

**Poster #21-53****NpO<sub>2</sub>(s) Dissolution Under Vadose Zone Conditions**

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A novel field experiment at Savannah River Site (SRS), the Radionuclide Field Lysimeter Experiment (RadFLE<sub>x</sub>), is the basis of investigation of neptunium migration and geochemical behavior in the vadose zone. These studies probe the effect of oxidation state on neptunium transport, the effect of source characteristics on release mechanisms, and the effect of colloids on transport. With a long half-life and potentially high environmental mobility, neptunium geochemistry is of paramount importance for risk assessment and environmental health and safety, but field-scale evidence of neptunium transport from sources of varying oxidation state has yet to be reported. The specific release from NpO<sub>2</sub>(s) is of interest because typical conceptual models based on uranium oxidation would predict surface oxidation of neptunium oxide as a rate-limiting step in transport of neptunium away from the source region.

Field data indicated that downward migration of Np from a NpO<sub>2</sub>(s) source was due to transport of 1) soluble neptunyl, NpO<sub>2</sub><sup>+</sup> ions and 2) eigen colloids of NpO<sub>2</sub>(s). Both mobile species were proposed to be formed during oxidative dissolution of NpO<sub>2</sub>(s). Based on these observations, a hypothesis for new experiments was developed wherein dissolution of polycrystalline phases occurs via alteration of phases along grain boundaries and formation of mobile colloids or polynuclear aqueous species. New NpO<sub>2</sub>(s) sources were placed in lysimeters and three depths and exposed for one year. Electron microscopy verified alteration of NpO<sub>2</sub>(s) through formation of granules along grain boundaries (Figure 1). Complimentary laboratory-based dissolution studies were initiated under vadose zone conditions (~pH 5, oxic conditions), used to mimic environmental conditions the source was exposed to in field lysimeters. Both aqueous and solid phases are monitored to identify the rate and mechanisms involved in NpO<sub>2</sub>(s) dissolution.

This work is motivated by a lack of dissolution studies of NpO<sub>2</sub>(s), particularly non-hydrated or amorphous phases, at environmentally relevant conditions. Specifically, there is a need for greater understanding of the mechanisms of NpO<sub>2</sub>(s) dissolution, including grain boundary formation, relative importance of presence of oxygen and water on grain boundary formation and dissolution, rates of dissolution in presence and absence of oxygen, and potential impact of colloidal species. Overall, these efforts seek to validate observed field data and bridge understanding of NpO<sub>2</sub>(s) dissolution from field to nano scale.