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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 initial work performed on a research grant awarded to S.J. Traina, when the PI was on the faculty at the Ohio State University. This work was performed under a subcontract from The Ohio State University to UC Merced subsequent to the S.J. Traina's move to the latter institution. This represents approximately 50% of the work associated with the original grant. These activities are being continued under a direct award to UC Merced.

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 ($pK_1^H=10.89$) and three hydroxamate groups ($pK_2^H=9.70$, $pK_3^H=9.03$, and $pK_4^H=8.30$), 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 (Fe0) 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.

Approach and Results

Uranyl (U^{VI}) solutions (10^{-1} to 10^{-5} M) were reacted with 0.1 M zerovalent iron powder (Fe^0) at variable molal ratio (1 to 10^5) and pH (1 to 5), and 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. Then dissolution studies were conducted by equilibrating the U solids with DFB as a function of pH, molality and temperature.

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. Generally >60% U disappeared from all the solutions, and typically pH 5 favored >90% of U-solid formation (Table 1). At a particular pH, such as 5, the percent of U_{solid} formation augmented with increasing U molality. The solution U disappearance kinetics followed a first order reaction with a half-life close to 5 hr ($r^2 = 0.99$). The solid phase formation appeared to be a combination of partial reduction, adsorption and precipitation processes, depending on the pH and molal conditions. Saturation indices (SI) computation suggested that Schoepite at different hydration levels and also α and β U-oxides were the predominant solids formed after equilibration.

Table 1. Solid phase U formation (U_{solid}) under variable reaction conditions.

<u>ID</u>	<u>pH</u>	<u>%U_{solid}</u>	<u>$M U^{VI}$</u>	<u>$M Fe^0$</u>
S_a	3	74	0.00001	0.1
S_b	5	89	0.00001	0.1
S_c	3	63	0.0001	0.1
SL3	5	96	0.001	0.1
S2	3	94	0.02	0.1
S3	5	95	0.02	0.1
SL2	1	65	0.1	0.1
S0	3	65	0.1	0.1
S6	5	99	0.1	0.1

The U solids were characterized for spatial maps and solid phases by a Scanning Transmission X-ray Microscopy system (Figure 1). 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 $[(UO_2)_8O_2(OH)_{12} \cdot 12H_2O]$ 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.

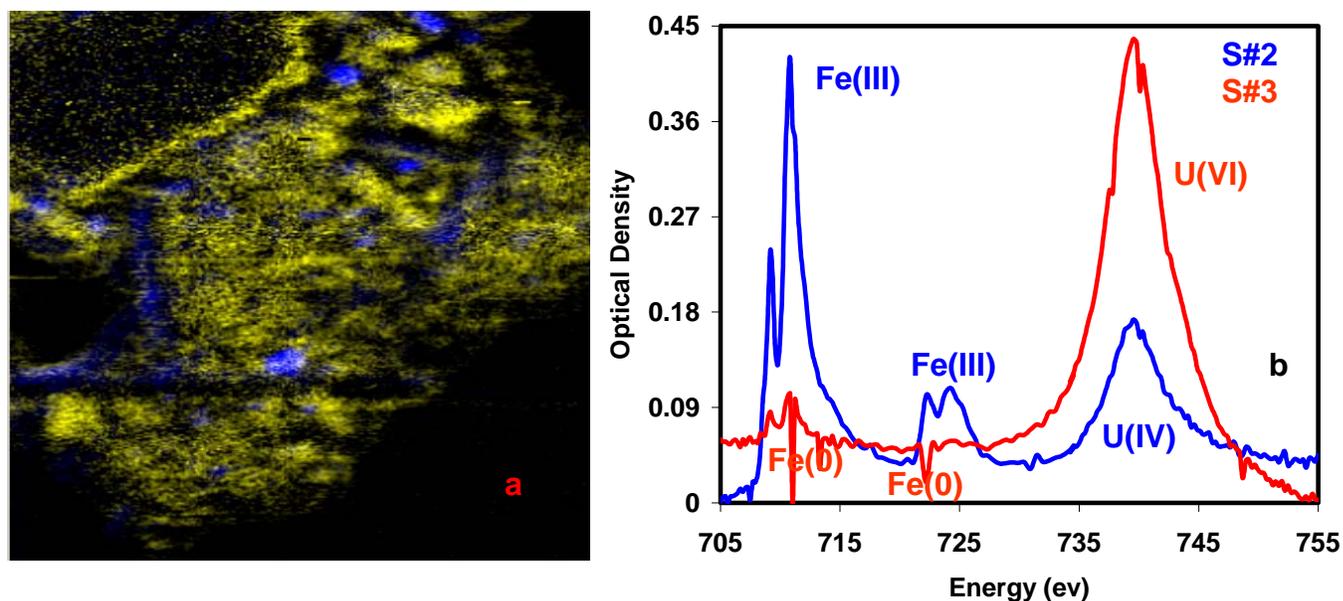


Figure 1. U solid phase characterization by STXM: (a) Spatial structural map (U – yellow, Fe – blue); (b) Energy spectrum.

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.

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	
ID	pH _f	pH _e	U dissolution %		U:DFB
			H ₂ O	DFB	(mole)
S#L2	1	5.7	4	25	13
S#2	3	6.2	2	32	9
S#6	5	6.9	0.5	21	11

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. 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.

Currently a journal manuscript is in preparation, and three conference abstracts (for AGU, ALS and SSSA meetings) have been presented.

Research Products

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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