Kinetics of U(VI) reduction control kinetics of U(IV) reoxidation

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Introduction

U(IV) and U(VI) are both present in uranium-bearing aquifers. The U(VI) fraction is typically the most mobile species. Reduction of U(VI) to U(IV) can immobilize uranium and have implications for its mobility and bioremediation. Our study examined the bioreduction of U(VI) by Shewanella putrefaciens and its impact on U(IV) reoxidation. The effects of electron donor concentration on U(VI) reduction kinetics were also studied.

Figure 1: Hypothesized bioreduction rate-dependent differences in U(IV) products

The effect of U(VI) bioreduction rate on the subsequent reoxidation of biogenic U(IV)

Preparation of U(VI) via different rates of bioreduction

Rheological cells of Shewanella putrefaciens (S. putrefaciens) were incubated in buffered (pH 6.8) medium containing 1 mM uranyl actate and 5 mM sodium lactate. Cells were pasteurized to remove any extracellular U(IV) precipitate. The effect of electron donor concentration on U(VI) reduction kinetics was examined. The rates of U(VI) reduction were correlated with the electron donor concentration.

Figure 2. Bioreduction of U(VI) by various cell densities of S. putrefaciens CN32

Evolution of biogenic U(IV) by various cell densities of S. putrefaciens CN32

Figure 3. Bioreduction of U(VI) by various cell densities of S. putrefaciens CN32

Results and Discussion

U(IV)fast, U(IV)med, and U(IV)slow containing inoculations exhibited different colors after complete reduction of U(VI) (Figure 3). Carefully controlled rates of U(VI) reduction may yield U(IV) precipitates that are more resistant to oxidation than rapidly formed (and smaller) U(IV) particles.

Visual characteristics of biogenic U(IV)

Figure 4. Differences in color of U(VI)-reducing inoculations after complete reduction (U(VI))

- Not clear if this occurs in all incubations.
- Relates rapidly-formed U(IV) was correspondingly more susceptible to biological and abiotic oxidation coupled to reduction of a variety of oxidants (Figure 5).

Column preparation, characteristics, and run conditions

Column setup included initial incubations of U(VI) with and without added oxidant to determine U(VI) reoxidation rates. The effect of electron donor concentration on U(VI) reduction kinetics (assuming 50% porosity) was studied. The pore volume of each column was 26.4 ml. Pore volume of each column was 52 g. The effect of electron donor concentration on U(VI) reduction kinetics was also examined.

Figure 5. Biological and abiotic oxidation of U(IV)fast, U(IV)med, and U(IV)slow

- Asses the rates of U(IV) reoxidation in FRC sediment column material upon completion of column experiments.

Ongoing and future work

Further work will include studies of the effect of electron donor concentration on U(VI) reduction kinetics and the potential for U(IV) to reoxidize in the presence of oxidants. The effect of electron donor concentration on U(VI) reduction kinetics and the potential for U(IV) to reoxidize in the presence of oxidants.

Figure 6. Differences in color of U(VI)-reducing inoculations after complete reduction (U(VI))

- May be attributed to differences in U(IV) natural crystallinity or simply to the differences in cell density of each inoculation.
- U(IV) deposited extracellularly (Figure 6).

- Asses the potential for U(IV) to reoxidize in the presence of oxidants.

- Determination of U(IV)-cellular material interactions (by EXAFS with collaborators at University of Central Florida).