Biogeochemistry of plutonium and uranium in intertidal sediments

M. AL-BOKARI[1], J. R. LLOYD[2], M. J. KEITH-ROACH[3] AND F. R. LIVENS[4]

[1]Centre for Radiochemistry Research, University of Manchester, UK (albokari2003@hotmail.com)
[2]School of Earth, Atmospheric and Environmental Sciences, University of Manchester, UK (jon.lloyd@manchester.ac.uk)
[3]School of Earth, Ocean & Environmental Sciences, University of Plymouth, UK (miranda.keith-roach@plymouth.ac.uk)
[4]Centre for Radiochemistry Research, University of Manchester, UK (francis.livens@manchester.ac.uk)

Intertidal sediments of the NE Irish Sea basin contain elevated levels of transuranic and other nuclides derived from the authorised low level discharges to sea made by the Sellafield fuel reprocessing plant. The majority of the discharges occurred more than 25 years ago and the radionuclides have now become incorporated in offshore and intertidal sediments. These sediments provide a rare opportunity to explore the behaviour of artificial radionuclides in the natural environment. Microbially-driven redox cycling occurs in the sediments and this has been linked to seasonal variations observed in transuranic element solubilities.

Poised microcosm experiments were established using these sediments, and nitrate-, iron- and sulfate-reducing conditions developed. Radionuclide concentrations were measured by alpha spectrometry (^{234,238}U; ^{238,239,240}Pu) and high resolution ICPMS (^{235,236}U). The microbial communities were characterised by DNA/RNA extraction and PCR amplification, followed by cloning and sequencing.

In the poised microcosms, plutonium solubility is enhanced approximately 6-fold in both nitrate- and iron-reducing systems, with smaller changes in uranium solubility. Neither uranium nor plutonium are affected by sulfate-reducing conditions. ^{234}U is more soluble than ^{238}U, consistent with the establishment of disequilibrium, but this effect is even greater for the artificial isotope ^{236}U, which can be used as an indicator for technogenic uranium.

The onset of nitrate-, iron- or sulfate-reducing conditions is accompanied by substantial shifts in microbial community structure, and both DNA- and RNA data give similar outcomes. In nitrate- and iron-reducing conditions, the communities are dominated by known nitrate- and iron-reducing organisms respectively. In the sulfate-reducing microcosms, known sulfate-reducers comprise only a small proportion of the community.

References

OJ Marsden, L Abrahamsen, ND Bryan, JP Day, LK Fifield, C Gent, PS Goodall, K Morris & FR Livens (2006) *Sedimentology,* **53**, 237-248

Keith-Roach, M.J., Day, J.P., Fifield, L.K., Bryan, N.D. & Livens, F.R. (2000) Environ. Sci. Technol. **34**, 4273-4277

Solubility measurements of Neptunium-incorporated soddyite

DANIEL S. ALESSI, JEREMY B. FEIN, TORI Z. FORBES, PETER C. BURNS, JENNIFER E. S. SZYMANOWSKI, AND JENALEE U. ALMES

Department of Civil Engineering and Geological Sciences, University of Notre Dame, Notre Dame, IN, 46556, USA (dalessi@nd.edu)

Spent nuclear fuel is likely to alter to uranyl minerals under the oxidizing conditions of a geological repository. Radionuclides, such as neptunium, may become incorporated into these secondary uranyl mineral structures, potentially altering the solubility of the phases and hence the mobilities of U and Np in the repository environment. Soddyite ($(UO_2)_2(SiO_4)(H_2O)_2$) forms as an alteration product of spent nuclear fuel in laboratory settings (e.g., Finch *et al*., 1999), and significant concentrations of Np can be incorporated within soddyite (Klingensmith and Burns, 2007). The solubility and thermodynamic properties of pure soddyite have been studied (Gorman-Lewis *et al*., 2007). It is unclear, however, what effect Np(V) incorporation into the mineral structure of soddyite will have on the mineral solubility or on the extent to which Np is released from the phase.

We synthesized soddyite in the presence of 10 to 600 ppm aqueous Np(V) and measured the release of U, Np, and Si as a function of time under controlled pH conditions. XRD and FTIR analyses demonstrated that soddyite remained the only stable uranyl phase during the course of the experiments. We use the data to constrain the value of the apparent solubility product of soddyite as a function of Np concentration in the mineral. These values can be used to predict the extent of Np release from Np-bearing soddyite phases, and therefore are useful for modelling Np mobility under repository conditions.

References

Finch, R.J., Buck, E.C., Finn, P.A., Bates, J.K., 1999. In *Scientific Basis for Nuclear Waste Management XXII*, Materials Research Society Symposium Proceedings, 556, 431-438.

Gorman-Lewis, D., Mazeina, L., Fein, J.B., Szymanowski, J.E.S., Burns, P.C., Navrotsky, A., 2007. *J. Chem. Thermodynamics* **39**, 568-575.

Klingensmith, A.L., Burns, P.C., 2007. *American Mineralogist*, accepted.