of these iron-oxide-silicate coatings. The specific objectives were (a) to evaluate the molecular mechanisms of silicate adsorption by iron oxide; (b) to evaluate the effects of silicate on the bulk and surface properties of iron oxides; and (c) to evaluate the effect of silicate on metal-cation adsorption properties by iron oxides.

Iron oxides were prepared according to the procedures described by Atkinson et al. (1968) and Tejedor-Tejedor and Anderson (1990). It involved mixing of 0.3 mol L⁻¹ Fe(NO₃)₃ and 0.6 mol L⁻¹ Na(OH) solutions into a 2 L polyethylene bottle and aged for 2 days at room temperature. The suspension was alkalinized to pH 12.5 with Na(OH) and the resulting precipitate was aged for 6 more days at 60°C. After aging, the sample was washed with d-H₂O by centrifuging-decanting and dialyzing. The suspension was then freeze-dried.

X-ray diffraction analysis confirmed that the iron oxide sample was goethite (α-FeOOH) as indicated by the presence of intense d-spacings at 0.422, 0.246, and 0.271 nm (Figure 5). FT-IR absorption at 897 and 797 cm⁻¹ also confirmed that the iron-oxide was goethite (Figure 6). This iron oxide had a specific surface area of 85 m² g⁻¹ (determined by N₂-BET) and a point of zero charge (ZPC) of 8.3, which was also characteristic of goethite.

Figure 5. X-ray diffractogram of the laboratory-prepared iron oxide (goethite) sample.

Figure 6. FT-IR diffuse reflectance spectra of the laboratory-prepared iron oxide (goethite) sample.

Silicate adsorption on the iron oxide was evaluated using a batch equilibrium approach. It involved mixing of iron oxide suspension (the freeze-dried iron oxide was first resuspended in $\text{d-H}_2\text{O}$) with varying amount of Si (0.0 to 3.4 mmol L^{-1} Si) in 250mL polyethylene centrifuge tubes. Each of the test tubes was adjusted to a given pH (pH 4 to 8) in a background electrolyte of 0.1 N NaNO_3 . Equilibration was conducted under a nitrogen (N) gas environment. After a 24 h equilibration the pH of the suspension was measured, the samples were centrifuged and Si concentration in the supernatant was analyzed colorimetrically according to the procedures outlined by Clesceri et al. (1989). The silicate adsorption isotherm was constructed based on the

relationship between Si in the equilibrium solution and that adsorbed on the iron oxide. The Si adsorbed on the iron oxide was calculated based on the difference between the initial and final (after equilibrium) Si concentrations.

Figure 7 showed that the plot of adsorbed silicate on iron oxide versus equilibrium silicate in the solution produced a curvilinear line. This revealed that there was a relatively high affinity for silicate by the iron oxide. The mechanism most likely involves ligand exchange in which hydroxyl surface groups are replaced by silicate (Dzombak and Morel, 1990). Regardless of the equilibrium silicate concentration, adsorption of silicate increased with increasing pH (Figure 7). In order to evaluate the maximum pH for silicate adsorption, we conducted a silicate adsorption experiment from pH 4 to about 13. It was found that the maximum silicate adsorption occurred at pH around 9 (Figure 8), which is the pK_a of silicic acid.

Figure 7. Adsorption of silicate by the laboratory-prepared iron oxide (goethite) at different pH.

Figure 8. Adsorption of silicate by the laboratory-prepared iron oxide (goethite) at different pH and Si concentrations.

WORK PLANNED

For the next six-month period we plan to further characterize the mechanisms of silica-iron oxide reactions using FT-IR, XRD, XPS (X-ray Photoelectron Spectroscopy), TEM (Transmission Electron Microscopy), and TGA (Thermogravimetric Analysis) for understanding pyrite silica-coating formation. We also plan to include in these studies kinetics and dissolution of silica-iron oxide reactions and the metal-cation adsorption properties of silica-coated-iron oxides.

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Hazardous Substance Plan

Anticipated Substances/Chemicals to be Used

NO ADDITIONAL HAZARDOUS SUBSTANCES WERE GENERATED SINCE THE LAST REPORTING. WE STILL ANTICIPATE USING THE MATERIAL BELOW IN THE FUTURE.

- * Description of Substance/Chemical
1-1-2-2 Tetrabromoethane
- * EPA Hazardous Waste Number
No known number. Classified as a toxic, non-regulated waste material.†
- * EPA Hazard Code
No known code.†
- * Anticipated Quantity to be purchased, utilized or generated
5 kg (22 lb.)
- * Anticipated Hazardous Waste Transporter
Midwest Environmental Transport (OH 0000000539)
- * Anticipated Hazardous Waste Disposal Facility Contractor and Location
(City/Municipality, State)
Environmental Enterprises Inc., Cincinnati, Ohio (OHD 083377010)
- * Anticipated Treatment Method
Ensco incinerator

Hazardous Waste Report

Purchased, utilized or generated Waste

NO ADDITIONAL HAZARDOUS SUBSTANCES WERE GENERATED SINCE THE LAST REPORT.

- * Description of Substance/Chemical
- * EPA Hazardous Waste Number
- * EPA Hazard Code
- * Actual Quantity purchased, utilized or generated

* Actual Hazardous Waste Transporter

* Actual Hazardous Waste Disposal Facility Contractor and Location (City/Municipality, State)

* Actual Treatment Method

† Information regarding the EPA Hazardous Waste Number and the EPA Hazard Code was received from Kevin Baker, Assistant Director of Waste Management, University of Kentucky, Lexington, KY 40546. If this information differs from what DOE expects, please advise us how to procure the correct information.