FATE OF NEPTUNIUM IN AN ANAEROBIC, METHANOGENIC MICROCOSM

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ABSTRACT

Neptunium is found predominantly as Np(IV) in reducing environments, but as Np(V) in aerobic environments. Currently, it is not known how the interplay between biotic and abiotic processes affects Np redox speciation in the environment. To evaluate the effect of anaerobic microbial activity on the fate of Np in natural systems, Np(V) was added to a microcosm inoculated with anaerobic sediments from a metal-contaminated freshwater lake. The consortium included metal-reducing, sulfate-reducing, and methanogenic microorganisms, and acetate was supplied as the only exogenous substrate. Addition of more than 10^{-5} M Np did not inhibit methane production. Total Np solubility in the active microcosm, as well as in sterilized control samples, decreased by nearly two orders of magnitude. A combination of analytical techniques, including VIS-NIR absorption spectroscopy and XANES, identified Np(IV) as the oxidation state associated with the sediments. The similar results from the active microcosm and the abiotic controls suggest that microbially produced Mn(II/III) and Fe(II) may serve as electron donors for Np reduction.

INTRODUCTION

The migration of neptunium isotopes, especially ^{237}Np, away from nuclear waste sites and repositories presents a significant long-term health risk. Recent evidence suggests that, among the actinides present in nuclear waste streams, Np may have the highest bioavailability, because its stable oxidation state in aerobic biological systems, Np(V), is also the most soluble and mobile actinide oxidation state [1-4]. While Np(V) is the most stable oxidation state under aerobic conditions, significant evidence indicates that neptunium is found predominantly as Np(IV) in natural reducing environments [1, 5-9].

Microbial processes can have a significant impact on actinide speciation in the subsurface [10-13]. In anaerobic environments, actinides may be utilized directly as electron acceptor substrates for energy generation or may participate in redox reactions with other microbially reduced compounds [10, 11, 13-20]. The former mechanism requires the presence of living microorganisms, while the latter may proceed whether the organisms are alive or dead. However, even though the latter electron transfer is an abiotic process, the source of reducing capacity in the system is still biological.

The purpose of this study is to assess the fate of Np in the presence of an anaerobic, methanogenic microbial consortium isolated from lake-bottom sediments. To evaluate the effect of anaerobic microbial activity on the fate of Np in natural systems, Np(V) was added to live and sterilized microcosms inoculated with anaerobic sediments from a metal-contaminated freshwater lake. The consortium included metal-reducing, sulfate-reducing, and methanogenic microorganisms. In this work, we show that the predominant Np oxidation state under biotic and abiotic conditions is Np(IV), suggesting that microbially produced Fe(II) or Mn(II/III) may serve as the source of electrons for Np reduction.

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EXPERIMENT

Origin of live sediments

Lake DePue, a backwater lake of the Illinois River, is located in Northern Illinois, east of LaSalle-Peru. Industrial chemical operations, including zinc smelting and sulfuric acid/diammonium phosphate fertilizer production, began in 1903 and continued through 1992. Several residual sources of contamination, identified by the Environmental Protection Agency, include: residue and waste piles, lithopone waste material ridges, cinder fill areas, contaminated soils, lagoons, cooling ponds, and gypsum stack ponds. All of these sources have been found to contain elevated levels of zinc, lead, arsenic, cadmium, chromium, and copper. These residuals have also led to metal contamination of the aquatic system. Contaminants flow into Lake DePue through surface water runoff and groundwater migration.

The lake is shallow (approximately 2 m) and is characterized by high primary productivity and high suspended solids. Since Lake DePue is a backwater lake, it often has drastic volume changes during periods of high precipitation. The water column remains oxic during most of the year, but on some occasions the bottom waters became oxygen depleted. Average concentrations of total metals present in the water column are: Zn = 7000 nM, Pb = 140 nM, Cd = 20 nM, and Cu = 700 nM. The ranges of metal concentrations in the sediments are: Zn = 1000-350,000 ppm, Pb = 120-2000 ppm, Cd = 50-1000 ppm, and Cu = 300-100,000 ppm.

Growth conditions and microcosm setup

To prevent contamination by foreign microorganisms, sediments were sampled using sterile techniques in late November 1997 and sealed anaerobically in glass containers. In an anaerobic chamber, 125 mL of sediment slurry was inoculated into 1 liter of defined growth medium containing (in g/L) 0.8 NaCl, 1.0 NH_4Cl, 0.1 KCl, 0.1 KH_2PO_4, 0.165 $MgCl_2 \bullet 6H_2O$, 1.361 NaAcetate, 1.5 N-tris(hydroxymethyl)methyl-2-aminoethanesulfonic acid (TES) buffer, and 10 mL/L of a Wolin vitamin solution [21]. For the non-actinide experiments, NaAcetate (10 mM) and MnO_x (15 mM), prepared by permanganate oxidation of Mn(II) to yield mixed Mn(III/IV) oxide [22], were added to the sediments at regular intervals as electron-donor and -acceptor substrates, respectively. The microcosms were kept at a constant temperature of 30°C.

For the Np experiments, two microcosms (one control and one receiving Np additions) were prepared in a similar manner. In an anaerobic chamber, approximately 5 mL of sediment slurry was inoculated into 95 mL of the growth medium described above. Both microcosms were supplemented with NaAcetate and MnO_x for several weeks, and then MnO_x additions were suspended; after that point NaAcetate was added periodically as the sole substrate. Filter-sterilized, anoxic Np(V), prepared as a stock solution by electrolytic reduction of Np(VI), was added periodically to one microcosm. The other microcosm received no Np addition. Both microcosms received identical acetate additions. Due to the special requirements necessary for handling vessels containing actinides, all vessels with Np were kept in the dark at 25°C.

Abiotic microcosms were prepared in an anaerobic chamber by transferring 0.5 mL of sediment and 5 mL of solution from the non-Np control microcosm into two 30-mL serum bottles, which were subsequently crimp-sealed with rubber stoppers. One bottle was sterilized by autoclaving three times. The other bottle was sterilized by irradiation at the ^{60}Co gamma source at Argonne National Laboratory (ANL). The radiation dose was 0.2 Mrad. No gas production was observed following sterilization by either method. Following sterilization, each bottle was purged with a sterile N_2/CO_2 (70:30) gas mixture and pressurized to 1 psig. After the

gas purge, 7 mL of sterile methane gas was injected into the headspace of each bottle to approximate the headspace atmosphere (~15% CH_4 in the non-actinide vessels) in the live microcosms. Sterile, anoxic Np(V) stock was added to each bottle with a needle syringe. The abiotic microcosms were kept in the dark at 25°C.

Analytical methods

The non-actinide reactor was sampled at regular intervals for dissolved Fe and Mn. The microcosm headspace was sampled with a gas-tight syringe and analyzed for CH_4 on a gas chromatograph (EG&G CARLE Series 100) equipped with a HayesSep column using thermal conductivity detection. Dissolved Mn and Fe were determined with spectroscopic techniques from filtered reactor aliquots: Mn was determined by the formaldoxime method at 450 nm [23] and Fe by the ferrozine method at 562 nm [24]. As the formaldoxime method does not select against complexation of Fe, the Mn concentrations were corrected for the amount of Fe present. The pH was measured using a combination glass pH electrode. Alkalinity was determined by sample titration with HCl to below the endpoint of H_2CO_3 and subsequent Gran analysis [25].

The actinide microcosms were sampled for Np solubility by a needle syringe. In the live microcosm, samples were drawn for Np analysis before and after agitation of the sediments. The Np solubility in the live and abiotic microcosms was determined by energy-specific scintillation counting (Packard 2500) of 0.2-μm filtered vs. unfiltered aliquots of agitated solution. Samples for VIS-NIR spectroscopy (Varian CARY 5) were prepared by needle-syringe transfer of solution into a cuvette under a flowing stream of Ar.

X-ray absorption near-edge spectroscopy (XANES) analyses [26, 27] were performed on the MR-CAT undulator beamline at the Advanced Photon Source (APS). Samples were prepared in a nitrogen glovebox by centrifuging (6000 rpm x 30 minutes) aliquots of sediment slurry in 0.5-mL microcentrifuge tubes. Following centrifugation, a section of the centrifuge tube containing sediment was clipped off and encapsulated in polystyrene plastic. After encapsulation, the samples were removed from the glovebox and mounted for XANES analysis. Standards of various Np oxidation states were prepared by recovering solids from the following syntheses: $Np(IV)F_4$ by addition of excess fluoride to Np(IV); $NaNp(V)O_2CO_3$ by titration of Np(V) stock with 0.1 M sodium carbonate to pH 7; and Np(VI)-phosphate by addition of excess phosphate to Np(VI) stock and adjustment of pH to 8.

RESULTS AND DISCUSSION

Key biological processes

In the live microcosms, two key biological processes dominate acetate degradation and electron flow. Metal-reducing bacteria gain energy for growth by coupling the oxidation of organic substrates to the reduction of metal ions, most commonly Fe^{3+} and Mn^{4+} [28-32]. This process can be represented qualitatively by:

$$\text{Acetate} + \text{Me(oxidized)} \Rightarrow CO_2 + \text{Me(reduced)} + \text{biomass} \qquad (1)$$

In the case of utilization of Fe(III) and Mn(III/IV) as electron acceptors, metal reduction causes an increase in solubility, because the reduced forms of the metals are more soluble than the oxidized forms [28, 30, 32-34].

In non-actinide vessels, acetate and Mn(III/IV) were supplied as the electron-donor and

-acceptor substrates. Figure 1 shows that utilization of oxidized Mn as an electron acceptor caused an initial increase in the concentration of dissolved Mn species. Similarly, Figure 1 shows that the concentration of soluble Fe also increased in the first 30 days, even though Fe was not added to the microcosm. The increase in Mn and Fe solubility follows the trends observed for biological metal reduction in other systems, suggesting that Fe was liberated from the sediments due to the action of metal-reducing bacteria.

The second major biological process in the microcosms was methane production. Acetoclastic methanogens derive energy for growth by cleaving acetate to form methane and carbon dioxide:

$$\text{Acetate} \Rightarrow CO_2 + CH_4 + \text{biomass} \qquad (2)$$

Reactions (1) and (2) cause the pH increase often associated with methanogenic systems; volatile acids are converted to methane and weaker carbonic acid, which can evolve from solution as CO_2 when a gas phase exists. Additionally, reductive dissolution of oxidized metal oxy-hydroxides releases base equivalents to the system [33].

Methane was produced in all the live microcosms as long as acetate was supplied, and the pH increased to 10.1 (data not shown). Figure 1 illustrates the relationships among alkalinity, total carbonate concentration, and soluble Fe and Mn concentrations in the vessels. Addition of NaAcetate as a substrate and dissolution of Fe oxy-hydroxide minerals and MnO_x initially increased the alkalinity in the vessels. Figure 1 also shows that conversion of acetate to CO_2 increased the total carbonate concentration in solution. However, after 110 days, the alkalinity in the vessels showed a decreasing trend. Similarly, after 40-60 days, the concentration of soluble Mn and Fe decreased and stabilized afterwards, even though MnO_x was continually added as an electron acceptor. Since precipitation of metal carbonates removes base equivalents from solution, the decrease in soluble metal concentrations and alkalinity in conjunction with increasing carbonate concentrations suggests that Fe(II) and Mn(II) precipitated as carbonate phases. In the pH range of 9-10, carbonates are the stable Fe(II) and Mn(II) solids in alkaline, anaerobic systems with elevated carbonate concentrations [33].

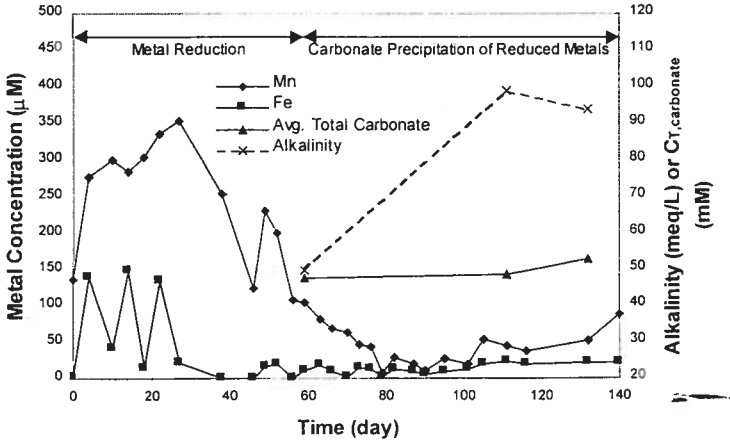

Figure 1. Concentration of soluble Mn, Fe, total carbonate, and alkalinity in non-actinide methanogenic microcosms fed NaAcetate and MnO_x as electron-donor and -acceptor substrates. All points are the average from two vessels. The increase in metal solubility was caused by utilization of the metals as electron acceptors in energy-generating biological reactions. The decrease in metal solubility after 60-80 days correlated with an increase in total carbonate and a decreasing alkalinity trend in the reactors, suggesting that the reduced metals were precipitated as carbonate phases.

Np solubility in live and abiotic microcosms

Unlike Fe and Mn reduction, in the absence of strong complexing ligands, reduction of Np from Np(V) to Np(IV) causes precipitation of sparingly soluble hydroxide solid phases and a decrease in metal solubility [1, 6, 35, 36]. Thus, one key indicator of Np(V) reduction to Np(IV) can be a significant decrease in actinide solubility. The partitioning of Np in the live microcosm over the course of the experiment is shown in Figure 2. The Np solubility decreased by approximately two orders of magnitude in the microcosm, even as additional Np(V) was added to the vessel. About 50-55% of the insoluble actinide was associated with the sediments; a significant fraction remained suspended in the solution above the sediments. The suspended Np did not pass a 0.2-μm filter, indicating that it was associated with particles or mobile microbial cells. There was no Np partitioning observed in sterilized, anaerobic growth medium without sediment; all the added Np remained soluble (data not shown).

Figure 3 compares the solubility of Np in the live microcosm to results obtained from the sterilized vessels. In all three vessels, total Np solubility decreased by approximately two orders of magnitude. The average soluble Np concentration among the three vessels was $2.26 \pm 0.95 \times 10^{-7}$ M. Since there was no active microbial activity in the sterilized vessels, the similarity in final Np solubility among the three microcosms suggests that an abiotic process was responsible for Np partitioning into the sediments.

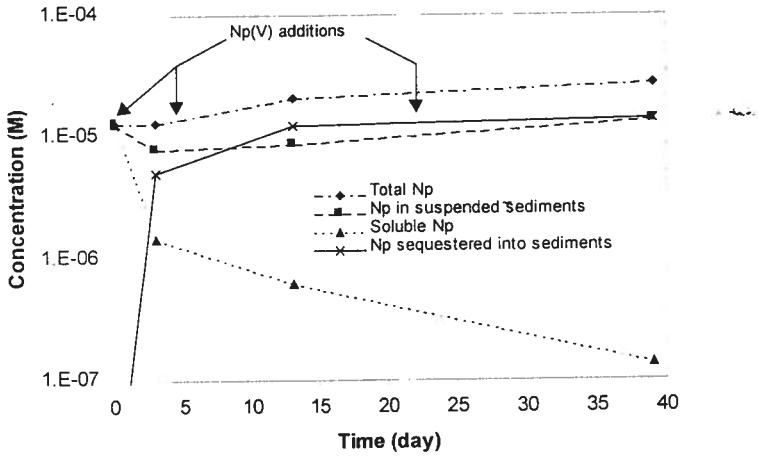

Figure 2. Partitioning of Np in the methanogenic microcosm. Soluble Np is defined as the quantity passing a 0.2-μm filter. The soluble Np in the vessel decreased by two orders of magnitude. Approximately 50-55% of the Np was sequestered into the sediments; a significant fraction of the actinide remained associated with suspended particles or microbial cells.

Oxidation state of Np in the microcosms

The Np partitioning noted in the microcosms could have been caused by any of several mechanisms. The Np(V) could have precipitated from solution or sorbed [37-39] onto the sediment particles as an Np(V) species. Conversely, the Np could have been reduced to Np(IV), either in solution or while sorbed onto the sediment surface. The Np(IV) formed from Np(V) reduction could then either precipitate from solution or sorb onto the sediments [1].

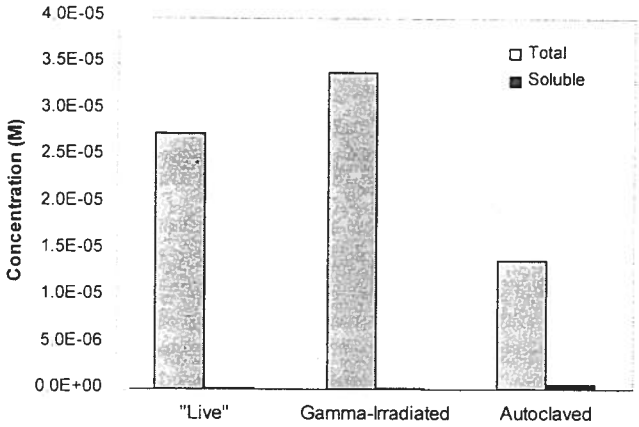

Figure 3. Neptunium partitioning in live and abiotic microcosms. In all three vessels, soluble Np decreased to approximately 10^{-7} M. The similarity in final Np solubility suggests that an abiotic mechanism affected Np partitioning.

Several complementary methods were used to investigate the mechanism causing Np partitioning in the microcosms. Figure 4 shows the VIS-NIR spectrum of Np in the live microcosm taken within 10 minutes after addition, but before the sediments were agitated. The bands at 980 and 990 nm correspond to the $Np(V)O_2^+$ and $Np(V)O_2CO_3^-$ species, respectively [40-44]. The small band at 960 nm indicates rapid formation of an Np(IV) species [35, 45]. However, spectra taken several days after Np addition showed only a small, broad band centered at 980 nm (data not shown) that prevented identification of individual Np species. Also, spectra obtained from filtered solutions only showed the presence of small amounts of the Np(V) aquo species (data not shown).

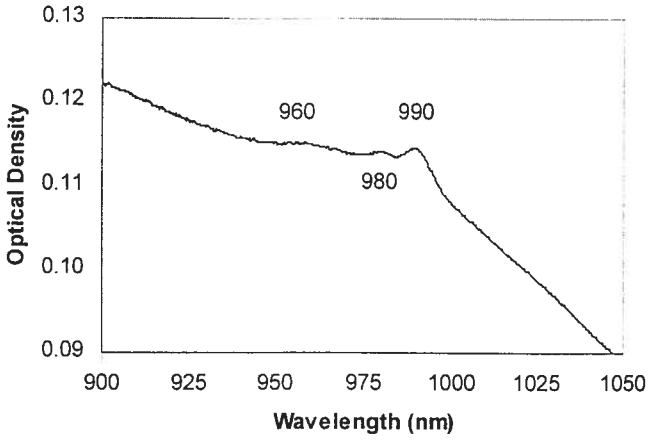

Figure 4. VIS-NIR absorption spectrum of Np in the live microcosm 10 minutes after addition and before the sediments were agitated. The 980 and 990 nm bands correspond to Np(V) species. The 960 band indicates rapid reduction of Np(V) to Np(IV). Scatter from organic matter and biomass in the microcosm caused the high-sloping background absorbance.

Evidence for formation of Np(IV) in solution does not preclude partitioning of Np(V) into the sediments. Furthermore, formation of Np(IV) in solution was only investigated by VIS-

NIR spectroscopy for the live microcosm. To determine Np redox speciation in all three vessels, XANES analysis was used to determine the primary oxidation state of Np associated with the sediments. Figure 5 shows the XANES spectrum of Np associated with sediments obtained from the gamma-irradiated microcosm compared to spectra from Np solids of known oxidation state. The spectrum shown in Figure 5 is qualitatively consistent with XANES obtained from the Np(IV) solid. Since the majority of the Np in the three microcosms partitioned into the sediments, nearly all of the Np added to the system as Np(V) was reduced to Np(IV). However, sufficient data are not available to determine if the sediment-associated Np(IV) is present as a solid precipitate or a sorbed species.

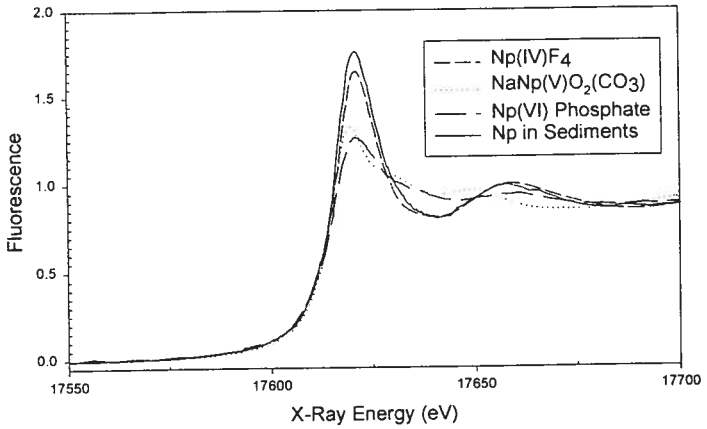

Figure 5. XANES spectrum of the L_{III} edge of Np associated with sediments in the gamma-irradiated microcosm, compared to spectra obtained from Np solids of known oxidation state. The shape and edge position of the spectrum match those of the Np(IV) solid, indicating that most of the Np partitioned into the sediments was present as Np(IV).

The rapid reduction of Np in solution observed in the biotic microcosm suggests that an abiotic compound, either a reduced metal, suspended particles, or an extracellular material produced by microorganisms, participated in the redox transformation of Np. Furthermore, although organic matter and mineral surfaces in the sediments may contribute to Np reduction [15, 20, 46], the spectrum shown in Figure 4 suggests that the redox transformation also occurred in solution. Previous work by Lieser [1, 47] showed that Np(V) is rapidly reduced to Np(IV) by Fe(II). Figure 1 shows that the long-term concentration of soluble Fe in the methanogenic microcosms is on the order of 20 μM, and additional reducing capacity may be available in the system from the formation of Fe(II)-carbonate solids. Thus, reduced Fe may play a key role in redox transformation of Np(V) in anaerobic systems. Alternatively, although reduction of Np(V) to Np(IV) by Mn(II/III) in solution is not thermodynamically feasible, sorbed Mn(II/III) species often play important roles in trace metal redox cycling in biological systems [48]; so reduced Mn species may be participating in Np reduction. Future studies will assess the individual roles of reduced Mn and Fe species in Np reduction.

CONCLUSIONS

In this work we showed that Np reduction from Np(V) to Np(IV) occurs in microcosms inoculated with methanogenic lake-bottom sediments, with subsequent association of Np with the sediments as either a sorbed species or a solid phase. Our results suggest that Np reduction in these microcosms is primarily an abiotic process caused by reducing agents present due to microbiological activity. A possible electron donor, based on previous studies, is microbially reduced Fe(II). However, more research is needed to determine if Fe(II), sorbed Mn(II/III) species, or another microbially produced compound causes Np reduction. Similarly, additional work is needed to determine the speciation of Np associated with particulate matter in solution. Because Np reduction in anaerobic systems has important implications for Np mobility in the environment, future studies must assess the individual roles of organic matter, mineral surfaces, biological processes, and reduced metals in Np reduction in anoxic natural systems.

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