

Spectroscopic Investigation of Uranyl Surface Species in Amorphous Ferric Oxyhydroxide Gravel

Permeable Reactive Barriers



Yuji Arai† and C. C. Fuller‡

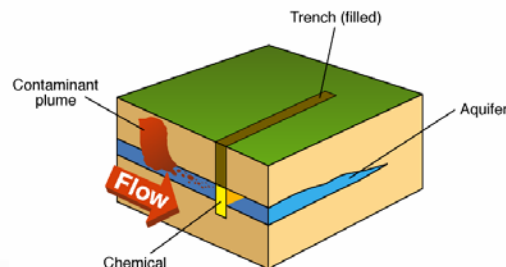


†Dept. of Entomology, Soils and Plant Sciences, Clemson University, Clemson, SC 29634

‡U.S. Geological Survey, Water Resource Division, Menlo Park, CA 94025, USA

Abstract

Understanding the uranium(U) sorption processes in permeable reactive barriers (PRB) is critical in modeling reactive transport for evaluating PRB performance at the Fry Canyon demonstration site in Utah, USA. To gain insight in the U sequestration mechanism in the amorphous ferric oxyhydroxide (AFO) coated gravel PRB where $pCO_2 = 1-2 pCO_2 \%$ and dissolved sulfate $\sim 3.9-18mM$, U(VI) sorption processes on AFO PRB were studied using X-ray Absorption spectroscopy (XAS). The XAS analysis of core materials indicates that no sulfate ligands contributes to the surface speciation of U(VI) sorbed at the AFO-water interface. Instead, a mixture of bis-carbonato inner-sphere and tris-carbonato outer-sphere U(VI) ternary surface species was found in all core samples. The study suggests that the bicarbonate coordination on U(VI) surface species might be important in evaluating the sulfate rich environment in the AFO PRB at the study site.



Schematic diagram of a reactive barrier. (Modified from Morrison and Spangler, 1992)

Objectives

As part of the evaluation of U solid-state speciation in aged field AFO PRB samples, we investigated the effects of sulfate ligand on U surface species in the aged AFO PRB using X-ray Absorption spectroscopy (XAS).

Introduction

The long-term (9 yr) performance of an AFO based PRB has been tested at the Fry Canyon demonstration site in southeastern Utah, USA, the site of an abandoned uranium upgrader operation. Ground water (GW) entering the AFO PRB had dissolved U (as U(VI)) concentrations that ranged from 4 to 130 μM at $pH \sim 7.1$. Evaluating the reaction processes resulting in U sequestration by the AFO PRB, such as determining surface complex species, is critical to development and application of meaningful reaction terms in solute transport models for U at the site. In addition to carbonate alkalinity ($\sim 3.4 mM$), the GW has elevated levels of dissolved sulfate ($\sim 13 mM$) with other chemical components (conc. in mM: Na ~ 8 , Mg ~ 5.4 and Ca ~ 9.3). Sulfate may influence uranyl sorption processes on AFO surfaces via 1) competitive adsorption between sulfate and the anionic U(VI)-carbonato aqueous species and or 2) competitive formation of U(VI)-sulfate/carbonato ternary surface species.

Methods

Five core samples were kept/handled in the argon environment prior to the sectioning processes. The mineralogy of aged AFO PRB is predominantly goethite and AFO. Room temperature U L_{III} edge (17166 eV) fluorescence spectra were collected at beamline 11-2 at Stanford Synchrotron Radiation Laboratory, Menlo Park, CA. The samples were kept under the continuous argon gas purge during the measurements.

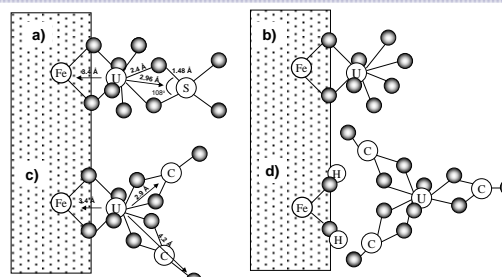


Figure-1: Ball-and-stick representation of some of U(VI) surface species on the iron octahedral structure of ferrihydrite surfaces that are considered in the XAS model. a) Mono-sulfate U(VI) ternary complex via bidentate mononuclear U(V)-O-Fe linkage b) Binary inner-sphere U(VI) surface species via bidentate mononuclear U(V)-O-Fe linkage c) Bis-carbonato U(VI) ternary complex via bidentate mononuclear U(V)-O-Fe linkage d) Tris-carbonato U(VI) outer-sphere complex

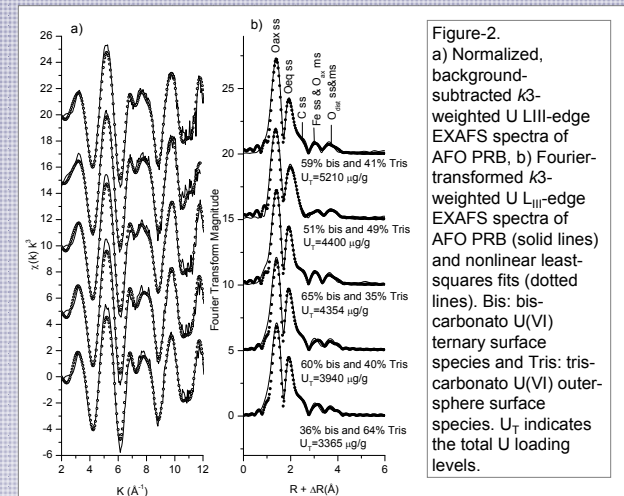


Figure-2. a) Normalized, background-subtracted k^3 -weighted U L_{III} -edge EXAFS spectra of AFO PRB. b) Fourier transformed k^3 -weighted U L_{III} -edge EXAFS spectra of AFO PRB (solid lines) and nonlinear least-squares fits (dotted lines). Bis: bis-carbonato U(VI) ternary surface species and Tris: tris-carbonato U(VI) outer-sphere surface species. U_T indicates the total U loading levels.

Research Findings

As demonstrated in our previous study (Arai et al, 2006), our CN correlated XAS model was used to differentiate the U(VI)-carbonato from U(VI)-sulfate ternary species. $U-O_{dist}$ SS and MS shells were only correlated with carbonato complexes, and were not correlated with U-S SS shell of sulfate ternary and binary species. In this model, we set the "total fraction (f) = 1" as a summation of all fractions of surface species (i.e., $1 = fs + fb + fmono + fbis + ftris$), where mono-sulfate (fs), binary inner-sphere (fb), mono-carbonato ternary ($fmono$), and bis-carbonato ternary ($fbis$), and tris-carbonato outer-sphere surface species ($ftris$). Ball-and-stick representation of some of U(VI) surface species is shown in Figure-1. The results show a mixture of bis-carbonato U(VI) ternary and tris-carbonato U(VI) outer-sphere species (Figure-2). There is no evidence for the sulfate ternary species, suggesting a transition between air and 2% pCO_2 systems where sulfate ternary surface species were no longer important.

References

Arai et al. 2006. 70, 10, 2492-2509. *Geochimica et Cosmochimica Acta*.