

Speciation of uranyl adsorbed on gibbsite: A time-resolved laser-induced fluorescence spectroscopic study

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This study was carried out to identify spectroscopically-distinct species of uranyl adsorbed on gibbsite and quantify effects of pH and ionic strength variations on them. The technique of Time-Resolved Laser-Induced Fluorescence Spectroscopy (TRLIFS) was employed for that purpose. To improve the resolution of the vibronic lines of uranyl, TRLIFS measurements were carried out in cryogenic conditions. Deconvolution based on evolving factor analysis (EFA) was employed to discern the presence and contributions of non-identical emitters.

EFA showed that three main species contributed to the emission of uranyl. These included two components (referred to as Species A and B) affected by pH only, and an additional species C affected by both pH and ionic strength variations. Species A had the shortest decay time and was predominant at pH < 5.0. The emission of Species B was predominant at pH > 5.0, had a longer decay time and exhibited a red shift. This was interpreted as an indication that Species B was a deprotonated form of Species A. Species A and B were concluded to be bound via inner-sphere complexation. Species C had the longest decay time and apparently was bound via outer-sphere complexation. Because the spectrum of species C exhibited subtle changes at pHs close to the p.z.c. of gibbsite and high ionic strengths, it was concluded that it was likely to represent an envelope for several subspecies whose contributions are determined by both the surface charge and aqueous uranyl speciation.

The results show that TRLIFS of uranyl enhanced by EFA can be employed to probe the nature of uranyl species adsorbed on gibbsite and determine effects of surface and solution chemistries on their predominance. Because the emission spectra of uranyl species present on the surface of gibbsite were different from those on other representative surfaces (for instance, silica), it was concluded that detailed TRLIFS analysis for uranyl adsorbed on more complex environmentally important surfaces, notably aluminosilicates, potentially allows determination of contributions of dissimilar adsorption sites.

Reduction and retention processes within arid subsurface environments

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Introduction

Chromium and technetium are redox active metals that are significant threats to groundwater quality at U.S. Department of Energy sites. The oxidized forms of these metals, chromate [Cr(VI)] and pertechnetate [Tc(VII)], are highly soluble and mobile in the environment, while the reduced forms, Cr(III) and Tc(IV), are relatively insoluble and immobile. Chromate and pertechnetate reduction may be initiated by reduced mineral phases, dissolved Fe(II), sulfide, reduced organic matter or bacteria. Often the only potential reductant of Cr(VI) and Tc(VII) in arid subsurface environments, such as the Hanford Site in eastern Washington, is ferrous-bearing mineral phases. Beneath tank SX-108 at the Hanford Site, ⁹⁹Tc distribution was almost identical to NO₃⁻, while some retardation of Cr was observed (Zachara, 2004).

Results and Discussion

Here we examine Cr(VI) and Tc(VII) reduction by synthetic magnetite and Hanford formation sediments under hydrodynamic conditions. The amount of Cr(VI) reduced by magnetite was dependent on influent concentration. Cr(VI) reduction was only observed when the sediments were pre-treated with 0.5 M HCl, or when the column feed solution contained 10 M NaOH. Micro-X-ray absorption spectroscopy and micro-X-ray diffraction show that Cr(III) is associated with iron rich phyllosilicates, serpentinite minerals, and magnetite. Chromate reduction by Hanford sediments is inhibited by a passivating layer; however, once this layer is removed the sediments are capable of significant chromate reduction. We expect similar results for Tc(VII) reduction by magnetite and Hanford sediments.

Reference

Zachara, J. M.; Smith, S. C.; Szecsody, J. E.; Traina, S. J.; Warner, J. A., *Geochim. Cosmochim.* **2004**, *68*, 13-30.