![ESRF logo]	**Experiment title:** Influence of common groundwater oxyanions on the structure and arsenic sorption reactivity of Fe(II,III) oxides generated by Fe(0) electrocoagulation	**Experiment number**: 26-01-1122
Beamline: BM26A	**Date of experiment**: from: 26 January, 2018 to: 30 January, 2018	**Date of report**: 7 Feb, 2018
Shifts: 12	**Local contact(s)**: Dipanjan Banerjee	*Received at ESRF:*

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Report:

1) Objectives. The objective of this experiment (26-01-1122) was to determine the impact of co-occurring oxyanions common in groundwater, i.e. phosphate (P), silicate (Si), and arsenate (As(V)), on the structure of Fe(II,III) oxides generated by Fe(0) electrocoagulation (EC). In our previous work at DUBBLE, we applied Fe K-edge EXAFS to identify the formation conditions of magnetite (Mag), carbonate green rust (GR-CO_3), and lepidocrocite (Lp). In this work, we produced Mag, GR-CO_3 and Lp (3 mM total Fe) using these formation conditions, but modified systematically the electrolyte solution by adding P, Si, or As at concentrations ranging 0.03 to 1 mM, which corresponds to P:Fe, Si:Fe, and As:Fe molar ratios of 0.01 to 0.33. In addition, the impact of 1 mM $MgCl_2$ or $CaCl_2$ was examined in binary electrolyte solutions (i.e. solutions containing both oxyanions and bivalent cations). We collected Fe K-edge XANES and EXAFS spectra for a sample matrix of over 50 experimental conditions. However, in this report, only Fe K-edge EXAFS spectra for a subset of the data set are given. In addition, we note that As K-edge EXAFS data of most of the corresponding As-containing samples have been collected, with plans to finish the As K-edge XAS data set later in 2018.

2) Methods. Fe K-edge XAS data (XANES and EXAFS) of filtered suspensions were recorded in transmission mode out to k of 13 Å^{-1} at the DUBBLE beamline (BM26A) of the ESRF. Spectra were recorded at room temperature using ion chambers for measurements of I_0 and I_t. The X-ray beam diameter was 1 (vert) x 8 (horz) mm and the beam was detuned 40%. The XANES region was measured with 0.35 eV steps, whereas step sizes of
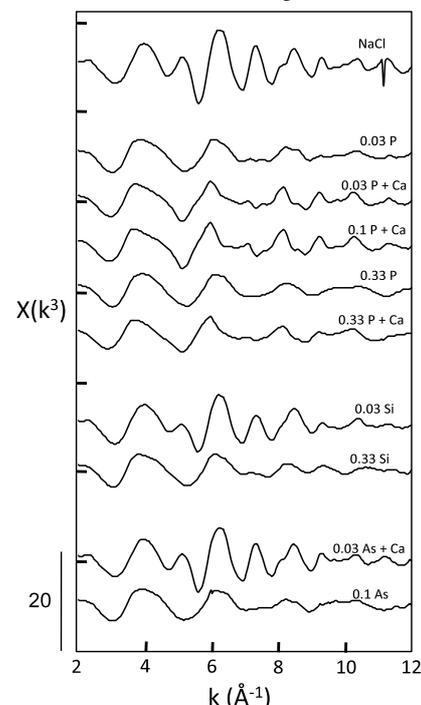

Figure 1: Impact of P, Si, and As(V) on magnetite formation by Fe(0) EC. Samples were produced in NaCl or $CaCl_2$ electrolytes with initial P, Si, or As concentrations equivalent to oxyanion:Fe molar ratios of 0.03, 0.1, and 0.33.

0.05 Å^{-1} were used for the EXAFS region. Two to 6 scans were collected for each sample. Data reduction and analysis was performed with the SixPack software. Shell-by-shell fits of experimental samples were performed by varying the coordination number (*CN*), change in threshold energy (*ΔE$_0$*), interatomic distance (*R*), and the mean squared displacement parameter (*σ^2*) in each fit.

3) Results and Conclusions. Figure 1 shows the impact of P, Si, and As on the solids generated using the EC formation conditions of Mag. The top spectrum was generated in a 10 mM NaCl electrolyte in the absence of oxyanions and bears fingerprints indicative of Mag, including the symmetric first oscillation from 3-4 Å^{-1} and the second distinct oscillation centred near 5 Å^{-1}. By contrast, the presence of P at P:Fe molar ratios ≥ 0.03 completely alters the EXAFS spectrum in favour of a more disordered phase that shares little similarity in the EXAFS line shape and phase relative to that of Mag. The Fourier transformed EXAFS spectra (not shown) of all P series samples, regardless of the presence or absence of CaCl$_2$, indicated the presence of a single Fe-Fe path in the second shell, which is also inconsistent with the structure of Mag. Interestingly, shell-by-shell fits of the P series samples revealed a local Fe coordination environment consistent with GR, which has a theoretical CN_{Fe-Fe} = 6 and R_{Fe-Fe} = 3.17 Å based on the crystal structure. For example, the fit of the 0.03P+Ca sample yielded R_{Fe-Fe} = 3.18 ± 0.02 Å (CN_{Fe-Fe} = 1.7 ± 0.8). Therefore, we conclude that the presence of P at P:Fe ratios as low as 0.03 inhibits the formation of Mag by Fe(0) EC in favour of a poorly ordered GR phase, which is consistent with the bluish colour of these solids. By contrast, Figure 1 shows that the presence of Si and As at molar ratios of 0.03 did not inhibit Mag formation. At Si:Fe and As:Fe above 0.1, the EXAFS spectra resembled that of the high P samples, which suggests the formation of a similar poorly ordered oligomeric arrangement of Fe(II) and Fe(III) polyhedra at high oxyanion:Fe ratios.

Figure 2 shows the influence of P at P:Fe ratios of 0.03 and 0.33 on the solids formed under conditions that lead to Lp (10 mM NaCl and low iron production rate, IPR), Mag (10 mM NaCl, high IPR), and GR-CO$_3$ (2 mM NaHCO$_3$, high IPR). The formation of Mag was most significantly impacted by P, with nearly complete inhibition of Mag at P:Fe of 0.03. By contrast, the EXAFS spectra of solids produced at P:Fe of 0.03 under conditions leading to GR-CO$_3$ maintained features consistent of GR-CO$_3$. In addition, features of Lp were still observed in the EXAFS spectrum of solids produced at P:Fe = 0.1. These results indicate that the formation of Mag by Fe(0) EC is more sensitive to P than GR-CO$_3$ and Lp, which can be explained by the different crystal morphologies and structures of these minerals: Mag forms dense cubic crystals, whereas GR and Lp are layer type minerals.

4) Future Experiments. Both Mag and GR are likely unstable in the presence of dissolved oxygen, but the timescales of mineral transformation for each phase is expected to vary. In the next stage of this research, we will examine the structural transformations of Mag and GR during aging in aerobic and anaerobic environments over hour, day, week, and month timescales. We will submit a proposal to DUBBLE in April, 2018 to collect As and Fe K-edge XAS data probing the transformation products and fate of As during aging of EC-generated Mag and GR.
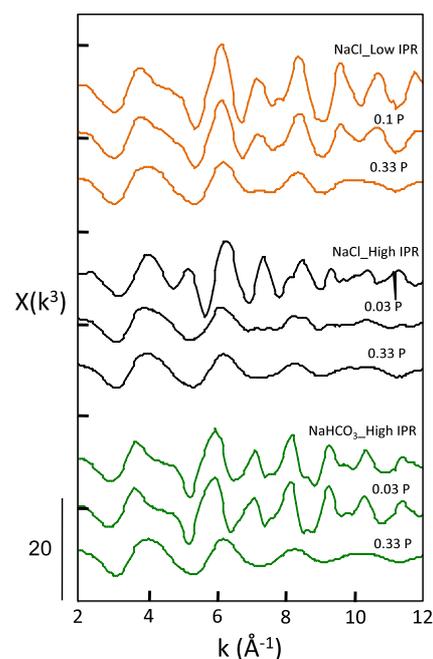

Figure 2: Fe K-edge EXAFS spectra showing the influence of co-occurring P on the solids generated using the EC formation conditions of Lp (orange), Mag (black), and GR-CO$_3$ (green).