

Fate of Neptunium in an Anaerobic, Methanogenic Microcosm

RECEIVED
SEP 28 1999
OSTI

J.E. Banaszak and D.T. Reed

Argonne National Laboratory
Chemical Technology Division
9700 South Cass Avenue
Argonne, IL 60439

S.M. Webb, B.E. Rittmann, J.-F. Gaillard

Northwestern University
Department of Civil Engineering
Evanston, IL 60208

The submitted manuscript has been created by the University of Chicago as Operator of Argonne National Laboratory ("Argonne") under Contract No. W-31-109-ENG-38 with the U.S. Department of Energy. The U.S. Government retains for itself, and others acting on its behalf, a paid-up, nonexclusive, irrevocable worldwide license in said article to reproduce, prepare derivative works, distribute copies to the public, and perform publicly and display publicly, by or on behalf of the Government.

To be presented at

Material Research Society Conference
Boston, Massachusetts
November 30-December 4, 1998

This work is supported by the U.S. Department of Energy, Office of Environmental Restoration and Waste Management, under Contract W-31-109-ENG-58.

This work not performed at Argonne National Laboratory.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, make any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

FATE OF NEPTUNIUM IN AN ANAEROBIC, METHANOGENIC MICROCOSM

J. E. Banaszak,^{1,2} S. M. Webb,¹ B. E. Rittmann,¹ J.-F. Gaillard,¹ and D. T. Reed²

¹Department of Civil Engineering, Northwestern University, Evanston, IL 60208

²Chemical Technology Division (CMT), Argonne National Lab, Argonne, IL 60439, reedd@cmt.anl.gov

ABSTRACT

Neptunium is found predominantly as Np(IV) in reducing environments, but Np(V) in aerobic environments. However, currently it is not known how the interplay between biotic and abiotic processes affects Np redox speciation in the environment. In order 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 fresh water 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. In order 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 fresh water 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.

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 EPA, 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 L of defined growth medium containing (in g/L) 0.8 NaCl, 1.0 NH₄Cl, 0.1 KCl, 0.1 KH₂PO₄, 0.165 MgCl₂ · 6H₂O, 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 (10mM) and MnO_x (15mM), 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 this 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 ⁶⁰Co 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 N₂/CO₂ (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% CH₄ 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 CH₄ on a gas chromatograph 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 H₂CO₃ and subsequent Gran analysis [25].

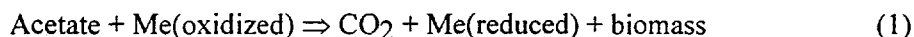
The actinide microcosms were sampled for Np solubility by needle syringe. In the live microcosm, samples were drawn for Np analysis before and after agitation of the sediments. Np solubility in the live and abiotic microcosms was determined by energy-specific scintillation counting (Packard 2500) of 0.2- μ m 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) 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. Np standards of various oxidation states were prepared by recovering solids from the following syntheses: Np(IV)F₄ by addition of excess fluoride to Np(IV); NaNp(V)O₂CO₃ 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 Fe³⁺ and Mn⁴⁺ [28-32]. This process can be represented qualitatively by:



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:



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 CO₂ 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 relationship between 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 CO₂ increased the total carbonate concentration in solution. However, after 110 days, the alkalinity in the vessels showed a decreasing trend. Similarly, after 50-60 days, the concentration of soluble Mn and Fe decreased, and stabilized after 80 days, 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, the stable solids in alkaline, anaerobic systems with elevated carbonate concentrations [33].

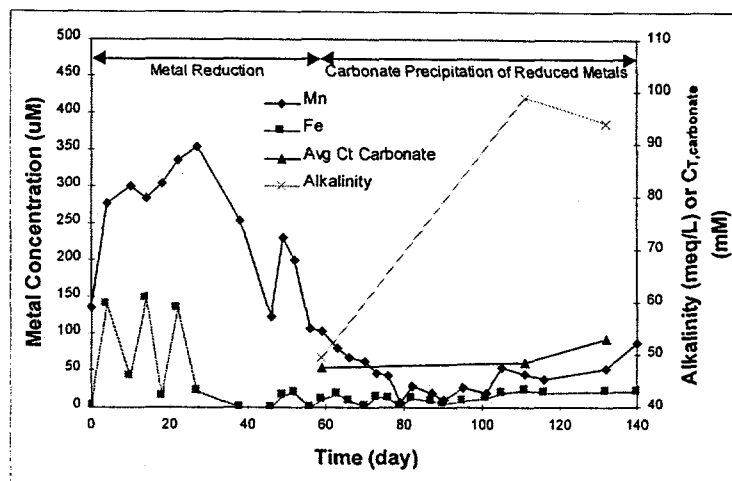


Figure 1. Concentration of soluble Mn, Fe, total carbonate, and alkalinity in non-actinide methanogenic microcosms fed NaAcetate and MnO_x as electron-donor and -acceptor substrates. All points are the average from two vessels. The increase in metal solubility was caused by utilization of the metals 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 decreased alkalinity 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. 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 particulates 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.

Oxidation state of Np in the microcosms

The Np partitioning noted in the microcosms could have been caused by any of several

mechanisms. 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].

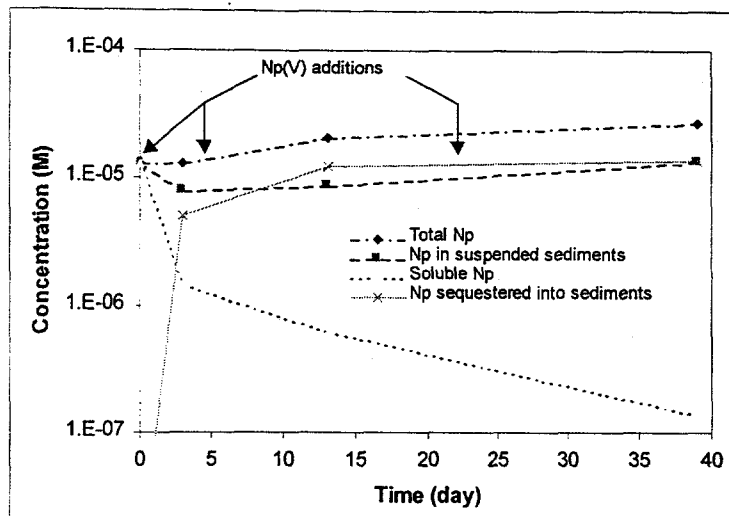


Figure 2. Partitioning of Np in the methanogenic microcosm. Soluble Np is defined as the quantity passing a 0.2- μm filter. The soluble Np in the vessel decreased by two orders of magnitude. 50-55% of the Np was sequestered into the sediments; a significant fraction of the actinide remained associated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

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 $\text{Np(V)O}_2\text{CO}_3^-$ 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).

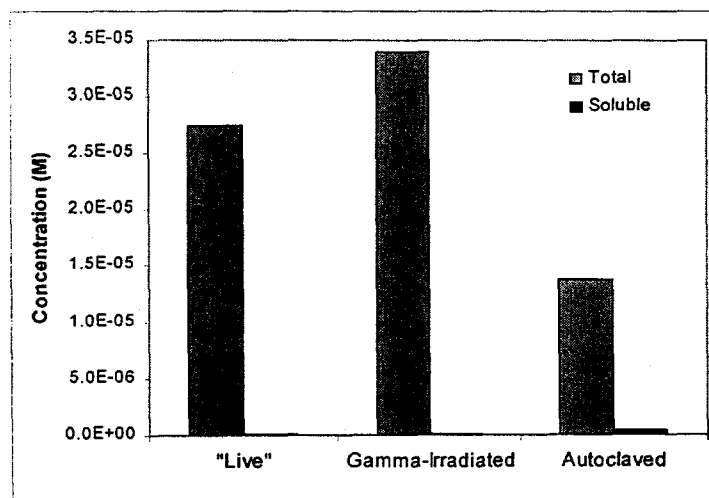


Figure 3. Np partitioning in live and abiotic microcosms. In all three vessels, soluble Np decreased to approximately 10^{-7} M. The similarity in final Np solubility suggests that an abiotic mechanism affected Np partitioning.

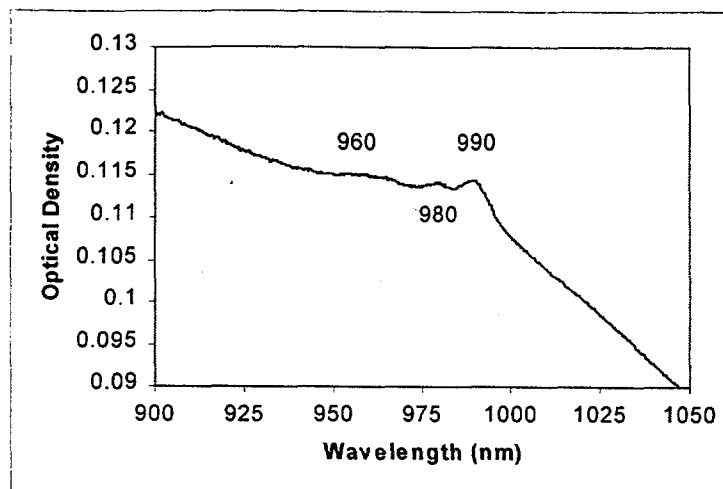


Figure 4. VIS-NIR absorption spectrum of Np in the live microcosm 10 minutes after addition and before the sediments were agitated. The 980 and 990 nm bands correspond to Np(V) species. The 960 band indicates rapid reduction of Np(V) to Np(IV). Scatter from organic matter and biomass in the microcosm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

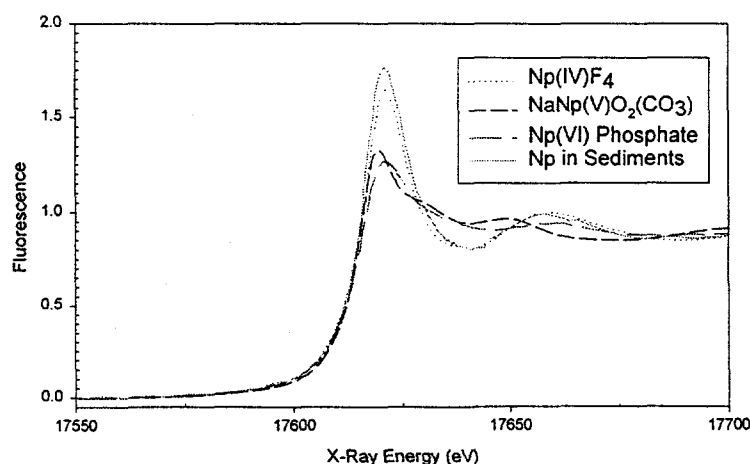


Figure 5. XANES spectrum of the LIII edge of Np associated with sediments in the gamma-irradiated microcosm, compared to spectra obtained from Np solids of known oxidation state. The shape and edge position of the spectrum match those of the Np(IV) solid, indicating that most of the Np partitioned into 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 particulates, 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 μ M, 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.

ACKNOWLEDGMENTS

The authors would like to acknowledge the assistance of Scott Aase of CMT for XANES sample preparation, Jeremy Kropf of CMT/MR-CAT for XANES analyses, and Tory Steed of the Chemistry Division at ANL for the gamma irradiation. This work was funded by Argonne National Laboratory directed research funds to investigate actinide speciation in environmental systems and by the U.S. Department of Energy Co-contaminant Chemistry Subprogram of the Subsurface Science program. The continued support of Dr. Frank Wobber (DOE/ES/OBER) is gratefully acknowledged. Use of the Advanced Photon Source was supported by the U.S. Department of Energy, Basic Energy Sciences, Office of Energy Research, under Contract No. W-31-109-Eng-38. The MR-CAT beamlines are supported by the member institutions and the U.S. DOE-BES-OER under Contracts DE-FG02-94ER45525 and DE-FG02-96ER45589.

REFERENCES

1. Lieser, K. H. and U. Mühlenweg, *Radiochimica Acta* **43**, 27 (1988).
2. Taylor, D. M., *The Science of the Total Environment* **83**, 217 (1989).
3. Wildung, R., personal communication, 1997.
4. Thompson, R. C., *Radiation Research* **90**, 1 (1982).
5. Pratopo, R. M., H. Moriyama, and K. Higashi, in "Proceedings of the 1989 Joint International Waste Management Conference", Vol. 2, p. 309, 1989.
6. Hakanen, M. and A. Lindberg. (1995). "Technetium, Neptunium and Uranium in Simulated Anaerobic Groundwater Conditions." *YJT-95-02*, Voimayhtiöiden Ydinjätetoimikunta (Nuclear Waste Commission of Finnish Power Companies), Helsinki.
7. Lieser, K. H., *Radiochimica Acta* **70/71**, 355 (1995).

8. Silva, R. J. and H. Nitsche, *Radiochimica Acta* **70/71**, 377 (1995).
9. von Gunten, H. R. and P. Benes, *Radiochimica Acta* **69**, 1 (1995).
10. Francis, A. J., *Journal of Alloys and Compounds* **213/214**, 226 (1994).
11. Francis, A. J. and C. J. Dodge, *Environmental Science and Technology* **24**, 373 (1990).
12. Macaskie, L. E., J. R. Lloyd, R. A. P. Thomas, and M. R. Tolley, *Nuclear Energy-Journal of the British Nuclear Energy Society* **35**, 257 (1996).
13. Banaszak, J. E., D. T. Reed, and B. E. Rittmann, *Journal of Radioanalytical and Nuclear Chemistry* (accepted).
14. Barton, L. L., K. Choudhury, B. M. Thomson, K. Steenhoudt, and A. R. Groffman, *Radioactive Waste Management and Environmental Restoration* **20**, 141 (1996).
15. Choppin, G. R. and L. F. Rao, in "Transuranium Elements - A Half Century" (L. R. Morss and J. Fuger, eds.), p. 262. American Chemical Society, Washington, DC, 1992.
16. Francis, A. J., C. J. Dodge, F. Lu, G. P. Halada, and C. R. Clayton, *Environmental Science and Technology* **28**, 636 (1994).
17. Gorby, Y. A. and D. R. Lovley, *Environmental Science and Technology* **26**, 205 (1992).
18. Lovley, D. R., E. J. P. Phillips, Y. A. Gorby, and E. R. Landa, *Nature* **350**, 413 (1991).
19. Lovley, D. R., E. E. Roden, E. J. P. Phillips, and J. C. Woodward, *Marine Geology* **113**, 41 (1993).
20. Reed, D. T., S. Aase, D. Wygmans, and J. E. Banaszak, *Radiochimica Acta* (in press).
21. Wolin, *Journal of Biological Chemistry* **238**, 2882 (1963).
22. Murray, J., *Journal of Colloid and Interface Science* **46**, 357 (1974).
23. Chiswell and Halloran, *Talanta* **38**, 641 (1991).
24. Stookey, *Analytical Chemistry* **42**, 779 (1970).
25. Dryssen, D. and L.G. Sillen, *Tellus*, **19**, 113., *Tellus* **19**, 113 (1967).
26. Conradson, S. D., *Applied Spectroscopy* **52**, 252A (1998).
27. Konigsberger, D. C. and R. Prins, (eds.), "X-ray Absorption: Principles, Applications, Techniques of EXAFS, SEXAFS, and XANES." John Wiley and Sons, New York, 1988.
28. Lovley, D. R., *Annual Review of Microbiology* **47**, 263 (1993).
29. Lovley, D. R., M. J. Baedeker, D. J. Lonergan, I. M. Cozzarelli, E. J. P. Phillips, and D. I. Siegel, *Nature* **339**, 297 (1989).
30. Nealson, K. H. and D. Saffarini, *Annual Reviews in Microbiology* **48**, 311 (1994).
31. Myers, C. R. and K. H. Nealson, *Science* **240**, 1319 (1988).
32. Lovley, D. R., *Microbiological Reviews* **55**, 259 (1991).
33. Stumm, W. and J. J. Morgan, "Aquatic Chemistry," p. 1022. John Wiley & Sons, Inc., New York, 1996.
34. Zajic, J. E., "Microbial Biogeochemistry," p. 345. Academic Press, New York, 1969.
35. Fahey, J. A., in "The Chemistry of the Actinide Elements" (J. J. Katz, G. T. Seaborg, and L. R. Morss, eds.), Vol. 1, p. 443. Chapman and Hall, New York, 1986.
36. Nakayama, S., T. Yamaguchi, and K. Sekine, *Radiochimica Acta* **74**, 15 (1996).
37. Girvin, D. C., L. L. Ames, A. P. Schwab, and J. E. McGarrah, *Journal of Colloid and Interfacial Science* **141**, 67 (1991).
38. Triay, I. R., C. R. Cotter, M. H. Huddleston, D. E. Leonard, S. C. Weaver, S. J. Chipera, D. L. Bish, A. Meijer, and J. A. Canepa. (1996). "Batch Sorption Results for Neptunium Transport through Yucca Mountain Tuffs." *LA-12961-MS*, Los Alamos National Laboratory, Los Alamos.
39. Tochiyama, O., H. Yamazaki, and T. Mikami, *Radiochimica Acta* **73**, 191 (1996).
40. Clark, D. L., S. D. Conradson, S. A. Ekberg, N. J. Hess, D. R. Janecky, M. P. Neu, P. C. Palmer, and C. D. Tait, *New Journal of Chemistry* **20**, 211 (1996).
41. Clark, D. L., S. D. Conradson, S. A. Ekberg, N. J. Hess, M. P. Neu, P. D. Palmer, W. Runde, and C. D. Tait, *Journal of the American Chemical Society* **118**, 2089 (1996).
42. Neck, V., W. Runde, J. I. Kim, and B. Kanellakopoulos, *Radiochimica Acta* **65**, 29 (1994).
43. Bidoglio, G., G. Tanet, and A. Chatt, *Radiochimica Acta* **38**, 21 (1985).
44. Runde, W., M. P. Neu, and D. L. Clark, *Geochimica et Cosmochimica Acta* **60**, 2065 (1996).
45. Carnell, W. T. and H. M. Crosswhite, in "The Chemistry of the Actinide Elements" (J. J. Katz, G. T. Seaborg, and L. R. Morss, eds.), Vol. 2, p. 1235. Chapman and Hall, New York, 1986.
46. Yaozhong, C., T. Bingmei, and L. Zhangji, *Radiochimica Acta* **62**, 199 (1993).
47. Lieser, K. H., *Chemiker-Ztg* **110**, 215 (1986).
48. Lienemann, C.-P., M. Taillefert, D. Perret, and J.-F. Gaillard, *Geochimica et Cosmochimica Acta* **61**, 1437 (1997).