

## Poster #205

### Characterization of Redox Mediated Alterations in $\text{PuO}_2(\text{s})$ , $\text{NH}_4\text{PuO}_2\text{CO}_3(\text{s})$ and $\text{NpO}_2(\text{s})$ Sources in Multi-Year Field Lysimeter Studies

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The RadFLEx (Radionuclide Field Lysimeter Experiment) at the DOE Savannah River Site is examining long-term vadose zone transport of Np and Pu under natural conditions. In this experiment,  $\text{Pu(IV)O}_2$ ,  $\text{Np(IV)O}_2$ ,  $\text{Np(V)O}_2\text{NO}_3$ , and  $\text{NH}_4\text{Pu(V)O}_2\text{CO}_3$  sources (as 1-10 mg solids sandwiched between glass fiber filter papers) are buried midway in a sandy clay loam soil filled 61 cm long x 10 cm diameter lysimeters. Pu lysimeters were deployed in triplicate and Np lysimeters in duplicate for multi-year retrieval and analysis. Additionally, a set of archived sources were preserved in the laboratory under inert conditions. Leachate is collected from these lysimeters approximately every three months to provide a measure of radionuclide transport.

Comparison with data from previous field lysimeter experiments with plutonium originating from  $\text{Pu(VI)}$  sources was transported significantly further than  $\text{Pu(IV)}$  sources. New experiments with a soluble  $\text{NH}_4\text{Pu(V)O}_2\text{CO}_3$  source indicated relatively little transport of Pu after 2.5 years with greater than 95% of the plutonium remaining within the source. X-ray absorption spectroscopy (XAS) analysis of initial source archived in an inert atmosphere and sources exposed to lysimeters indicate some reduction to  $\text{Pu(IV)}$  within the sources leading to the formation of  $\text{Pu(IV)O}_2$ . Thus, there appears to be an auto-reduction of  $\text{NH}_4\text{Pu(V)CO}_3$  to  $\text{Pu(IV)O}_2$  even under inert conditions. However, solvent extraction on archived and field-deployed sources show the archived source still contains around 40%  $\text{Pu(V)}$  whereas the same source from a field lysimeter deployed for 2.5 years contained less than 10% of  $\text{Pu(V)}$ . Laboratory studies have shown that the presence of sediment accelerates the reduction of  $\text{Pu(V)}$  to  $\text{Pu(IV)}$ .

A second set of lysimeters contain  $\text{Np(IV)O}_2$  and  $\text{Np(V)O}_2\text{NO}_3$  sources for comparison with the Pu sources. Aqueous Np was measured in the effluent from duplicate  $\text{Np(V)O}_2\text{NO}_3$  bearing lysimeters within 18 months of deployment whereas Np was not measured in the effluent of initially  $\text{Np(IV)O}_2$  lysimeters for 4 years. After recovery of one  $\text{Np(V)}$  and one  $\text{Np(IV)}$  source after 4 years of exposure, more than 99% of the total Np was leached from the initially  $\text{Np(V)O}_2\text{NO}_3$  source and approximately 50% was leached from the initially  $\text{Np(IV)O}_2$  source. Transport from the  $\text{Np(IV)O}_2$  source was not expected due to the low solubility of source material. However, as this was observed, it is likely that the source has oxidized from  $\text{Np(IV)}$  to  $\text{Np(V)}$  while in contact with oxidizing rainwater. The concentrations of Np in the soil from the  $\text{Np(IV)O}_2$  source are an order of magnitude lower than in the  $\text{Np(V)O}_2\text{NO}_3$  source, suggesting that the entirety of the source has not oxidized. Electron microscopy and x-ray absorption spectroscopy (XANES/EXAFS) analysis of the source materials have verified oxidation of  $\text{Np(IV)}$  to  $\text{Np(V)}$  as well as a shift from a crystalline to an amorphous phase. Our current efforts are relating these observed changes in source oxidation state to the migration of Pu and Np within the lysimeters.

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