



	Experiment title: Behaviour of arsenic during the co-precipitation of Fe(II,III) oxides generated by Fe(0) electrocoagulation	Experiment number: 26-01-1104
Beamline: BM26A	Date of experiment: from: 28 April, 2017 to: 2 May, 2017	Date of report: 12 June, 2017
Shifts: 12	Local contact(s): Dipanjan Banerjee	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): Case van Genuchten (PI)*, Utrecht University Simon Mueller*, Utrecht University Thilo Behrends, Utrecht University Peter Kraal, Utrecht University		

Report:

1) Objectives. The objective of this experiment (26-01-1104) was to evaluate the redox behaviour and sorption mechanism of As during the in-situ production of the Fe(II,III) oxides, carbonate green rust (GR-CO₃) and magnetite, generated by Fe(0) electrocoagulation (EC). We obtained As K-edge XANES and EXAFS spectra for a matrix of experimental samples produced by varying key electrochemical and solution parameters, including the Fe(II) production rate, pH and As:Fe ratio. In addition, we collected As K-edge XANES and EXAFS spectra of a suite of As(III) and As(V)-bearing reference minerals and adsorption standards, including As(III) and As(V) adsorbed to GR and magnetite. In our previous DUBBLE experiments (26-01-1083), we used Fe K-edge EXAFS spectroscopy to identify the formation controls of GR-CO₃ and magnetite by Fe(0) EC. Therefore, we generated GR-CO₃ and magnetite samples (3 mM total Fe) following our previous results in the presence of 1125 and 11250 ppb As(III) (initial As:Fe ratios of 0.5 and 5 mol%). In this report, only As K-edge XANES spectra for a subset of reference material and experimental samples are given, but we note that EXAFS spectra for most of the proposed samples were also collected.

2) Methods. As K-edge XAS data (XANES and EXAFS) of filtered suspensions were recorded in fluorescence mode out to k of 13 Å⁻¹ at the DUBBLE beamline (BM26A). Spectra were recorded at 80 °K using a Ge fluorescence detector. 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 Å⁻¹ were used for the EXAFS region. Four to 12 scans were collected for each sample or reference compound, depending on data quality. Data reduction and analysis was performed with the SixPack software. The average oxidation state of As in experimental samples was quantified by performing linear

combination fits (LCFs) of the As K-edge XANES spectra using the XANES spectra of As(III) and As(V) adsorption references.

3) Results and Conclusions. Figure 1 shows the XANES spectra of As(III) and As(V) adsorption standards (A) and experimental samples (B and C). For each experimental sample, the As(III) and As(V) fractions derived by LCFs are given. In addition, the residual As concentration in solution at the end of the reaction is also shown. Comparison of the LCF-derived As fractions among experimental samples reveals a number of important trends. Regardless of the solid phase produced, increasing solution pH from 7 to 9 increased the extent of As(III) oxidation. Furthermore, for a given As:Fe ratio, the production of purely Fe(III) precipitates (orange spectra in Fig. 1C) resulted in greater As(III) oxidation than Fe(II,III) oxides (green spectra in Fig. 1C). Both of these trends are consistent with the competition between Fe(II) and As(III) for the reactive oxidants produced during Fe(0) EC treatment. Comparing the As K-edge XANES spectra of GR-CO₃ and magnetite samples (green and black spectra in Fig. 1B) shows that slightly more As(III) oxidation occurs during GR-CO₃ formation. However, more importantly, the As K-edge XANES spectra for the magnetite samples display major post-edge oscillations near 11880 and 11892 eV (highlighted by the arrows in Fig. 1B), which are absent in all other experimental or reference XANES spectra. These differences indicate significant changes in the As coordination environment when As is present during the formation magnetite relative to GR-CO₃ or Fe(III) precipitates. The post-edge XANES features in the magnetite samples are consistent with As incorporation into the structure of magnetite, likely by substitution for tetrahedral Fe.

4) Future Experiments. Based on these results, we plan to investigate the stability of As co-precipitated with magnetite, GR-CO₃ and Fe(III) precipitates by performing sequential chemical extractions on the solid phase using NaCl, PO₄³⁻ and citric acid. In addition, a proposal was submitted to DUBBLE in April, 2017 to evaluate the impact of common groundwater ions, including PO₄³⁻ and SiO₄⁴⁻, on the structure and As sorption reactivity of EC-generated magnetite and GR-CO₃ (Fe and As K-edge XAS).

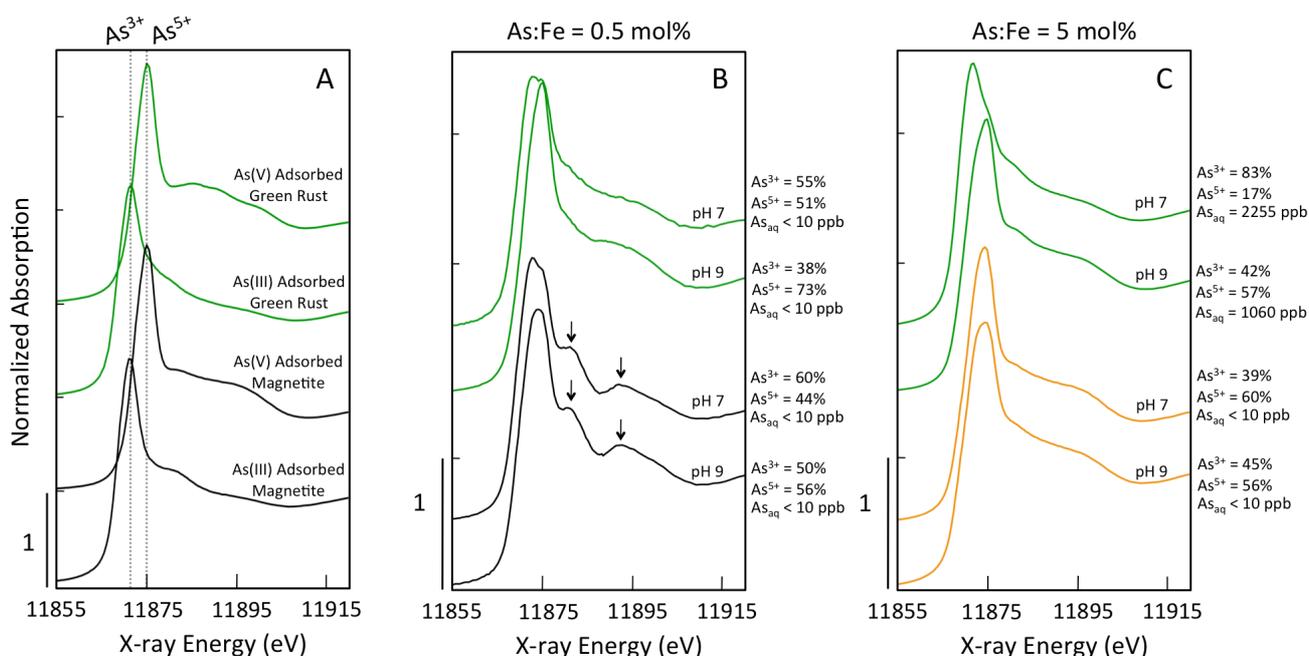


Figure 1: As K-edge XANES spectra of (A) As(III) and As(V) adsorption references, and experimental samples generated at As:Fe ratios of (B) 0.5 mol% and (C) 5 mol%. The XANES spectra in black, green and orange represent solid phases of magnetite, GR-CO₃ and Fe(III) precipitates, respectively.