Controls on the formation of Fe(II,III) (hydr)oxides generated by Fe(0) electrolysis

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The formation pathways of Fe(II,III) (hydr)oxides, such as magnetite and green rust, have been extensively studied because of their unique properties (e.g. magnetic ordering, redox and sorption reactivity). These minerals can be formed by application of an electric current to Fe(0) metal, which generates Fe(II) at a rate proportional to the current. This method, called Fe(0) electrocoagulation (EC), has been proposed for low cost arsenic treatment. By selectively producing Fe(II,III) (hydr)oxides, Fe(0) EC could exploit their unique reactivity (e.g. multinuclear arsenic retention modes, magnetic particle separation) to substantially improve treatment. However, the Fe(II,III) (hydr)oxide formation conditions, with respect to EC operating parameters and solution composition, are unknown.

In this presentation, we elucidate the (electro)chemical controls on the formation of Fe(II,III) (hydr)oxides produced by Fe(0) EC. We generated Fe(II,III) (hydr)oxides (3 mM total Fe) at a range of iron(II) production rates (IPR, 30 to 300 µM min^{-1}) in solutions with a range of composition (10 mM NaCl or $NaHCO_3$; pH 7-10). The impact of dissolved oxygen (DO) was evaluated by performing experiments where DO was held constant from 0.1 to 3.0 mg L^{-1} (controlled system) and where DO was allowed to drift (open system). The major and minor solid phases were quantified by iterative transformation factor analysis of Fe K-edge EXAFS spectra.

Our results show that a narrow DO range separates the Fe(II,III) (hydr)oxide and Fe(III) (hydr)oxide domains. In NaCl solutions at all tested pH, magnetite formed at DO = 0.3 mg L^{-1} and was the dominant Fe phase at DO = 0.1 mg L^{-1}. In $NaHCO_3$ solutions, a similar dependence on DO was observed but carbonate green rust formed instead of magnetite. Pure Fe(II,III) phases formed only in open system experiments at the highest IPR (10-fold greater than the DO replenishment rate), which resulted in rapid DO depletion. 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.