

Kinetics of coupled Fe(II)-catalysed ferrihydrite transformation and U(VI) reduction

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The Fe(II) accelerated transformation of ferrihydrite to more crystalline Fe(III) oxides such as goethite has implications for the environmental mobility of uranium and other toxic elements. In this study we used X-ray absorption spectroscopy (XAS) on samples obtained from both batch and real time experiments to measure the kinetics of ferrihydrite transformation to goethite and U(VI) reduction across a range of Fe(II) concentrations.

Linear combination fitting of Fe K-edge Extended X-ray Absorption Fine Structure (EXAFS) and U L(III)-edge X-ray Absorption Near Edge Structure data revealed similar time scales of ferrihydrite transformation and U(VI) reduction to U(V) for each treatment, inversely proportional to Fe(II) concentration. The higher rate of U(VI) reduction by Fe(II) on pure goethite than the ferrihydrite/goethite system suggested that it is the associated enhanced rate of goethite formation, rather than the higher Fe(II) itself that causes faster U reduction. The use of quick-scanning XAS, which allowed the collection of Fe K-edge EXAFS spectral data to $k = 15 \text{ \AA}^{-1}$ in < 1 minute for the real time experiments, provided improvements in experimental efficiency.

As predicted by calculations using the Nernst equation and solubility products of the relevant Fe(III) oxides, the oxidation-reduction potential of the systems also declined on time scales similar to the transformation of ferrihydrite to goethite, further providing evidence for the strong reducing power of Fe(II) associated with goethite and that the presence of goethite is necessary for U(VI) to be reduced.

The effect of Sb(V) on the transformation of ferrihydrite to goethite, hematite, and feroxyhyte

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Antimony is released into the environment in some natural and man-induced processes. [1]. Yet, its impact on the transformation processes of heavy metal-adsorbing minerals remains poorly understood. In acid-mine drainage systems and shooting ranges, the adsorption of antimony by iron oxides such as ferrihydrite can play a major role. The poorly crystalline 2-line ferrihydrite represents one of the most common Fe oxides in these settings and can transform to goethite ($\alpha\text{-FeOOH}$) or hematite ($\alpha\text{-Fe}_2\text{O}_3$) with time [2]. The rate of transformation depends on the pH, temperature, and on the ions and molecules present during the transformation process [3]. This study focuses on the transformation of synthetic ferrihydrite to crystalline iron oxides in the presence of Sb(V). Transformations were carried out for 1-16 days at 70 °C and at pH 4, 7 and 12, with different concentrations of Sb(V) (0.00, 0.23, 0.75, 2.25 and 6.00 mM Sb). Samples taken from aqueous suspensions were washed, dried, and characterized by X-ray diffraction (XRD) and atomic absorption spectroscopy (AAS). At pH 12, goethite (Sb concentrations up to 3.7 mg Sb/g) is favored and the transformation is completed after one day. Only a concentration of 6 mM Sb retarded the transformation, where even after 8 days only 50 % of the ferrihydrite was transformed into goethite. Transformations at pH 7 led to a mixture of 75 % hematite and 25 % goethite (4.3 mg Sb/g). However, at concentrations of 6 mM Sb, feroxyhyte ($\delta\text{-FeOOH}$) (9.1 mg Sb/g) was favored instead. At pH 4, hematite (32.3 mg Sb/g) was favored except for concentrations of 6 mM Sb, where again feroxyhyte (141.1 mg Sb/g) occurred. We assume that increased Sb concentrations favor feroxyhyte and indicate the incorporation of Sb into the structure of feroxyhyte.

- [1] Filella *et al.* (2007) *Earth-Sci Rev* **80**, 195-217. [2] Cudennec & Lecerf (2006) *J Solid State Chem* **179**, 716-722. [3] Cornell (1987) *Pflanzenern Bodenk* **150**, 304-307.