

Mapping arsenic-induced changes on the green rust surface at the nanoscale

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Green rust (GR) phases consist of Fe^I-Fe^{III} hydroxide sheets with hydrated interlayer anions (e.g., Cl⁻, CO₃²⁻, SO₄²⁻). Due to their nanoparticulate nature and a zero point of charge around pH 8, they are excellent sorbents for toxic oxyanions such as arsenic (As). We have recently shown that synthetic GR sulfate (GR_{SO4}) has a high sorption capacity for As(III) and As(V), which are among the highest for Fe-bearing mineral phases in subsurface environments [1].

Synchrotron X-ray absorption spectroscopy (XAS) studies have further shown that As(III) and As(V) adsorb to GR surfaces as inner sphere complexes [2-4]. The exact mechanisms for the interaction between As species and GR phases are, however, still poorly understood.

Here, we extend our knowledge of these interactions by mapping the distribution of As(III) and As(V) (500 ppm) reacted with synthetic GR_{SO4} using energy dispersive X-ray (EDX) imaging in the scanning transmission electron microscope (STEM). The STEM-EDX maps showed redox state-dependent As distribution and morphological changes in the GR_{SO4} surfaces. In addition, high energy X-ray diffraction and pair distribution function (PDF) analysis revealed that the initial GR_{SO4} did not transform to other Fe-bearing phases, and XAS analyses of the same samples indicated that both As(III) and As(V) were bound as bidentate, binuclear inner-sphere surface complexes. Overall, these results give new important insights on how As species are sequestered on the surface of GR, and on the potential role of GR phases in controlling the mobility of As in contaminated environments.

References: [1] Perez et al. 2019, *Sci Total Environ*, 648, 1161. [2] Randall et al., *GCA*, 2001, 65(7), 1015. [3] Jönsson et al. 2008, *Chem Geol*, 255(1-2), 173. [4] Wang et al., *ES&T*, 2014, 48, 14282.