

Title: A Silica/Fly Ash Based Technology for Controlling Pyrite Oxidation DATE:

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OBJECTIVE: The objective of this project is to develop methodology for applying silica coatings, using metasilicate and/or fly ash, on the surface of pyrite for passively inhibiting pyrite oxidation. The principal thrust of the project is to understand the surface chemistry of pyrite with respect to bicarbonate pyrite surface complexes and their role in enhancing the rate of pyrite oxidation abiotically and how one may use such knowledge to induce formation of silicate coatings on the surface of pyrite. Surface chemistry of pyrite will be studied employing FT-IR spectroscopy while coating application methods would involve miscible displacement techniques using pyrite films and pyrite leaching columns of various sizes in the laboratory and in the greenhouse.

WORK DONE AND CONCLUSIONS:

- An accepted mechanism explaining enhancement of nonmicrobial pyrite oxidation in high pH environments is OH^- involvement in an inner-sphere electron transfer process. In this process, an OH^- and an electron are exchanged simultaneously between pyrite surface- $\text{Fe(III)} (\text{OH})_n^{n-3}$ and pyrite surface disulfide. This study was carried out to elucidate the potential role of $\text{CO}_2/\text{CO}_3^{2-}$ on nonmicrobial pyrite oxidation. FT-IR spectroscopic evidence demonstrated that pyrite exposed to humidified CO_2 plus O_2 formed pyrite surface- HCO_3^- complexes.
- A study was carried out to elucidate the potential role of HCO_3^- on pyrite oxidation. Evidence obtained from our previous studies, using FT-IR spectroscopy, demonstrated that pyrite exposed to humidified CO_2 plus O_2 formed pyrite surface- $\text{Fe(II)}-\text{HCO}_3^-$ complexes. Based on the above results, it was postulated that HCO_3^- , having the potential to form pyrite surface $\text{Fe(II)}-\text{HCO}_3^-$ complexes, would promote abiotic pyrite oxidation by accelerating oxidation of Fe(II) . Ferric iron (Fe(III)) would oxidize the disulfide ($-\text{S}_2$) by accepting its electrons. Using a miscible displacement technique, oxidation of FeS_2 with H_2O_2 was carried out in the absence or presence of NaHCO_3 . The data showed that NaHCO_3 increased significantly the oxidation rate of FeS_2 .
- The feasibility of controlling pyrite oxidation by creating a ferric hydroxide-silica coating that would prevent either O_2 or Fe^{3+} from further oxidizing pyrite was investigated in bench-scale studies. 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. Ferric hydroxide-silica coating formation involved leaching pyrite at room temperature with a solution containing H_2O_2 , NaOAc , and soluble silicate. It was postulated 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-silica coating on the surface of pyrite was induced and inhibited pyrite oxidation under acid conditions. Long-term field-column studies are presently underway to examine the durability of such coatings.

- Pyrite microencapsulation by silicate, a novel approach for controlling acid mine drainage (AMD) production, is currently under development in our laboratory. Although under laboratory conditions these approaches have been shown to be effective, testing under natural conditions for possible field application is necessary. An outdoor leaching column experiment is currently under observation to evaluate the effects of both conventional and microencapsulation approaches for controlling pyrite oxidation. The experiment consists of control, limestone, and silicate treatments on mine spoil samples contained in polyvinyl chloride leaching columns (18" high and 6" in diameter) and set up in the field. Preliminary results indicate that, after a fourteen month period in the field, application of silicate coatings significantly reduced pyrite oxidation. Among the approaches tested, the silica coatings seemed to be superior. However, long term meticulous monitoring and evaluation are needed.

SIGNIFICANCE TO FOSSIL ENERGY PROGRAM: DOE is currently sponsoring research on clean fossil energy focussed on the development of economically viable technologies in controlling oxidation of pyrite and acid mine drainage production. Currently, there are no technologies available to ensure that no acid mine drainage production would take effect in mining sites containing pyritic geologic waste. The current project is directed at understanding the mechanisms by which alkaline substances, used to treat acid mine drainage, could accelerate pyrite oxidation and how we may develop pyrite microencapsulation technologies using silicate and/or fly ash to actually slow down the pyrite oxidation process.

PLANS FOR THE COMING YEAR:

- Investigations on the effect of oxidants on pyrite silica-oxide coating.
- Investigations on the use of fly ash to induce pyrite coatings.
- Investigations on stability of pyrite coatings and effectiveness.

II. HIGHLIGHT ACCOMPLISHMENTS

- Spectroscopic studies revealed the mechanisms by which carbonate/bicarbonate complexes are forming on the surface of pyrite.
- Wet chemistry evidence have been produced showing that carbonate/bicarbonate complexes forming on the pyrite surface catalyze its oxidation.
- Bench scale procedures have been developed to coat pyrite with silicate.
- Bench scale studies have shown that silicate coatings inhibit pyrite oxidation passively.
- Spectroscopic and wet chemistry studies have shown that the pyrite coating is composed of an iron oxide layer containing physically adsorbed silicate ions on its surface.

III. ARTICLES AND PRESENTATIONS

- Evangelou, V. P., A. K. Seta and L. M. McDonald. 1996. Acid mine drainage: Chemistry, Prediction, and Control. Encyclopedia of Environmental Analysis and Remediation. John Wiley & Sons, Inc., New York. In Press.
- Evangelou, V. P., M. Vandiviere and M. Chappel. 1996. Remediation of acid drainage through surface coating of iron sulfides. III Brazilian Symposium on Rehabilitation of Degraded Lands (III Sinrad), May 18 to 23, 1997, Minas Gerais State.
- Seta, A. K., and V. P. Evangelou. 1996. Pyrite microencapsulation: Potential for abatement of acid mine drainage. In Proceedings of 13th annual Am. Soc. Surface Mining and Reclamation, Knoxville, TN, May 18, 1996.
- Seta, A. K., and V. P. Evangelou. 1997. Influence of bicarbonate on pyrite oxidation rates. Under internal review. To be submitted to J. Geoch. Explor.
- Seta, A. K., and V. P. Evangelou. 1997. FT-IR evidence of bicarbonate-pyrite surface complex formation: Implication on rate of oxidation. Under internal review. To be submitted to J. Geoch. Explor.
- Evangelou, V. P., A. K. Seta. 1997. Infrared spectroscopic and wet chemistry evidence on HCO₃ catalyzing pyrite oxidation. American Chemical Society, Geochemistry Division, meetings, San Francisco, Ca. April 13-17.

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