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Long-term Aging of Actinide Solid Sources Exposed to Environmental Conditions

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Exposure of actinide bearing solid phases to environmental conditions may result in a myriad of chemical or physical modifications including dissolution/precipitation, oxidation/reduction, and/or recrystallization/amorphization. Each of these reactions may have an impact on the long-term fate and transport of actinides in the environment. To better understand such processes, a series of field lysimeter experiments have been deployed to monitor the changes in chemical and physical properties of a variety of Pu and Np bearing solid phases including:

$\text{Pu(V)NH}_4\text{CO}_3(\text{s})$, $\text{Pu(IV)(C}_2\text{O}_4)_2(\text{s})$, $\text{Pu(III)}_2(\text{C}_2\text{O}_4)_3(\text{s})$, $\text{Pu(IV)O}_2(\text{s})$, $\text{Np(IV)O}_2(\text{s})$, and $\text{Np(V)O}_2\text{NO}_3(\text{s})$.

Lysimeters were deployed in triplicate to allow for destructive sampling after 2.5-4, 10 and 20 years.

To date, the 2.5-4 year sampling has occurred. X-ray absorption spectroscopy (XAS) of a $\text{Pu(V)NH}_4\text{CO}_3(\text{s})$ source archived in an inert atmosphere and the same source recovered from field lysimeter indicates some reduction to Pu(IV) leading to the formation of Pu(IV)O_{2+x} in both cases. However, solvent extraction of the archived source indicates that around 40% of the source remained in as Pu(V) while the field-deployed source contained less than 10% Pu(V). Thus, source reduction was accelerated when exposed to environmental conditions. Migration of Pu from a $\text{Pu(IV)O}_2(\text{s})$ source was much lower than the migration observed in previous field lysimeter experiments using $\text{Pu(VI)O}_2(\text{NO}_3)_2(\text{s})$. However, a small fraction of Pu is believed to have migrated due to transport of colloidal species.

Of the four lysimeters containing $\text{Pu(V)NH}_4\text{CO}_3(\text{s})$ sources, two were placed in soil amended with 10% natural organic matter (NOM by weight). Relatively little transport of Pu has been observed with greater than 95% of the plutonium remaining within the source. However, the lysimeter containing 10% NOM exhibited less transport than the unamended lysimeter indicating that sorption to NOM or formation of ternary complexes could be retarding Pu transport.

Complementary laboratory studies have been performed to examine the role of NOM. Batch sorption experiments examining the influence of citric acid on Pu sorption to goethite and gibbsite suggest the formation of ternary mineral-NOM-Pu complexes that enhance Pu sorption at low pH. Similar ternary complexes are hypothesized to influence Pu migration in the field experiments. Reactive transport models based on the Pu-NOM-mineral experiments are under development.