

Aqueous Complexation Reactions Governing the Rate and Extent of Biogeochemical U(VI) Reduction

Scott C. Brooks^{1*}, Wenming Dong¹, James K. Fredrickson², Kenneth M. Kemner³, and Shelly Kelly³

¹Oak Ridge National Laboratory, Oak Ridge, TN 37831-6038, ²Pacific Northwest National Lab, Richland, WA 99352, ³Argonne National Lab, Argonne, IL 60439

Collaborators: Kent Orlandini³, John Zachara²

Abstract

Laboratory research has shown that dissimilatory metal reducing bacteria (DMRB) can effectively reduce oxidized uranium (U(VI)) to the sparingly soluble U(IV) with the concomitant precipitation of UO₂ phases. Despite the promise of bioreduction as a remediation strategy, the factors that enhance or inhibit the rate and extent of biogeochemical U(VI) reduction under representative environmental conditions are not well defined. Before effective biomobilization can be realized, the factors governing contaminant reactivity in multicomponent systems must be better understood. Only recently has the quantification of a few key interactions been established. For example, we recently reported the inhibition of bacterial U(VI) reduction by DMRB in the presence of environmentally realistic concentrations of soluble calcium (Ca) (Brooks et al., 2003). This finding has significant implications for field applications of bioreduction because Ca²⁺ is a dominant soluble and cation-exchangeable species in soils and aquifers. We propose to identify and quantify the important biogeochemical reactions that also equilibrate with the U-carbonate solution species and may inhibit or enhance U(VI) reduction. Initially, cation exchange resins, with well-defined Ca²⁺ selectivities, will be employed to establish the distribution of Ca-U-carbonate species in the presence of varying amounts of cation-exchangeable forms of Ca²⁺; other potentially important competing cations in the exchange equilibria (e.g., Mg²⁺, Sr²⁺) will be examined in later phases of the proposed research. Concurrent with the measurement of the competing equilibria among soluble and cation exchangeable phases, the reduction of the major cation-U-carbonate species will be studied using both abiotic and microbial agents. Our state-of-the-art measurement techniques (XAS, XRFs, EDX, TEM, radioisotopes, ICPMS, and KPA) will be applied to quantify these soluble complexes and precipitated phases. By understanding these important key equilibria, more predictable and effective approaches can be established for in situ bioremediation of U under realistic field conditions.

Determination of the formation constants of ternary complexes of uranyl and carbonate with alkaline earth metals (Mg²⁺, Ca²⁺, Sr²⁺, Ba²⁺) (Dong and Brooks, in review)

The formation constants of ternary complexes (MUO₂(CO₃)₂²⁻ and M₂UO₂(CO₃)₃⁰) of uranyl and carbonate with alkaline earth metals (M²⁺ denotes Mg²⁺, Ca²⁺, Sr²⁺, and Ba²⁺) were determined using an anion exchange method by varying the metal concentration (0.1-5 mM) at pH 8.1 and a constant ionic strength (0.1 M NaNO₃) at equilibrium with atmospheric CO₂ (Fig 1). The MUO₂(CO₃)₂²⁻ and M₂UO₂(CO₃)₃⁰ complexes are simultaneously formed for Ca²⁺ and Ba²⁺, while Mg²⁺ and Sr²⁺ only form the MUO₂(CO₃)₂²⁻ complex under our experimental conditions. The cumulative stability constants determined are provided in Table 1. Based on the formation constants obtained in this study, speciation calculations indicate that at low Ca²⁺ concentration (< 2.5 mmol/L) CaUO₂(CO₃)₂²⁻ is more important than Ca₂UO₂(CO₃)₃⁰ and that the Ca₂UO₂(CO₃)₃⁰ distribution increased with increasing [Ca²⁺]. Uranium sorption onto anion exchange resins is inhibited by the formation of the neutral Ca₂UO₂(CO₃)₃⁰ species.

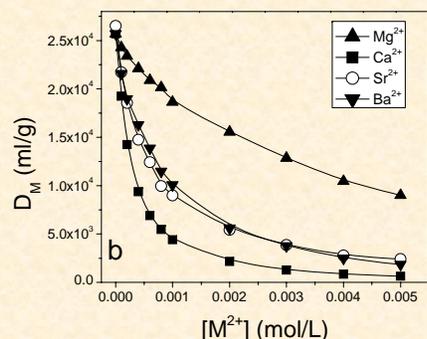


Figure 1 Uranium sorption by anion exchange resin as a function of alkaline earth element concentration. The extent of U sorption is represented by the distribution coefficient, D_M. Decreased values of D_M with increasing metal concentration are indicative of the formation of neutral M₂UO₂(CO₃)₃⁰ and poorly sorbing MUO₂(CO₃)₂²⁻ complexes.

Table 1. Formation constants of the MUO₂(CO₃)₂²⁻ (aq) and M₂UO₂(CO₃)₃⁰ (aq) complexes.

	log β ₁₁₃ (I = 0)	log β ₂₁₃ (I = 0)	Reference
Mg ²⁺	26.11 ± 0.04	---	This work
Ca ²⁺	27.18 ± 0.06	30.70 ± 0.05	This work
	---	29.41 ± 0.7 ^a	Bernhard et al. (1996)
	25.6 ± 0.25 ^a	30.79 ± 0.24 ^a	Bernhard et al. (2001)
	---	29.8 ± 0.7 ^a	Kalmykov and Choppin (2000)
Sr ²⁺	26.86 ± 0.04	---	This work
Ba ²⁺	26.68 ± 0.04	29.75 ± 0.07	This work

^a = revised to reflect the new recommended value for formation constant of UO₂(CO₃)₃⁴⁻ in Guillaumont et al. (2003)

Influence of EDTA and pH on Bioreduction of Uranium(VI) in the Presence of Calcium Ions (Dong et al., in prep)

Previously, we reported that the aqueous Ca₂UO₂(CO₃)₃⁰ complex can effectively inhibit U(VI) bioreduction (Brooks et al., 2003). In this study, the bioreduction of U(VI) was investigated in the presence of 2.5 mM Ca and varying EDTA concentration (1.75-2.5 mM) and pH (6.5 and 7.1) under anoxic conditions. The rate and extent of U(VI) bioreduction increased with increasing EDTA concentration (Fig 2). These observations are consistent with decreased Ca₂UO₂(CO₃)₃⁰ concentration due to the competitive complexation of Ca²⁺ by EDTA. The reduced U(IV) was observed in the forms of uraninite and U(IV)-EDTA complexes in the absence and presence of EDTA, respectively (Fig 3). Faster U(VI) reduction with increased pH is consistent with a lower predicted Ca₂UO₂(CO₃)₃⁰ concentration at pH 7.1. U(VI) speciation calculation and EXAFS analysis were applied to confirm our hypothesis that aqueous complexation controlled U(VI) bioreduction through the reactions of Ca²⁺ with UO₂(CO₃)₃⁴⁻ and EDTA.

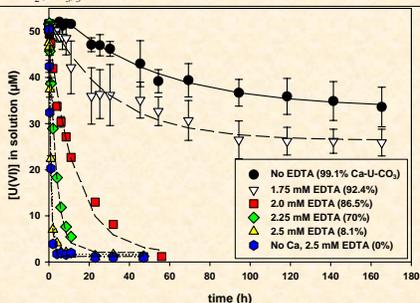


Figure 2 U(VI) bioreduction by *S. putrefaciens* CN32 at pH 6.5 as a function of EDTA concentration. As the concentration of EDTA in solution is increased, the fraction of U(VI) in the Ca-U(VI)-CO₃ complexes decreased and the rate and extent of U(VI) reduction increased.

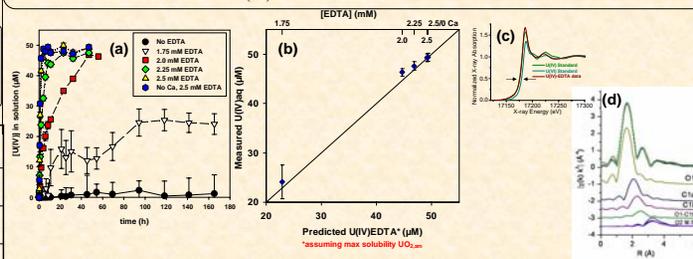


Figure 3 (a) In the presence of EDTA biogenic U(IV) remained in solution as an U(IV)-EDTA complex. (b) Equilibrium solubility calculations suggest that a U(IV) solid phase with a higher solubility than UO₂ (Guillaumont et al., 2003) controlled [U(IV)]. (c) U-XANES analyses confirmed that U in the samples was predominantly U(IV) and, (d) the absence of U-U backscattering demonstrates that it is not nanoparticulate U that passed the 0.2 μm pores in the filter.

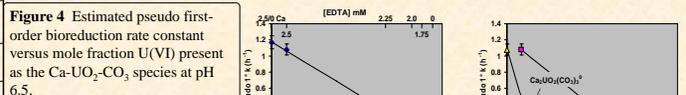


Figure 4 Estimated pseudo first-order bioreduction rate constant versus mole fraction U(VI) present as the Ca-UO₂-CO₃ species at pH 6.5.

Effects of pH, EDTA, and Ca²⁺ on Biogenic U(IV) Solids and U(IV)-EDTA Oxidation (Dong and Brooks, in prep)

The effects of pH, EDTA and Ca²⁺ on oxidation of biogenic U(IV) solids and U(IV)-EDTA complexes were investigated at acidic (pH 1) and weakly alkaline (pH 8.1) conditions under atmospheric conditions (21% O₂). The U(IV) solids and U(IV)-EDTA were prepared by the bioreduction of U(VI) in the absence and presence of EDTA and Ca²⁺ under anaerobic conditions. The oxidation rate of U(IV) solids and U(IV)-EDTA increased with increasing pH and decreasing [Ca] (Table 2 and Fig 5). The results are well-described by a pseudo first-order reaction. EDTA decreased the oxidation rate at pH 1 and increased the rate at pH 8.1 (Fig 6). In acidic media, treatment of samples suspected of containing a mixture of U(VI) and U(IV) with appropriate [EDTA] can stabilize the U(IV), suggesting a potential means to improve the determination of U(IV) from the difference of U(VI) and total U in kinetic phosphorescence analysis.

Table 2. Effects of pH and [Ca] on biogenic U(IV) oxidation rate. Given below are the estimated pseudo first-order rate constants (h⁻¹) for U(IV) oxidation.

	U(IV) solid		U(IV)-EDTA ([EDTA] = 0.25 mM)	
	No Ca	0.25 mM Ca	No Ca	0.25 mM Ca
pH 1	0.124 ± 0.005	0.056 ± 0.003	0.005 ± 0.0001	0.0068 ± 0.0003
pH 8.1	0.196 ± 0.007	0.133 ± 0.007	1.880 ± 0.070 (pH = 7.7)	1.270 ± 0.090

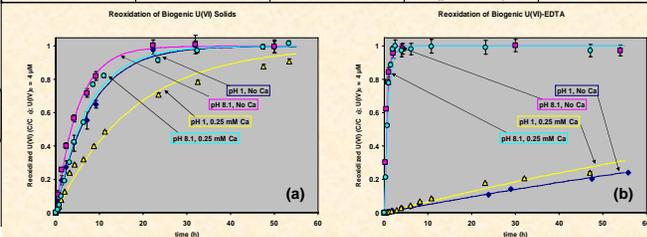


Figure 5 Reoxidation of biogenic (a) U(IV) solids and (b) U(IV)-EDTA in aqueous solution open to atmospheric O₂.

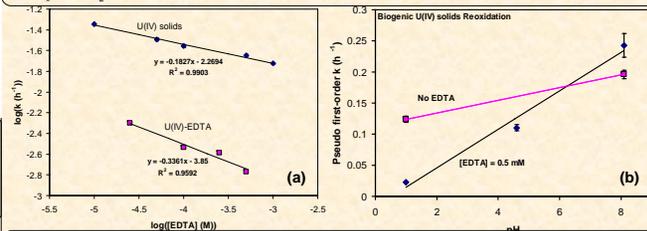


Figure 6 (a) First-order rate constant for reoxidation of biogenic U(IV) solids and U(IV)-EDTA in aqueous solution open to atmospheric O₂ as a function of [EDTA] at pH 1. (b) Effect of EDTA on biogenic U(IV) solids reoxidation as a function of pH.

Literature Cited
 Bernhardt G., Goppel G., Brendler V., and Nitsche H. (1996) Speciation of uranium in seepage waters of a mine tailing pile studied by time-resolved laser-induced fluorescence (TRLFS). *Radiochim. Acta* 74, 87-91.
 Bernhardt G., Goppel G., Reich T., Brendler V., Amann S., and Nitsche H. (2001) U(VI)-carbonate complex formation. Validation of the Ca₂UO₂(CO₃)₃ species. *Radiochim. Acta* 89, S11-S18.
 Brooks S. C., Fredrickson J. A., Carroll S. L., Kennedy D. W., Zachara J. M., Plymale A. E., Kelly S. D., and Fredrickson S. (2003) Inhibition of bacterial U(VI) reduction by calcium. *Environ. Sci. Technol.* 37(9), 1850-1858.
 Dong W. and Brooks S. C. (in review) Determination of the formation constants of ternary complexes of uranyl and carbonate with alkaline earth metals (Mg²⁺, Ca²⁺, Sr²⁺, and Ba²⁺) using anion exchange method. *Environ. Sci. Technol.*
 Guillaumont R., Engstrand T., Neck V., Fuger J., Palmer D. A., Grenthe I., and Raab M. H. (2003) Update on the Chemical Thermodynamics of Uranium, Neptunium, Plutonium, Americium, and Technetium. Elsevier.
 Kalmykov S. N. and Choppin G. R. (2000) Mixed Ca²⁺-UO₂²⁺-CO₃²⁻ complex formation at different ionic strengths. *Radiochim. Acta* 88, 603-606.