Neptunium substitution in synthetic uranophane and soddyite

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ABSTRACT

Alteration of spent nuclear fuel in a geological repository under oxidizing conditions may result in uranyl compounds and incorporation of Np-237 into uranyl alteration phases could impact repository performance. Powders of synthetic soddyite, (UO₂)₂(SiO₂)₂(H₂O)₆, and uranophane, Ca[[(UO₂)₃(SiO₂)OH]₂(H₂O)₆], were synthesized under mild hydrothermal conditions in the presence of Np⁵⁺. Synthesis experiments were conducted at various temperatures and pH of the initial solutions. Powders of soddyte exhibit increasing Np concentration with the synthesis temperature at a pH of 4, consistent with substitution of Np⁵⁺ for U⁶⁺ in the structure. In contrast, the general decrease of the Np concentration in powders of uranophane with increasing synthesis temperature is inconsistent with incorporation of Np⁵⁺ into the structure of uranophane. These results further support the possibility that uranyl phases that form in a geological repository may impact Np mobility, but also demonstrate that additional studies of the impact of the crystal structure on incorporation are needed.

Keywords: Soddyite, uranophane, neptunium, nuclear waste, Yucca Mountain

INTRODUCTION

Geological disposal of nuclear waste poses a daunting range of scientific and engineering challenges (Macfarlane and Ewing 2006). A repository should prevent a range of radionuclides with vastly different chemical properties from being transported into the environment. The proposed repository at Yucca Mountain, Nevada is intended for the disposal of about 70,000 metric tons of spent nuclear fuel in the unsaturated zone of a welded tuff sequence. Following failure of canisters that encapsulate the waste, contents may be exposed both to air and water.

Studies of natural analogues (e.g., Finch and Ewing 1992; Pearcy et al. 1994), as well as laboratory-scale studies of spent nuclear fuel (Wilson 1990; Finn et al. 1996; Finch et al. 1999; McNamara et al. 2005) and unirradiated UO₂ (Wronkiewicz et al. 1992, 1996) indicate that spent fuel is unstable under moist oxidizing conditions, and alteration rates may be appreciable. The most important alteration products of spent fuel under such conditions are a suite of uranyl minerals, with uranyl oxide hydrates forming early, followed by uranyl silicates or uranophases, depending upon the composition of the water (Finch et al. 1999). Uranyl silicates commonly form due to alteration of uraninite, UO₂³⁻, and the uranyl silicates uranophane, Ca[(UO₂)₃(SiO₂)OH]₂(H₂O)₆, boltwoodite, (K,Na)[(UO₂)₃(SiO₂ OH)]₂(H₂O)₆, haixweite, Ca[(UO₂)₃SiO₂(2OH)]_{2}(H₂O)₆, and soddyte, (UO₂)₂(SiO₂)(H₂O)₂, have been found as alteration products of spent fuel or UO₂ in laboratory experiments (Wilson 1990; Finch et al. 1999; Wronkiewicz et al. 1992, 1996).

Burns et al. (1997a) proposed that uranyl minerals that form as alteration products of spent fuel in a geological repository could incorporate various radionuclides into their structures, thereby potentially impacting the future mobility of these radionuclides. Of particular interest is ²³⁷Np because of its long half life (2.14 × 10⁶ years) and potential mobility in groundwater. The most stable oxidation state of Np in solution is pentavalent. Burns et al. (1997a) suggested, on the basis of crystal-chemical arguments, that Np⁵⁺ could substitute for U⁶⁺ in crystal structures of uranyl phases, but a charge-balance mechanism would be required. More recent studies of Np crystal chemistry (e.g., Forbes and Burns 2005, 2006; Forbes et al. 2006) indicate a divergence of the crystal chemistry of Np⁵⁺ from that of U⁶⁺. Both cations occur as approximately linear actinyl ions, (NpO₂)⁺ and (UO₂)²⁺. The O atoms within the uranyl ion form strong enough bonds to U⁶⁺ to satisfy most of their bonding requirements (Burns et al. 1997b), and these O atoms seldom bond to another U⁶⁺ cation or another cation of higher valence. The Np⁵⁺ neptunyl ion has a lower formal valence and the bond valences of the bonds in the ion are lower than those in the uranyl ion (Burns et al. 1997a). The bonding requirements of the neptunyl ion O atoms are a good match with the equatorial positions of other neptunyl polyhedra. The sharing of a neptunyl ion O atom with another neptunyl ion, so that the apical ligand of one bipyramid atoms are a good match with the equatorial positions of other neptunyl polyhedra. The sharing of a neptunyl ion O atom with another neptunyl ion, so that the apical ligand of one bipyramid corresponds to an equatorial vertex of another, is common. The bond strengths within the Np⁵⁺ neptunyl ion are lower than those in the U⁶⁺ uranyl ion, and this may impact substitution of Np⁵⁺ for U⁶⁺ in uranyl minerals.

Burns et al. (2004) studied incorporation of Np⁵⁺ into powders of uranyl phases synthesized under mild hydrothermal conditions. They found incorporation of significant Np in powders of uranophane and the Na analog of compeigneacite, Na₃[(UO₂)₂(OH)]₃(H₂O), but not in metaschoepite, [(UO₂)₄O(OH)]₃(H₂O)₆, and β-UO₃(OH). As the latter two phases contain electronneutrals sheets of uranyl polyhedra and no charged species in their interlayers, whereas the former two contain cations in their...