Characterization of Redox Mediated Alterations in PuO$_2$(s), NH$_4$PuO$_2$CO$_3$(s) and NpO$_2$(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, Pu(IV)O$_2$, Np(IV)O$_2$, Np(V)O$_2$NO$_3$, and NH$_4$Pu(V)O$_2$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 sources have shown plutonium originating from Pu(VI) sources was transported significantly further than Pu(IV) sources. New experiments with a soluble NH$_4$Pu(V)O$_2$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 Pu(IV) within the sources leading to the formation of Pu(IV)O$_2$. Thus, there appears to be an auto-reduction of NH$_4$Pu(V)CO$_3$ to 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% Pu(V) whereas the same source from a field lysimeter deployed for 2.5 years contained less than 10% of Pu(V). Laboratory studies have shown that the presence of sediment accelerates the reduction of Pu(V) to Pu(IV).

A second set of lysimeters contain Np(IV)O$_2$ and Np(V)O$_2$NO$_3$ sources for comparison with the Pu sources. Aqueous Np was measured in the effluent from duplicate Np(V)O$_2$NO$_3$ bearing lysimeters within 18 months of deployment whereas Np was not measured in the effluent of initially Np(IV)O$_2$ lysimeters for 4 years. After recovery of one Np(V) and one Np(IV) source after 4 years of exposure, more than 99% of the total Np was leached from the initially Np(V)O$_2$NO$_3$ source and approximately 50% was leached from the initially Np(IV)O$_2$ source. Transport from the 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 Np(IV) to Np(V) while in contact with oxidizing rainfall. The concentrations of Np in the soil from the Np(IV)O$_2$ source are an order of magnitude lower than in the Np(V)O$_2$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 Np(IV) to 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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