Surface Complexation of Neptunium with Iron Oxides

James L. Jerden and A. Jeremy Kropf, Chemical Engineering Division, Argonne National Laboratory

Introduction

- Our work focuses on developing a predictive understanding of actinide release from a breached spent nuclear fuel waste package in a geologic repository.
- Our experiments focus on neptunium because it is anticipated to be the main long-term (greater than 75,000 years) dose-contributing radioelement for the proposed Yucca Mountain nuclear waste repository.
- Our results will facilitate the development of mechanistically based predictive models that are needed to assess the safety performance of nuclear waste repositories.

Challenges

- Once a commercial spent nuclear fuel waste package has been breached its metal structural components will corrode. Over thousands of years the spent fuel assemblies will be surrounded by a mass of iron oxides (Figure 1).
- The question is: as the spent fuel oxidizes and dissolves, how will the mass of iron oxide corrosion products influence radionuclide transport into the environment?
- The processes under investigation are: the adsorption (surface complexation) of neptunium onto mineral surfaces (Figure 2) and precipitation of neptunium as a separate mineral phase.

Our Approach

- We are studying neptunium interaction with iron oxides using inductively coupled plasma mass spectrometry (ICPMS, analyses by Argonne's Analytical Chemistry Laboratory) and x-ray absorption spectroscopy (XAS, done at Argonne's Advanced Photon Source MR-CAT beamline).
- ICPMS is used to determine the concentration of neptunium in simulated groundwater solutions before and after they have been reacted with iron oxides.
- XAS is used to obtain molecular structural information on the neptunium surface complexes that form at the solution/iron oxide mineral interface (Figure 3).

Results

- Early results indicate that in neutral groundwaters neptunium is readily adsorbed by the common steel corrosion products goethite and magnetite. Thus, in a corroding waste package neptunium transport will be retarded by interactions with iron oxides (Figures 4 and 5).

Physical/Chemical Scenario Under Investigation

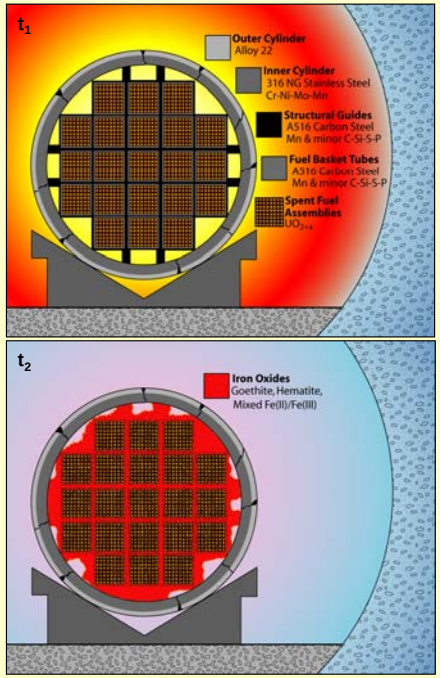

Figure 1. Cross-section through a geologic repository tunnel showing a breached waste package containing commercial spent nuclear fuel. Over thousands of years the metal components in the waste package weather to form a mass of iron oxides that surround the spent fuel.

Process Under Investigation

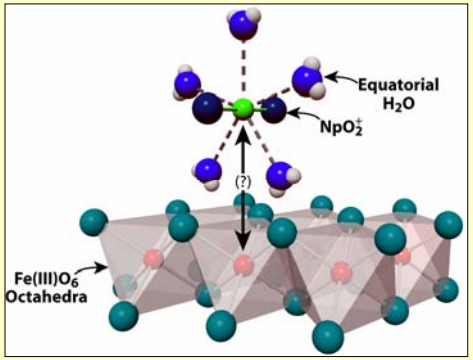

Figure 2. Molecular illustration of a neptunium solution complex interacting with an iron oxide mineral surface (example is goethite, α-FeOOH). Our goal is to determine the bond lengths and coordination environment around the neptunium at the mineral surface.

Experimental Approach

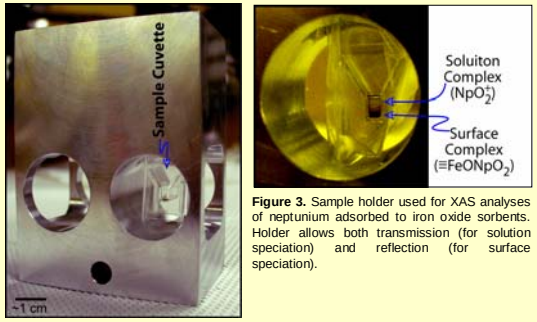

Figure 3. Sample holder used for XAS analyses of neptunium adsorbed to iron oxide sorbents. Holder allows both transmission (for solution speciation) and reflection (for surface speciation).

Solution Results

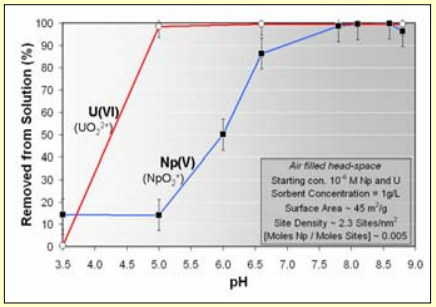

Figure 4. This plot shows the amount of neptunium and uranium removed from solution by the iron oxide goethite (α-FeOOH) under different pH conditions.

X-ray Absorption Results

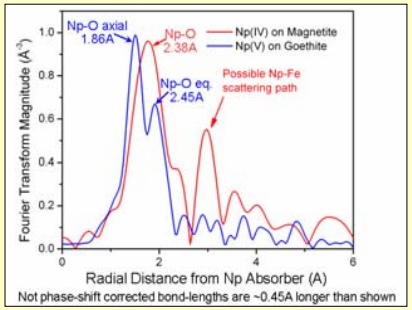

Figure 5. Example of processed XAS data showing a radial distribution function that yields information on bond-lengths within the neptunium surface complex.

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