Adsorption of Humic Acid onto Alumina: Conformational Changes

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Natural organic matter is a key component of both soils and sediments that is likely to be associated with mineral matter. Natural organic matter - mineral complexes typically represent more than 50% of the organic carbon in a soil and typically more than 70% of the OC in unlithified sediments. The behavior of NOM in the environment is affected by their interactions with minerals due to their possible fractionation and conformational changes. The objective of this study was to investigate these conformational changes and the mechanisms that produce them. The adsorption isotherms of a humic acid as well as its non-amphiphilic and amphiphilic components, onto alumina were determined. The adsorbed and remaining humic acid in solution at both low and high concentration was characterized by solid state NMR and UV spectroscopy. Data suggested that preferential sorption and changes in the mobility of aromatic carbon occur upon adsorption and these changes vary with concentration. Analysis of the data for the amphiphilic fraction of humic acid suggested that surfactant character plays an important role in the adsorption selectivity and conformational changes that occur upon adsorption onto alumina.

Electrochemical study of pyrite oxidation in oxygen-bearing solutions

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Pyrite (FeS_2) is the most common disulfide mineral. [1,2] Oxidation of FeS_2 in presence of dissolved oxygen results in the release of sulfuric acid and toxic trace metals in acid mine drainage, which is one of the most serious environmental problems. Inspite of this importance, the kinetics and mechanism of electron transfer from pyrite to oxidants are poorly understood. The aim of this study was to investigate the kinetics of FeS_2 interaction with dissolved oxygen using electrochemical techniques.

Electrochemical experiments were performed in a conventional three-electrodes electrochemical cell with a Pt counter electrode and saturated calomel reference electrode. The electrochemical parameters (exchange currents densities, charge transfer resistances, etc) of pyrite oxidation in air-saturated HCl solutions were measured as a function of pH (1.0 to 5.0) at temperatures from 25 to 40°C.

Preliminary analysis of the experimental data indicated that temperature has a notable effect on the rate of pyrite oxidation by dissolved O_2. The values obtained for activation energy decrease from 69 kJ mol^{-1} (at pH 5.0) to 33 kJ mol^{-1} (at pH 1.0), suggesting that pyrite oxidation is controlled by surface reaction at high initial pH, with diffusion of reactants and reaction products between surface and solutions gradually becoming rate-limiting at lower initial pH. The reaction order with respect to $[H^+]$ shows a small decrease from 0.15 at 25°C to 0.09 at 40°C. This variation can be attributed to the decrease of oxygen solubility at greater temperature.

Another important observation is that for oxidation by dissolved oxygen under similar experimental conditions (initial pH and temperature) the exchange currents densities (i_0) measured for pyrite are lower than those measured for iron monosulfide (FeS). For example, at initial pH 3.5 and 30°C temperature, i_0 of FeS oxidation is $1.19 \cdot 10^{-5}$ cm^{-1}, and i_0 of FeS_2 oxidation is $1.48 \cdot 10^{-6}$ cm^{-1}.

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