

Effects of Siderophore on Pyrite Oxidation

ELIZABETH B. CERKEZ¹, KAITLYN G. DUTTON¹, MARK A. KUKULA¹, ANN M. VALENTINE¹, AND DANIEL R. STRONGIN¹

¹Temple University, Department of Chemistry, Philadelphia, PA, USA

The oxidative dissolution of pyrite in water is a main contributor to the production of acid mine drainage (AMD). Oxidation of the mineral by ferric iron (Fe(III)) or dissolved oxygen (O₂) results in formation of ferrous iron (Fe(II)), sulfate, and protons. If the produced Fe(II) is reoxidized by dissolved O₂ then the primary oxidizing agent is reproduced, generating a cycle, where a significant amount of protons are produced per unit of pyrite oxidized. Thus, the oxidative dissolution of pyrite could be expected to be regulated by the removal/sequestration of Fe(II) and Fe(III) species.

In this work we demonstrate that the presence of iron chelating siderophores during pyrite oxidation limits both the rate and overall dissolution of pyrite under oxic and anoxic conditions over a wide range of pH. In particular, under oxic conditions we observe a 45-78% decrease in oxidation rate when the siderophore, desferrioxamine B (DFOB) is present, with an increasing effect as the pH is raised. Similarly, under anoxic conditions, we observe a 80-93% decrease in oxidation rate when DFOB is present. Furthermore, the use of a second siderophore, enterobactin, results in 86-94% decrease in oxidation rate at pH 8. We attribute the pH effect to the increase in binding affinity of the siderophore to Fe(III) and Fe(II) as the pH increases. Experimental results also show that pyrite exposed to DFOB and then introduced into a siderophore-free solution shows a decreased rate of oxidation in both anoxic and oxic waters. This experimental observation is attributed to the removal of Fe(III) species from the mineral surface during the DFOB pretreatment.

Analysis of the surface interaction between pyrite and DFOB was carried out using attenuated total reflectance Fourier transform infrared spectroscopy. Exposure of DFOB to an oxidized pyrite film shows vibrational modes indicative of DFOB-Fe(III) chelation, while the exposure of DFOB to a pristine pyrite film displays vibrational modes indicative of the unchelated DFOB moiety.

We conclude that the presence of siderophores both effectively clean Fe(III) impurities from the pyrite surface, preventing reaction initiation, and further chelates aqueous Fe(III) or Fe(II), which slows the overall rate of pyrite oxidative dissolution.