Incorporation of pentavalent neptunium into uranyl phases that may form as alteration products of spent nuclear fuel.

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Laboratory-scale simulations and studies of natural analogues have shown that alteration of spent nuclear fuel in a moist, oxidizing environment results in the formation of a variety of uranyl phases. Neptunium-237 has a half-life of 2.14 million years, and the pentavalent oxidation state is soluble in groundwater. Release of Np-237 from spent nuclear fuel in a geological repository may significantly impact the long-term performance of such a repository. Incorporation of Np, in the pentavalent oxidation state, into uranyl phases by substitution for hexavalent U is likely because of the similarity of the coordination environments of these two cations, but a charge-balance mechanism is required for substitution. A preliminary study has shown incorporation of pentavalent Np into powders of the uranyl silicate uranophane, and Na-compreignacite, a uranyl oxyhydrate [1].

Using synthesis experiments under mild hydrothermal conditions, we are examining the incorporation of pentavalent Np into selected uranyl oxyhydrates and silicates as a function of temperature and the pH of the mother solution. Analyses of powders of these uranyl phases has demonstrated both temperature and pH dependences for incorporation. Experiments are underway directed at the synthesis of single crystals of uranyl phases in the presence of 500-750 ppm pentavalent Np. The intent is to develop a basic understanding of the crystallographic and crystal chemical factors that impact incorporation of pentavalent Np into uranyl phases. Following synthesis, crystals are analyzed for Np using laser ablation ICP-MS. Preliminary results for Na-substituted metaschoepite indicate significant Np has been incorporated into the crystals. Additional phases under study include compreignacite, becquerelite, soddyite, zippeite, and $(UO_2)_3(PO_4)_2(H_2O)_4$.

[1] Burns, P.C., Deely, K.M. & Skanthakumar, S. (2003): Neptunium incorporation into uranyl compounds that form as alteration products of spent nuclear fuel: Implications for geologic repository performance. *Radiochimica Acta* 92, 151-159.