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Nucleation and growth of iron oxyhydroxide nanoparticles from solution: An *in situ* time-resolved Small Angle X-ray Scattering (SAXS) study

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Introduction

Poorly crystalline ferric (oxy)hydroxide nanoparticles (1-20 nm) occur ubiquitously throughout the near-earth surface environment, either suspended in groundwater or as a coating on mineral grains. The sorption and incorporation of trace elements, including pollutants (e.g. As^{5+}), from solution by these particles control their transport and bioavailability in many natural environments including acid mine drainage and contaminated land sites.

In this study we have used time-resolved Small Angle X-ray Scattering (SAXS) in conjunction with a rapid mixing stopped-flow cell to study, *in situ*, the formation of poorly-ordered ferric oxyhydroxide. The rates and mechanisms of particle formation were studied during the oxidative hydrolysis of a 0.1M Fe^{2+}-solution in the pH range 3-4.5 with or without 2.5mM phosphate present. Experiments were performed on station 6.2 of the Synchrotron Radiation Source (SRS), Daresbury laboratory.

Results and Discussion

Analysis of the SAXS data indicates that at pH 3-4.5 the initial precipitate consists of approximately spherical particles <5nm in size. The particle radii increase from ≈8Å to ≈20Å during the precipitation process (Fig 1). Reaction rate increases with increasing pH, but decreases when phosphate is present.

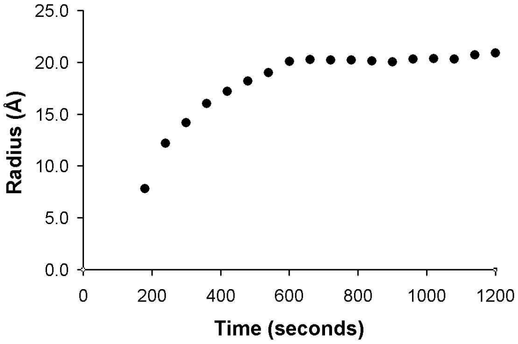

Figure 1. Particle radius as a function of time for iron oxyhydroxide formed at pH 3.

2.3.13

Combined infrared and potentiometric titrations of mineral suspensions

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Thermodynamic stabilities and rate laws derived from classical adsorption experiments suffer due to a lack of specific information about the manner in which the ligand or metal is bound to the surface. For this reason, geo and environmental scientists turn to spectroscopy to more accurately predict the fate of heavy metals, pesticides, radionuclides, and chemical warfare agents.

For many years, our laboratory supplemented careful potentiometric titrations with independent infrared spectroscopic measurements. The potentiometric titrations resulted in stoichiometric and thermodynamic information about ligand-mineral complexes. The infrared spectroscopy, while providing valuable structural information about the complexes, only resulted in semi-quantitative data that could verify the thermodynamic results from the potentiometry.

Now, we have bridged the gap between these two techniques by developing an *in situ* method for simultaneous potentiometric and infrared spectroscopic titrations of mineral suspensions. With this method, the infrared spectroscopy provides fully quantitative information about the concentrations of surface complexes, and this can be used to compute formation equlibria.

First, a mineral overlayer is deposited onto the surface of an internal-reflection element of a flow-through attenuated-total-reflectance (ATR) cell. Next, a potentiometric titration of a suspension of the mineral is performed, and this solution is continuously pumped through the ATR cell and over the mineral overlayer. With each addition of titrant, both the solution pH and the infrared spectrum at the aqueous-mineral interface are recorded. Finally, the accumulated data are evaluated using a factor analysis in which the spectra are fit according to a Surface Complexation Model comprised of the equilibrium, mass-balance, and surface-charge relations that describe the reactions in solution and at the mineral surface. The spectra of the surface complexes are isolated, and their stoichiometries and formation constants are determined.

Here, we describe this method in more detail. We also present the results of the application of this method to several systems of geochemical interest.