Pu(IV)(OH)₄(am) Reduction by DMRB

Pu(IV) has a long half-life (2.4 x 10⁴ years) and is of concern because of its chemical and radiological toxicity, high-energy alpha radioactive decay. A full understanding of its speciation and interactions with environmental processes is required in order to predict, contain, or remediate contaminated sites. Under aerobic conditions Pu is sparingly soluble, existing primarily in its tetravalent oxidation state. To the extent that prevalent and heterogeneous complexes and small colloidal species form they will increase the solubility of Pu in these circumstances. There is evidence that in both marine environments and terrestrial subsurface fractions of the plutonium in solution exist as hexavalent Pu(VI).

Given that the radionuclides of most concern to the NABIR program are generally more mobile in their oxidized forms (e.g., Pu(VI), Pu(VI), Pu(VI)), proposed biostabilization strategies are generally based upon either the sequestration of the oxidized form (e.g. actinide biosorption and bioaccumulation within ecosystems and biomes) or biomineralization of the reduced form (e.g., direct or indirect production of insoluble hydroxides by DMRB). The feasibility of these approaches is affected by the speciation of actinides under environmental conditions. For example, actinides can form complexes with co-contaminants (e.g. EDTA) or natural chelators like siderophores and biofilm. Resulting complexes can interact with bacteria in several ways to yield biostabilized products or more mobile forms that could persist. The goal of this work is to understand and optimize mechanisms for in situ immobilization of Pu species by naturally-occurring bacteria. We examined the ability of metal-reducing bacteria Geobacter metalloReducens GS15 and Shewanella oneidensis MR1 to reduce soluble Pu(IV) and Pu(VI) species under cell suspension conditions and examined the ability of these organometallic complexes to elicit biostabilization in cell-free systems.

We found that Pu(IV)(OH)₄(am) is reduced by cell suspensions of S. oneidensis (A) and G. metalloReducens GS15 (B). (A) Pu lives with the electron donor. (B) Live cells with the electron donor. (C) Dead cells with no electron donor. (D) Heat killed cells control.

The ability of G. metalloReducens and S. oneidensis cell suspensions to enzymatically reduce Pu(IV)(OH)₄(am) and Pu(IV)(EDTA) was assessed by following changes in Pu concentration in the cultures over time.

Pu(VI)Accessibility to Bacterial Reduction

The ability of DMRB to reduce Pu(VI) was assessed by studying the reduction of Pu(VI) in the presence of several electron donors. Figure 1 shows that Pu(VI) is effectively reduced by cell suspensions of G. metalloReducens GS15 and S. oneidensis MR1. The reduction of Pu(VI) is more rapid in the presence of the electron donor and is less than 8% of the starting concentration.

The evolution of the Pu(III)/Pu(IV) ratios was monitored using in situ spectroscopy to determine the extent of Pu(VI) reduction. The data show a gradual decrease of Pu(VI) from 1450 to 450 nm with the concurrent increase in the absorption band corresponding to Pu(III) at 600 nm. Controls with live cells and no electron donor show the production of less Pu(III) compared to the Pu(III) produced in the cultures with no cells or dead cells show no reduction of Pu(VI).

The ability of G. metalloReducens and S. oneidensis cell suspensions to enzymatically reduce Pu(VI) was assessed by following changes in Pu concentration in the cultures over time.

The reduction of Pu(VI) by cell suspensions of G. metalloReducens (A) and S. oneidensis (B). (B) Pu(VI) EDTA was added in two steps, the first addition of 0.5 mM was at t=0 and the second addition of 1.0 mM was at t=480. Total Pu(VI) EDTA added was 1.50 mM. (C) Live cells with the electron donor. (D) Live cells with no electron donor. (E) Dead cells control. (F) Heat killed cells control.

In cultures with initial concentrations of 0.5 mM Pu(VI) EDTA almost all of the Pu(VI) was reduced to Pu(VI) EDTA in less than 40 minutes.

The evolution of the Pu(VI)/Pu(V) reduction was determined using in situ spectroscopy. The data show a gradual decrease of Pu(VI) from 1450 to 450 nm with the concurrent increase in the absorption band corresponding to Pu(V) at 600 nm. Controls with live cells and no electron donor show the production of less Pu(V) compared to the Pu(V) produced in the cultures with no cells or dead cells show no reduction of Pu(V).

Variation of the optical absorbance spectra of solutions containing Pu(VI) EDTA complex with a cell suspension of G. metalloReducens.

Pu(VI)EDTA Reduction by DMRB

The reduction of Pu(VI) and Pu(V) by cell suspensions of G. metalloReducens (A) and S. oneidensis (B). (B) Pu(VI) EDTA was added in two steps, the first addition of 0.5 mM was at t=0 and the second addition of 1.0 mM was at t=480. Total Pu(VI) EDTA added was 1.50 mM. (C) Live cells with the electron donor. (D) Live cells with no electron donor. (E) Dead cells control. (F) Heat killed cells control.

The reduction of Pu(VI) by DMRB was assessed by studying the reduction of Pu(VI) in the presence of several electron donors. Figure 1 shows that Pu(VI) is effectively reduced by cell suspensions of G. metalloReducens GS15 and S. oneidensis MR1. The reduction of Pu(VI) is more rapid in the presence of the electron donor and is less than 8% of the starting concentration.

The evolution of the Pu(III)/Pu(IV) ratios was monitored using in situ spectroscopy to determine the extent of Pu(VI) reduction. The data show a gradual decrease of Pu(VI) from 1450 to 450 nm with the concurrent increase in the absorption band corresponding to Pu(III) at 600 nm. Controls with live cells and no electron donor show the production of less Pu(III) compared to the Pu(III) produced in the cultures with no cells or dead cells show no reduction of Pu(III).

The ability of G. metalloReducens and S. oneidensis cell suspensions to enzymatically reduce Pu(VI) was assessed by following changes in Pu concentration in the cultures over time.

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