XANES of Bio-Precipitated Np(IV) in Methanogenic and Sulfate-Reducing Systems

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Introduction

The effect of microbiological processes on the speciation of neptunium under subsurface conditions is being investigated.[1,2] Neptunium is an important subsurface contaminant on Department of Energy (DOE) lands. Methanogenic and sulfate-reducing bacteria (SRB) establish conditions in the subsurface that may reduce multivalent metals (e.g., neptunium in the +5 oxidation state), leading to precipitation and hence immobilization.

Methods and Materials

Methanogenic microcosms were isolated from lake-bottom sediments by the Microbial Ecology Laboratory at Northwestern University. The sulfate-reducing microcosm was isolated from creek bottom sediments by the Environmental Research Division at Argonne National Laboratory (ANL). Experiments were performed in ~ 150 ml bottles, at room temperature, in the dark. Lactate, pyruvate and hydrogen were added as the electron donor. Neptunium (V), at 0.01 mM concentrations, was added and monitored as a function of time to track oxidation state trends and precipitation.

X-ray absorption near-edge spectroscopy (XANES) analyses were performed on the MR-CAT undulator beamline at the Advanced Photon Source (APS) at ANL. Samples were prepared in a nitrogen glovebox by gravity centrifugation (6000 rpm and 30 min) in 10-ml centrifuge tubes. Following centrifugation, the biomass pellet was encapsulated in polystyrene plastic. After encapsulation, the samples were removed from the glovebox and mounted for XANES analysis. Neptunium standards of three oxidation states were prepared: $Np(IV)F_4$, $Np(V)O_2NaCO_3$, and Np(VI)-phosphate.

Results

The results of this research show that anaerobic bacteria, especially methanogens and sulfate reducers, actively precipitate neptunium from solution. This work is the first documented report of microbially driven Np(V) reduction. For mixed cultures, neptunium precipitation was most rapid when cultures were supplemented with hydrogen as the electron donor in lieu of pyruvate. For pure cultures, the rate of precipitation depended on the metabolic activity. Neptunium precipitation was most rapid when hydrogen or lactate was supplied as an electron donor. Precipitation of neptunium did not require the addition of sulfate as an electron acceptor, as growing cultures were always able to drive neptunium precipitation. The exact mechanism for this process is, for this reason, the subject of further study. The XANES analysis (see example in Fig. 1) of neptunium in the precipitate supported the view that neptunium was reduced to Np(IV) in all cases investigated.

Discussion

The discovery that anaerobic bacteria can drive reduction of Np(V) is an important result that has implications for neptunium mobility in anaerobic environments. Because SRB are common in anaerobic systems, if their ability to stimulate neptunium reduction is widespread, neptunium migration might be retarded significantly. However, more research is needed to determine the mechanism for neptunium reduction by SRB and other microorganisms and to investigate the stability of bio-precipitated neptunium in natural environments.

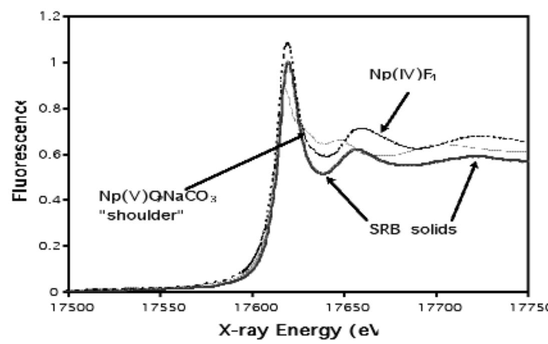

FIG. 1. Comparison of XANES spectra from neptunium precipitated during lactate fermentation to Np(IV) and Np(V) solid standards. The bio-precipitated neptunium spectrum lacks the near-edge shoulder associated with Np(V), indicating that Np(V) was reduced to Np(IV) during lactate fermentation.

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References

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