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Contaminant Organic Complexes: Their Structure and Energetics in Surface Decontamination

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Forward

The activities reported herein represent the work performed on this research grant subsequent to its transfer to UC Merced from the Ohio State University where Dr. Traina had been a faculty member.

Introduction

The Department of Energy has a goal of decontaminating an estimated 180,000 metric tons of metal wastes in various surplus facilities. Uranium (U) and other radioactive actinides and lanthanides are embedded within the mixed oxide structures of the passivity layers of corroded iron and steel. These toxic metals can be dissolved out of the surface layers by a naturally occurring bacterial siderophore called Desferrioxamine B (DFB). DFB is a trihydroxamate ligand with one amine ($pK_1 = 10.89$) and three hydroxamate groups ($pK_2 = 9.70$, $pK_3 = 9.03$, and $pK_4 = 8.30$), which chelates with metals through hydroxamate coordination. Complexation of DFB with U can be utilized in decontamination strategy of the passivity layers. Therefore, we have been studying reactions of uranyl U(VI) with zerovalent iron (Fe^0) followed by dissolution by DFB. The objectives were to determine the structure and speciation of solution and solid phases of U and to assess the effectiveness of DFB in U dissolution.

Methods:

Uranyl (U(VI)) solutions (10^{-2} to 10^2 M) were reacted with zerovalent iron powder (Fe^0) at variable molal ratio (1 to 10^5), pH (1 to 5), and temperatures (298 and 318 °K). The resulting solids were characterized under the ambient pressure using a soft Scanning Transmission X-ray Microscopic (STXM) technique at the Lawrence Berkeley National Laboratory ALS Beamline 11.0.2. Extended X-ray Absorption Fine Structure (EXAFS) spectroscopy of the L_{III} U was

conducted at the Stanford Synchrotron Radiation Laboratory in order to determine the coordination structure and bonding between U and other atoms. Scanning and Transmission Electron Microscopy were utilized to assess morphology, shape and particle size of Uranium crystallized into the passivity layers. With the goal of ascertaining a possible decontamination pathway, U(VI) solutions were reacted with Fe(0), and a siderophore (DFB) mediated dissolution of the resulting solids were studied. The dissolution studies were conducted by equilibrating the U solids with DFB as a function of pH, molality and temperature.

Results and Discussion:

Reaction of zerovalent iron, Fe(0), with U(VI) resulted in formation of U solids under variable pH and temperature conditions (Figure 1). U in solid phase increased with increasing Fe to U ratio, and nearly 40% of U was converted to solids when reacted with 20 mM Fe. Reaction with 100 mM Fe at pH 5, led to conversion of over 96% of reacting U to solid phase. Solid phase U formation was around 1.25 times greater at pH 5 than that at 1. Around 80 to 100% Fe remained in the solid phase after reacting with U. These reactions were rapid with an average 5 hr of half-life of solution phase U disappearance. The percent of solid U formation was initially higher at 318 °K than at 298 °K (STP); however, at both temperatures, >90% U solid formation occurred within 30 min at an ambient pH of 4 and at a 1:10 molal ratio of U and Fe; above 95% of Fe remained in the solid phase. The activation energy of U solid formation was about 6 KJ M⁻¹. All statistical correlations ($r = 0.95$ to 0.99) were significant within 1% confidence limit. Reactions between Fe(0) and U(VI) was essentially a redox reaction that resulted in reduction of Uranium to U(IV) and oxidation of iron to Fe(II) and primarily Fe(III). The oxidative states of U and Fe in solid phase were later ascertained using microscopic techniques.

Figure 1. Uranium solid phase formation under different reaction conditions: (a) 0.0001 to 100 mM U, 0.2 to 20 mM Fe, ambient pH 4; (b) 0.01 to 100 mM U, 100 mM Fe, pH 1 and 5; (c) 10 mM U, 100 mM Fe, ambient pH 4 (error bars are at 1 standard deviation level).

The zerovalent iron was effective in oxidizing the solution phase U(VI) at a wide concentration range (Table 1). Generally >60% U disappeared from all the solutions, and typically pH 5 favored >90% of U-solid formation. At a specific pH, the percent of solid U formation augmented with increasing U molality. For example, 89, 94, 95, and 99% of U solid was formed from 0.01, 1.0, 20, and 100 mM of originating Uranyl solutions, respectively, when they were reacted with 100 mM Fe(0) at pH 5. It is evident that at a constant pH and iron concentration, optimum U solid is formed (around 90% or more) irrespective of the geometric progression (up to 10,000 fold variation in our study) in the solution phase U concentrations. Change in pH had a notable impact on percent U solid formation, which was augmented at a relatively less acidic pH for all ranges of solution U concentrations. Saturation indices computation using a geochemical model (PHREEQC) suggested that Schoepite at different hydration levels and some alpha and beta U-oxides were the predominant U solids formed after equilibration. Ferric hydroxide, Goethite, and Hematite were the primary iron solids. These U and Fe solid phases were supersaturated at an ambient pH of 4.7, 298 °K temperature, and 1 mM U concentration.

Table 1. Effect of pH and U molality on solid phase U formation*.

pH	U in solution phase mM	U converted to solid phase %
3	0.01	74
5	0.01	89
3	0.1	63
5	1.0	94
3	20	94
5	20	95
1	100	63
3	100	65
5	100	99

*Reacted with 100 mM Fe(0). Supersaturated U and Fe solids: $\text{UO}_3 \cdot 8.5\text{H}_2\text{O}$, $\text{UO}_3 \cdot 9\text{H}_2\text{O}$, $\text{UO}_3 \cdot \text{H}_2\text{O}$, $\text{UO}_3 \cdot 2\text{H}_2\text{O}$, $\text{UO}_2(\text{OH})_2$, $\text{UO}_3 \cdot 9\text{H}_2\text{O}$, $\text{UO}_3 \cdot 2\text{H}_2\text{O}$; $\text{Fe}(\text{OH})_3$; FeOOH ; Fe_2O_3 .

The U solids were characterized for spatial maps and solid phases by a Scanning Transmission X-ray Microscopy system (Figure 2). The elemental mapping revealed that the relative distributions of U and Fe varied with the formation conditions of the solids. The images showed mixed and separate areas corresponding to both U and/or Fe. The Fe edges were detected around 710 ($L_3: 2p_{3/2}$) and 722 ($L_2: 2p_{1/2}$) eV, and showed patterns for 0 and III valence states. The relative preponderance of either of these valence states varied with samples. Occurrence of U reduction or precipitation was a function of the initial pH and molal conditions. The U edge was observed around 736 eV ($N_5: 4d_{5/2}$). The U valences were mostly at VI state, albeit with the presence of some IV state typically at lower molality and pH of the formation media. Depending on the formation conditions, the edges for the solids shifted slightly. Also kinks in edges were detected indicating Crystal Field Splitting. Species U(IV) was characterized by a lower optical/surface density and a greater spectral width than U(VI). Generally, U reduction was favored at low pH and molality, and precipitation occurred at higher boundaries of these formation conditions. However, mixed oxidation states were detected at different spatial regions in the same sample. Schoepite $[(\text{UO}_2)_8\text{O}_2(\text{OH})_{12} \cdot 12\text{H}_2\text{O}]$ was detected in the post-DFB-dissolution residues, which originated from both U^{IV} and U^{VI} type parent solids having identical U molality (0.02 M), indicating that DFB complexes with both U species.

Figure 2. U solid phase characterization by STXM: (a) Spatial structural map (U – yellow, Fe – blue), (b) Energy spectrum.

Dissolution studies were conducted by equilibrating the U solids with DFB as a function of pH, molality and temperature (Table 2). The differential concentration-time gradient ($\delta c/\delta t$) increased up to nearly 2 fold with the rise in temperature. This was evidently due to escalation in the U dissolution rate at the higher temperature. Solution U at 25 °C reached steady state after 24 hr and remained unchanged even after 72 hr of dissolution. At 10^{-3} M of DFB, a maximum value of 5 was reached for U dissolution gradient ($\delta U/\delta DFB$) per unit DFB molality rise. At STP (25 °C and 1 atmosphere), the U:DFB molal dissolution ratio was about 11 with a half-life ($t_{1/2}$) close to 100 hr. The $t_{1/2}$ increased by 2.5 fold with a 20°C rise in temperature. The activation energy for U dissolution by DFB was 36 kJ M^{-1} , and the amount dissolved was 6 to 40 times higher than that by water. Structural mapping and identification of solid phase species of uranium associated with iron are critical in understanding the remediation chemistry of the passivity layers. The data indicated that DFB effectively dissolved U formed under diverse chemical conditions.

Table 2. U Dissolution by DFB under variable reaction conditions.

T (°K)	k (h ⁻¹)	t _{0.5} (h)	M DFB	% U _{soln}
298.15	0.007	103	0	0.7
318.15	0.017	41	10 ⁻⁵	1.7
-----			10 ⁻⁴	9.3
E _{activation} = 36.3 kJ M ⁻¹			10 ⁻³	42
Max $\delta U/\delta DFB$ (~5) at 10 ⁻³ M of DFB			10 ⁻²	81

pH _f	pH _e	%U dissolution by		U dissolved by DFB
		H ₂ O	DFB	(M/M)
1	5.7	4	25	13
3	6.2	2	32	9
5	6.9	0.5	21	11

Figure 3. EXAFS characteristics of U structure in (a) solid and (b) solution phases.

Extended edge X-ray absorption spectroscopy, EXAFS, of U in the solid phase revealed that the U minerals were primarily consisted of Schoepite (U(VI)) and Uraninite (U(IV)) that remained mixed within the solids (Figure 3a). While preponderance of Schoepite precipitation was mainly observed for elevated U to Fe ratio in the reaction media, Uraninite was essentially detected under all reaction conditions, suggesting a plausible concurrence of both precipitation and reduction mechanisms. These mixed mineral phases were detected in the U residues even after dissolution with DFB. In solutions obtained after dissolution of U solids with DFB, the U EXAFS spectrum had a fingerprint match with the Schoepite type structure (Figure 3b). Thus, U in the post-dissolution phase remained hexavalently coordinated with the OH and DFB ligands. No U(IV) species were detected in the solution phase. This observation is consistent with greater thermodynamic instability of schoepite than Uraninite. Comparative analysis of the solid phase experimental data with FEFF computations predicted the presence of a third U mineral, Rutherfordine, in which U(VI) is also bonded with carbonate. This was possibly formed as a result of atmospheric carbon dioxide absorption by the reaction media. The EXAFS analysis revealed structural characteristics of U(VI) coordination milieu and the bond lengths of U and neighboring atoms. For solid U, the bond lengths of $U^{VI}-O$, $U^{IV}-O$, $U^{IV}-O-O-U^{IV}$, $U^{IV}-O-U^{IV}-O-U^{IV}$, and $U^{IV}-U^{IV}$ were 2.05, 2.30, 3.67, 4.67, and 6.02 Å, respectively, with around 0.004 Debye-Waller factor (σ^2), 4.66 reduced Chi-square, 0.0009 Uncertainty factor, and $0.949 r^2_{(amplitude \times \sigma^2)}$.

SEM **SEM** **TEM** **TEM** **EDS**

Figure 4. SEM, TEM, and EDS characterization of U in solid phase.

Morphological characteristics of U solids are shown in Figure 4. The SEM images showed platy structural growth of U solids mainly at acidic pH of 1 and 3. Cotton shaped U crusts were formed at pH 5. In conformity with the STXM elemental maps, distinct bright and dark spots were visible within the solids that primarily corresponded with U and Fe rich areas, respectively. However, all of the areas contained both elements at varying densities that were detected by Energy Dispersion Spectroscopy (EDS). Gray zones of water were observed surrounding the outer surface of mineral growths. No water was found within the structure. Some interstitial movements, probably caused by evaporation of water molecules, were observed. There was no structural collapse. The TEM micrographs showed flaky crystalline platelet structure of U minerals that were composed of nano and micro structural units with width and length as small as <50 and <500 nm, respectively. These microstructures are plausible constituents of a mixed phase of Shoepite, Uraninite, and Rutherfordine, as discussed in previous sections.

Results of this study, in combination with other work, will be useful for optimizing efficient U clean up strategies at iron and steel surplus facilities, and provide further insight for future work involving actinides and lanthanides. We would like to thank Drs. David Shuh and Tolek Tyliczszak of LBNL for helping with the STXM.

Technical Papers:

- Sharmasarkar S., D.K. Shuh, T. Tyliczszak, and S.J. Traina. 2004. STXM Analysis of U Solids Resulting from Uranyl and Zerovalent Iron Reactions. Advance Light Sources annual Conference, Abstract No. 173. Lawrence Berkley National Laboratory, Berkeley, CA
- Sharmasarkar S. and S.J. Traina. 2004. Structural Analysis of Solids Formed by Reacting U(VI) with Fe(0). American Geophysical Union Fall Meeting, Paper 10593, B53C-1003, San Francisco, CA
- Sharmasarkar S. and S.J. Traina. 2004. Reaction of U(VI) with Fe(0). Soil Chemistry Division, Soil Science Society of America Meeting, Abstract No. 5153, Seattle, WA