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

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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 bioremediation 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 bioremediation 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 cationic exchange species. The present study is designed to identify and quantify the important biogeochemical reactions that also occur with the U-carbonate solution species and that inhibit or enhance U(VI) reduction. Initially, cation exchange resins, with well-defined Ca2+ selectivities, will be employed to establish the distribution of 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, XRF, EIDX, TEM, radiocassette, ICPMS, and KPA) will be applied to quantify these soluble complexes and precipitated phases. By understanding these important equilibria, more predictable and effective approaches can be established for in situ bioremediation of U under realistic field conditions.

Table 1. Formation constants of the MO2(CO3)3− (aq) and M2UO2(CO3)3− (aq) complexes.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Log β25</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg2+</td>
<td>26.11 ± 0.04</td>
<td>This work</td>
</tr>
<tr>
<td>Ca2+</td>
<td>27.18 ± 0.06</td>
<td>This work</td>
</tr>
<tr>
<td>Sr2+</td>
<td>26.92 ± 0.04</td>
<td>This work</td>
</tr>
<tr>
<td>Ba2+</td>
<td>26.68 ± 0.04</td>
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Table 2. Effects of pH and [Ca] on biogenic U(VI) oxidation rate. Given below are the estimated pseudo first-order rate constants (h−1) for U(VI) oxidation.

<table>
<thead>
<tr>
<th>pH</th>
<th>[Ca] (mM)</th>
<th>k (h−1)</th>
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<tbody>
<tr>
<td>1</td>
<td>0.25 Ca</td>
<td>0.133 ± 0.007</td>
</tr>
<tr>
<td>8.1</td>
<td>0.25 Ca</td>
<td>0.196 ± 0.007</td>
</tr>
<tr>
<td>1</td>
<td>No Ca</td>
<td>0.124 ± 0.005</td>
</tr>
<tr>
<td>8.1</td>
<td>No Ca</td>
<td>0.133 ± 0.007</td>
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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, DM. Decreased values of DM with increasing metal concentration are indicative of the formation of neutral M2UO2(CO3)3− complexes.

Figure 2. U(VI) biodissolution 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) The presence of EDTA biogenic U(VI) remained in solution as an U(VI)-EDTA complex. (b) Equilibrium solubility calculations suggest that U(VI) solid phase with a higher solubility than UO2 (Guillaumont et al., 2003) is not U(VI). (c) U XANES analyses confirmed that U in the samples was predominantly U(VI) 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 biodissolution rate constants versus mole fraction U(VI) present as the Ca-CO3-CO3 species at pH 5.5.

Figure 5. Oxidation of biogenic (a) U(VI) solids and (b) U(VI)-EDTA in aqueous solution open to atmospheric O2. The rate of oxidation decreases as the U(VI) concentration increases.

Table 2. Effects of pH, EDTA, and Ca2+ on Biogenic U(VI) Oxidation (Dong and Brooks, 2001).

<table>
<thead>
<tr>
<th>pH</th>
<th>No EDTA</th>
<th>0.15 M EDTA</th>
<th>2.0 M EDTA</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.133 ± 0.007</td>
<td>0.196 ± 0.007</td>
<td>0.256 ± 0.007</td>
</tr>
<tr>
<td>8.1</td>
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Figure 6. (a) First-order rate constant for oxidation of biogenic U(VI) solids and U(VI)-EDTA complex open to atmospheric O2 as a function of [EDTA] at pH 1. (b) Effect of EDTA on biogenic U(VI) solids and U(VI)-EDTA complex. EDTA decreased the oxidation rate at pH 1 and increased the rate at pH 8.1. In acidic media, treatment of samples suspected of containing a mixture of U(VI) and U(IV) is appropriate [EDTA] can stabilize the U(IV) phase and create a potential means to improve the determination of U(VI) from the difference of U(VI) and total U in kinetic phosphorescence analysis.

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Figure 7. Oxidation of biogenic (a) U(VI) solids and (b) U(VI)-EDTA in aqueous solution open to atmospheric O2. The rate of oxidation decreases as the U(VI) concentration increases.

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