A 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 silicate and metal sorption on iron oxides.

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

SUMMARY OF TECHNICAL PROGRESS

1. Introduction

In the previous report (semi annual technical progress report on "Silica/fly ash-based technology for controlling pyrite oxidation", reporting period 03/01/96 to 08/31/96, 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 demonstrated through wet chemistry that this complex promotes pyrite oxidation by catalyzing the oxidation of Fe^{2+} to Fe^{3+} which serves as final electron acceptor in the process of 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. In previous work (Zhang and Evangelou, 1996) we demonstrated that under strong oxidizing conditions, e.g., presence of H_2O_2 , pyrite oxidized extremely slowly when pH was buffered in the range of 5 to 6. It was determined that the cause for this oxidation inhibition was formation of an iron oxide coating on the surface of pyrite. We also demonstrated (first semi annual technical report on "Silica/fly ash-based technology for controlling pyrite oxidation", reporting period 09/01/95 to 02/01/96, by Evangelou (1996)) that on this iron oxide we could deposit a silicate coating.

The purpose of our studies during this past six-month period was to evaluate the surface properties of iron-oxide-silicate coatings. The specific objectives were (a) to

evaluate the mechanisms and ability of hydrous ferric oxide (HFO) to adsorb silica (Si); (b) to evaluate the effects of Si on the bulk and surface properties of HFO; and (c) to evaluate the effect of Si on heavy-metal adsorption properties by iron-oxides.

2. *Synthesis and Characterization of hydrous ferric oxide (HFO)*

Two types of HFOs were used in these experiments. One type of HFO, referred to as HFO-1, was prepared by titrating 0.150 M $\text{Fe}(\text{NO}_3)_3$ with 0.450 M NaOH in a polyethylene beaker. The ferric hydroxide suspension was adjusted to pH 7 and aged for 3 days. After aging the suspension was washed with d- H_2O to remove excess salt. This was carried out by centrifuging and decanting. In the case where centrifuging was not adequate to separate the suspended ferric hydroxide, solids separation was attained by the dialysis membrane method. The HFO-1 gel was then stored as a stock suspension.

A second type of HFO, referred to as HFO-2, was prepared according to the procedures described by Atkinson et al. (1968) and Tejedor-Tejedor and Anderson (1990). It involved mixing 500 mL of 0.3 mol L^{-1} $\text{Fe}(\text{NO}_3)_3$ and 500 mL of 0.6 mol L^{-1} NaOH solutions into a 2 L polyethylene bottle and aged for 2 days at room temperature. The suspension was alkalinized to pH 12.5 with NaOH and the resulting precipitate was aged for 6 more days at 60 °C. After aging, the sample was washed with d- H_2O by centrifuging-decanting and dialyzing. The suspension was then freeze-dried and stored as a powder. All of the solutions used in these experiments were made in a nitrogen atmosphere glove box.

Physico-chemical and mineralogical properties of the HFO were characterized by potentiometric titration for zero point of charge, pH_{zpc} (Bowden et al., 1977; Sposito, 1981); FT-IR for surface properties determination; XRD for crystallinity determination; N_2 -BET for surface area determination, and XPS for element bonding energy analysis.

Figure 1 shows that HFO-1 is amorphous as indicated by the absence of x-ray diffraction peaks.

Figure 1. X-ray diffractogram of hydrous iron oxide 1 (HFO-1).

The FT-IR spectra in Figure 2 show that the most important vibrations are those in the approximately 3300 to 3100 cm^{-1} range, indicative of water stretches, and the 1619 cm^{-1} band indicative of the deformation band of water.

Figure 2. FT-IR diffuse reflectance spectra of hydrous iron oxide 1 (HFO-1).

The vibrations below the 1600 cm^{-1} are most likely Fe-O symmetric stretches. This iron oxide had a specific surface area of $188\text{ m}^2\text{ g}^{-1}$ as determined by N_2 -BET, and a zero point of charge (pH_{zpc}) of 8.9.

In the case of HFO-2, x-ray diffraction analysis confirmed that the solid formed was goethite ($\alpha\text{-FeOOH}$) as indicated by the presence of intense d-spacings at 0.422, 0.246, and 0.271 nm (Figure 3).

Figure 3. X-ray diffractogram of hydrous iron oxide 2 (HFO-2).

The FT-IR absorption bands at 897 and 797 cm^{-1} also confirmed that HFO-2 was goethite (Figure 4).

Figure 4. FT-IR diffuse reflectance spectra of hydrous iron oxide 2 (HFO-2).

This iron oxide had a specific surface area of $85 \text{ m}^2 \text{ g}^{-1}$ as determined by N_2 -BET, and a point of zero point of charge (pH_{zpc}) of 8.9.

2. *Si Adsorption on HFO*

Silicate adsorption on HFO was evaluated using a batch equilibrium approach employing suspensions. Freeze-dried HFO-2 was first resuspended in $\text{d-H}_2\text{O}$. Batch equilibrium involved mixing 20 mL of 20 g L^{-1} HFO-1 or HFO-2 suspensions with 20 mL of Si solution containing various amounts of Si (0.00, 0.25, 0.5, 0.94, 1.7, and 3.4 mM L^{-1} Si) in the form of sodium metasilicate, $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ in 250 mL polyethylene centrifuge tubes. Each of the tubes was adjusted to a given pH (pH 4 to 8) and in a background electrolyte of 0.1 N NaNO_3 . Equilibration was carried out 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. Silicate adsorption isotherms were constructed by plotting Si in the equilibrium solution against that adsorbed on the iron oxide. Adsorbed Si by the iron oxide was calculated by difference between the initial and final (before and after equilibrium) Si concentrations.

Figures 5 and 6 show that the plot of adsorbed silicate on HFO-1 or HFO-2 versus equilibrium silicate in the solution produced a curvilinear line which was strongly affected by pH.

Figure 5. Silicate adsorption isotherms of hydrous iron oxide 1 (HFO-1).

Figure 6. Silicate adsorption isotherms of hydrous iron oxide 2 (HFO-2) under various pH values.

The data show that as pH was increased affinity of the silicate by the HFO increased. This affinity increase by pH was greater for HFO-1 than for HFO-2. This was expected since the specific surface of HFO-1 was much greater than HFO-2. The mechanism responsible for this increase in Si affinity by the HFO due to pH could be explained by the fact that the pK_a of silicic acid is 9.2, which is the pH at which maximum Si adsorption on HFO would occur. Even though pH appears to play a role on Si adsorption maximum, the mechanism of the adsorption process is most likely independent of H^+ since it involves ligand exchange in which hydroxyl surface groups are replaced by silicate (Dzombak and Morel, 1990). The pH simply regulates the concentration of silicate ions affected by double layer interactions -a positively charged HFO surface interacting physically with negatively charged silicate ions.

The data in Figures 7 and 8 show the relationship between silicate adsorption and pH. It is clearly shown, as expected, that maximum Si adsorption took place near the pH

reflecting the pK_a of silicic acid. This pH of maximum silicate adsorption was more apparent in HFO-2 than in HFO-1.

Figure 7. Silicate adsorption isotherms of hydrous iron oxide 1 (HFO-1) under various pH values.

One would expect that the apparent strong surface interactions of silicate and iron oxide would have an influence on the surface charge properties of HFO. The data in

Figure 8. Surface coverage of hydrous iron oxide 2 (HFO-2) by silicate as a function of pH.

Figures 9 and 10 show that there is a linear relationship between pH_{zpc} and Si/Fe ratio on HFO.

Figure 9. Relationship between Si/Fe ratio on the surface of hydrous iron oxide 1 (HFO-1) and the surface's zero point of charge (pH_{zpc}).

Figure 10. Relationship between Si/Fe ratio on the surface of hydrous iron oxide 2 (HFO-2) and the surface's zero point of charge (pH_{zpc}).

This signifies that the pH_{zpc} of the HFO decreases as expected as adsorbed silica increases (Stoop, 1980). The decrease in pH_{zpc} was greater for HFO-2 than HFO-1. This greater decrease in pH_{zpc} for HFO-2 also suggests that in this case the Si-HFO interactions are stronger. However, adsorbed silica did not change the crystallinity of

HFO. These can be deduced from the similarities of the x-ray diffractograms, compare Figure 1 with Figure 11 and Figure 3 with Figure 12.

Figure 11. X-ray diffractogram of hydrous iron oxide 1 (HFO-1) at a surface Si/Fe ratio of 0.018.

Figure 12 X-ray diffractogram of hydrous iron oxide 1 (HFO-1) at a surface Si/Fe ratio of 0.013.

Decomposition of the Si (2p) x-ray photoelectron spectroscopy peak of the silicate-containing HFO are summarized in Table 1. These data show that the two HFOs (HFO-1 and HFO-2) differ in the Fe(2p) peaks, as expected, as well as in the Si(2p) and O peaks. The latter suggests that there are differences in the strength of silicate adsorption by the two HFOs.

Table 1. Average assignments of the Si (2p) and O(1s) x-ray photoelectron spectroscopy peaks of Si-containing HFO.

Sample	Fe (2p)	Si (2p)	O	OH	Si-O
			eV		
HFO-1 (Si/Fe = 0.018)	712.78	100.86	529.9	531.5	533.0
HFO-2 (Si/Fe = 0.013)	713.17	101.71	530.0	531.5	533.0

The FT-IR spectra shown in Figures 13 and 14 reveal that silicate adsorption by HFO takes place in a monodentate fashion.

Figure 13. FT-IR diffuse reflectance spectra of hydrous iron oxide 1 (HFO-1) under different levels of Si surface coverage.

Figure 14. FT-IR diffuse reflectance spectra of hydrous iron oxide 2 (HFO-2) under different levels of Si surface coverage.

The ν_3 vibrations of silicate is represented by a single absorption band. However, these ν_3 vibrations differ between the two HFOs in frequency (940 cm^{-1} for HFO-1 vs. 989 cm^{-1} for HFO-2). The higher frequency for HFO-2 suggests the interactions between silicate and HFO-2 are stronger.

3. Cadmium Adsorption on HFO-Si

Cadmium adsorption by HFO-Si was carried out by mixing 20 mL of HFO or HFO-Si complex suspensions, containing 0.4 mg HFO, with 20 mL of solution containing 0.379 mg L^{-1} Cd and adjusted to varying pH levels in a background electrolyte of 0.1 N NaNO_3 . After a 24 h equilibration, the pH of the suspension was measured, the samples were centrifuged and Cd concentration in the supernatant was analyzed using atomic absorption spectrophotometry, AAS. Equilibration was carried out under a nitrogen (N) gas environment. The amount of Cd adsorbed on the iron oxide was calculated by difference between initial and final (before and after equilibrium) Cd concentration in solution.

The data in Figures 15 and 16 show that the adsorption edge for Cd was affected by adsorbed silicate.

Figure 15. Surface coverage of hydrous iron oxide 1 (HFO-1), with and without silicate, by cadmium (Cd^{2+}) as a function of pH.

Figure 16. Surface coverage of hydrous iron oxide 2 (HFO-2), with and without silicate, by cadmium (Cd^{2+}) as a function of pH.

This Cd adsorption edge was more affected in HFO-2 than in HFO-1 which suggests also that silicate adsorption was stronger in HFO-2 than in HFO-1.

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