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Pyrite Surfaces – What a Difference a Day Makes

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The development of a new *in situ* cell to perform X-Ray Reflectivity experiments under electrochemical control has illuminated our understanding of pyrite surface oxidation. Because of the industrial (iron source) and environmental (acid mine drainage) importance of pyrite many studies relating to its surface reactivity have been made. Although much progress has been made, much is still unknown about the fundamental mechanisms involved in the oxidative dissolution/ decomposition of pyrite[1,2,3]. Overall reactions for the oxidative dissolution/ decomposition of pyrite in acid solution (Equation 1), where sulphate and soluble metal ions are produced, and at higher pH (Equation 2), where sulphate and iron oxides are produced are shown below.

(1) $FeS_2 + 8H_2O = Fe^{2+} + 2SO_4^{2-} + 16H^+ + 14e^-$

(2) $2FeS_2 + 19H_2O = Fe_2O_3 + 4SO_4^{2-} + 38H^+ + 30e^-$

The complexity of pyrite oxidation is immediately obvious from the above equations and involves several steps with sulphur in intermediate oxidation states between -2 and +6.

Electrochemistry allows us control over the oxidation reaction[3]. X-ray reflectivity studies allow us to measure changes in surface roughness, layer thickness, interfacial roughness and layer density with a great degree of sensitivity[4,5]. The work presented here is preliminary data from a study combining X-ray reflectivity, electrochemistry, fluid analysis (ICP-OES), Atomic Force and Scanning Electron Microscopies to investigate the surface oxidation of pyrite under conditions analogous to low temperature natural aqueous fluids.

It is well known that pyrite spontaneously oxidises in air. Development of this oxidised layer has been monitored via X-ray reflectivity. Figure 1 shows three reflectivity curves, from pyrite samples exposed to air for 10 minutes, 1 day and a week. The data shows that an apparently homogeneous oxidised layer between 50 and 70 Angstroms thick builds up over a weeks time.

To control the potential at the pyrite surface during reaction, the mineral is formed into a working electrode, with the pyrite surface polished. It has been found, from analysis of reflectivity data, that siton polishing of the pyrite surface produces a surface which is not compositionally representative of bulk pyrite. A layer which is less than 10 Angstroms in depth, and is of a higher density than pyrite (1.4 - 2 x ρ pyrite), is found at the surface. However, this layer does not appear to impede reaction at the pyrite surface/near surface.

In and *ex-situ* electrochemical reflectivity experiments were carried out at Daresbury Laboratory using siton polished pyrite as a working electrode, Ag/AgCl reference electrode, Pt counter electrode and a pH 6, 0.1M $NaNO_3$ electrolyte solution. All cell voltages quoted are versus the Ag/AgCl reference electrode.

When pyrite was exposed to a low overpotential (- 0.095V, 15 mins, + 2.9mC), a small quantity (0.05μM, ICP-OES) of sulphur was lost to solution. However, only trace (approx. 0.001 μM, ICP-OES) iron was lost. It is suggested that only sulphur is lost because the overpotential applied to the pyrite surface is insufficient to oxidise iron. Reflectivity curves suggest little change to the pyrite surface in terms of surface roughness during this reaction.

When higher overpotential is applied to the pyrite (+ 400mV, 20s) oxidation is more pervasive (+ 365mC). The extent of this oxidation reaction has three effects. Firstly at this overpotential iron is oxidised in addition to sulphur, although this is not stoichiometric (S/Fe 3.9, ICP-OES). Secondly the pH of the electrolyte solution is decreased due to oxidation reactions producing protons (see equations 1 and 2). Finally reflectivity data shows that the pyrite surface roughens considerably. On application of a further overpotential (+400mV, 20s) these trends continue with pervasive oxidation (1.6ºC), release of both sulphur and iron to solution (S/Fe 2.9, ICP-OES), decreased solution pH and increased surface roughening. By this stage the pyrite surface is covered with micron sized regions depleted in sulphur. Chemically this is evident in SEM back-scattered images of the sample after reaction, and topographically in AFM images of the same. In this case electrochemical oxidation is not homogenous unlike the previous example of air oxidation.

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