Ba(NpO2)(PO4)(H2O), its relationship to the uranophane group, and implications for Np incorporation in uranyl minerals

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ABSTRACT

Single crystals of Ba(NpO2)(PO4)(H2O) were obtained using hydrothermal synthesis techniques. The structure was determined using single-crystal X-ray diffraction data collected using MoKα radiation and an APEX II CCD detector and was refined on the basis of F2 for all unique data to R1 = 2.41%. Ba(NpO2)(PO4)(H2O) crystallized in monoclinic space group P21/n with a = 6.905(3), b = 7.108(3), c = 13.321(6) Å, β = 105.02°, and V = 631.4 Å3. The structure contains chains of edge-sharing neptunyl pentagonal bipyramids that link through phosphate tetrahedra to form infinite sheets. This sheet-type is identical to the anion topology of the uranophane group, in particular to that of oursinite, Co[(UO2)(SiO3OH)]4(H2O)6. Similarities between Ba(NpO2)(PO4)(H2O) and the uranophane group of minerals suggests a charge-balancing mechanism for incorporation of Np5+ into uranyl minerals.

Keywords: Neptunium, uranyl mineral, uranophane, nuclear waste, crystal structure, actinide

INTRODUCTION

A geologic repository for high-level nuclear waste, such as the proposed repository at Yucca Mountain, Nevada, is faced with the challenging task of controlling the fate of a chemically diverse suite of radionuclides, including 237Np (Lieser and Muhlenweg 1988; Silva and Nitsche 1995). Commercial spent nuclear fuel is composed of 95–99% UO2, with other actinides and fission products comprising the remainder (Johnson and Werne 1994). 237Np, with a half-life of 2.14 × 106 years, is one of the key contributors to the total potential radiation dose after thousands of years for the proposed repository at Yucca Mountain. Due to the significance of 237Np for the performance of a geologic repository, as well as its presence in sites contaminated by actinides, it is important to understand its fate and transport within natural systems (Kaszuba and Runde 1999; Lieser and Muhlenweg 1988; Silva and Nitsche 1995).

Laboratory studies and characterization of natural analogs indicate that commercial spent nuclear fuel is readily oxidized upon exposure to moist oxidizing conditions similar to those expected in the proposed repository at Yucca Mountain (Finch and Ewing 1992; Finch et al. 1999; Peary et al. 1994; Shoesmith 2000; Wronkiewicz et al. 1996). Interactions between spent fuel and groundwater of composition similar to that expected at Yucca Mountain results in extensive alteration of spent fuel, and formation of a variety of uranyl oxide hydrates and uranyl silicates (Finch et al. 1999; Finn et al. 1998). It is possible that such uranyl phases will significantly impact the mobility of uranium and any other radionuclide they incorporate.

Under oxidizing conditions, the dominant oxidation states of U and Np in solution are hexavalent and pentavalent, respectively (Antonio et al. 2001; Silva and Nitsche 1995). In both cases the cations are present in solutions and crystal structures as nearly linear dioxo cations, (UO2)2+ and (NpO2)+, with bond lengths ~1.8 Å (Burns et al. 1997b). The actinyl cations are further coordinated by four, five, or six equatorial ligands to create square, pentagonal, and hexagonal bipyramids (Burns et al. 1997a, 1997b).

The crystal structures of the uranyl phases that are expected to form when spent fuel is altered under moist oxidizing conditions are dominated by sheets of uranyl polyhedra and other polyhedra containing higher-valence cations. In particular, the uranyl silicates found in tests involving spent fuel and UO2 under unsaturated conditions (Finch et al. 1999; Wronkiewicz et al. 1996) contain uranophane-type sheets of uranyl pentagonal bipyramids and silicate tetrahedra, with low-valence cations and H2O groups located in the interlayer regions. On the basis of the geometric similarities of (UO2)2+ uranyl polyhedra and (NpO2)+ neptunyl polyhedra, Burns et al. (1997b) predicted that significant Np5+ could be incorporated into uranyl phases that form as spent fuel is altered, and suggested that such incorporation could impact the mobility of Np5+ in a geological repository. However, substitution of Np5+ for U5+ in a crystal structure requires a charge-balance mechanism that may involve another substitution at some other type of site in the crystal structure. More recently, incorporation of Np5+ into powders of synthetic uranophane and the Na analog of compreignacite has been demonstrated (Burns et al. 2004), although the charge-balance mechanism that permits incorporation is uncertain.

We are examining the crystal chemistry of Np5+ to better understand the fate of Np contamination in natural systems. This involves the synthesis and structural characterization of a variety of Np5+ compounds containing environmentally relevant cations and anions. Here we describe the synthesis and structure of a novel Np5+ phosphate that is structurally related...