



	Experiment title: Electrochemical and geochemical controls on the formation of mixed valent Fe(II,III) phases generated by Fe(0) electrocoagulation	Experiment number: 26-01-1083
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Report:

1) Objectives. The objective of this experiment (26-01-1083) was to determine the (electro)chemical controls on the formation of mixed valent Fe(II,III) oxides generated by Fe(0) electrocoagulation (EC), which is a low cost water treatment technology based on the electrolytic dissolution of Fe(0) electrodes. To this end, we collected Fe K-edge XANES and EXAFS spectra of reference minerals and a matrix of over 30 experimental samples that were produced by adjusting systematically a number of key EC operating parameters and solution variables. We generated 3 mM solid Fe (oxyhydr)oxide precipitates in Fe(0) EC experiments at a range of applied currents that correspond to iron(II) production rates (IPR) of 30 to 300 $\mu\text{M min}^{-1}$. Precipitates were also generated in both NaCl and NaHCO₃ solutions at a range of pH values from 7 to 10. Finally, to isolate the effect of the IPR and dissolved oxygen (DO) on mineral formation, we examined two systems: i) a controlled system where the DO was held constant over a range from 0.1 - 3.0 mg L⁻¹, and ii) an uncontrolled (open) system where the DO was allowed to drift. Although high-quality XAS data for the complete data set were collected without difficulty, we only report data for open system experiments in this document because of space constraints.

2) Methods. Fe K-edge XAS data (XANES and EXAFS) of filtered suspensions were recorded at room temperature in transmission mode out to k of 13.5 \AA^{-1} at the DUBBLE beamline (BM26A). The X-ray beam diameter was 1 (vert) x 3 (horz) mm and the beam was detuned 30%. The XANES region was measured with 0.35 eV steps, whereas step sizes of 0.05 \AA^{-1} were used for the EXAFS region. Two to 4 scans were collected for each sample or reference compound. An important consideration in our experiments was the sensitivity of

samples to atmospheric O₂ during data collection. However, our sample preservation method to eliminate artifacts due to oxidation during the experiment was confirmed by the identical spectrum of a green rust reference mineral measured at the start and end of the experiment. Data reduction was performed with the SixPack software and the EXAFS spectra were extracted using k³-weighting. The major and minor Fe phases formed in each experiment were quantified by principal component analysis (PCA) and iterative transformation factor analysis (ITFA) of the Fe K-edge EXAFS spectra using the ITFA program suite.

3) Results and Conclusions. Figure 1 shows the ITFA output for the EXAFS spectra of samples produced in open system experiments (chloride and carbonate solutions, pH 7 and 10). These spectra and ITFA output are representative of the data and modelling quality obtained for the controlled system experiments. Based on our results, we found that a narrow range of DO separates the domains of Fe(III) and Fe(II,III) oxide formation. In NaCl solutions at all tested pH in the controlled system (data not shown), magnetite formed at DO = 0.3 mg L⁻¹ and was the dominant Fe phase at DO = 0.1 mg L⁻¹. In NaHCO₃ solutions in the controlled system, a similar dependency on DO was observed, but carbonate green rust (GR-CO₃) formed instead of magnetite. Another interesting trend revealed by our data was that increasing pH from 7 to 10 lead to a systematic decrease in the concentration of lepidocrocite in favor of disordered hydrous ferric oxide (HFO), regardless of background electrolyte and DO concentration (Figure 1). Notably, the IPR did not impact the identity of the solid phase in the controlled DO system. However, in open system experiments, we found that the IPR was critical to the formation of Fe(II,III) oxides (Figure 1). Pure Fe(II,III) phases formed only at the highest IPR (10-fold greater than the DO replenishment rate), which resulted in rapid DO depletion. In general, our results suggest that the formation of Fe(II,III) oxides by Fe(0) EC hinges on maintaining DO < 0.3 mg L⁻¹, which can be achieved by increasing the IPR and minimizing air-water exchange during electrolysis.

4) Future Experiments. Having determined the formation conditions of Fe(II,III) oxides produced by Fe(0) EC, we will next use As K-edge XAS to evaluate the redox behavior and uptake mechanism of arsenic during coprecipitation with EC-generated GR-CO₃ and magnetite. These experiments are scheduled for 28 April, 2017 at BM26A (Proposal 26-01-1104).

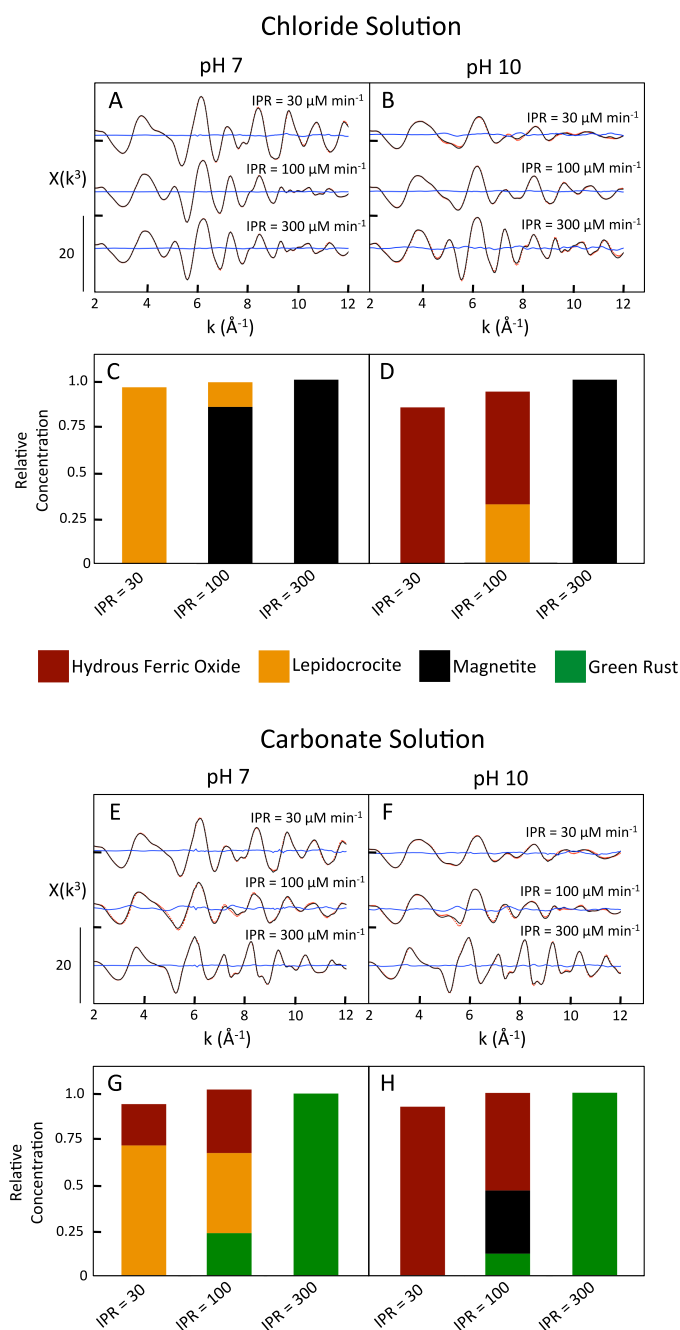


Figure 1: Fe K-edge EXAFS spectra (A, B, E, F) and ITFA-derived composition (C, D, G, H) of EC precipitates produced at different IPRs in chloride (top panels) and carbonate (bottom panels) solutions at pH 7 (left) and 10 (right). In A, B, E, and F, the black, red, and blue lines represent the data, reconstructed spectra, and residual, respectively. In C, D, G, and H, the green, black, yellow, and red columns represent CO₃-GR, magnetite, lepidocrocite and hydrous ferric oxide, respectively.