The crystal chemistry of neptunium sulfates and phosphates

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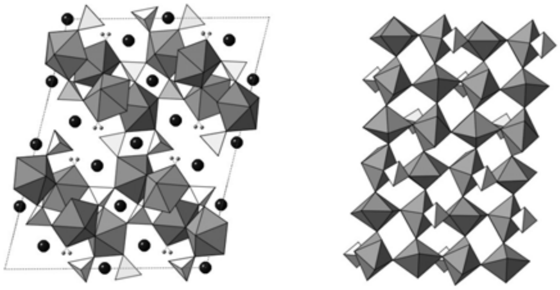
Background

Geologic repositories for nuclear waste, such as the proposed site at Yucca Mountain, Nevada, are faced with the challenging prospect of immobilizing a variety of radionuclides, including ^{237}Np, with very different chemical characteristics. Few structures of environmentally significant neptunyl compounds have been reported, therefore the basic crystallographic understanding of neptunium is lacking. Furthermore, a detailed understanding of the crystal chemistry of Np will provide a basis for studies of Np complexation in solution.

Figure 1: The crystal structures of $K(NpO_2)(SO_4)(H_2O)_{0.5}$ and $(NpO_2)_2(SO_4)(H_2O)_4$



Discussion of Results

Hydrothermal syntheses of Np(V) sulfates have resulted in several new structure types, including infinite chains, sheets, and frameworks of polyhedra. The similarities between Np(V) and U(VI) coordination polyhedra suggest that structural similarities between Np and U compounds should exist, however cation–cation interactions within Np(V) compounds result in significant structural differences. The Np(V) and Np(VI) phosphates have structures that are closely related to naturally occuring U(VI) compounds. A more detailed discussion of the crystal chemistry of environmentally relevant neptunium compounds will be presented.

Np^{5+} incorporation into U^{6+} phases that form as alteration products of spent nuclear fuel

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Incorporation of Np^{5+} into uranyl oxyhydrates predicted to form as alteration products of spent nuclear fuel may impart the future mobility of Np in the proposed geological repository at Yucca Mountain.

Method

Uranyl compounds were synthesized hydrothermally at temperatures from 80 to 140°C and solution pH ranging from 4 to 6. The temperature and pH dependence of Np^{5+} incorporation into soddyite, becquerelite, and uranophane were examined through the hydrothermal syntheses of these minerals from solutions containing ~200 ppm Np^{5+}. A double-containment method was used consisting of 7 mL Teflon cups with threaded screw-on tops. After tight closure, the cups were contained in 125 mL Teflon-lined Parr reaction vessels. 50 mL of ultrapure water was added to each vessel to provide counter pressure during heating. Following heating, the reaction vessels were allowed to cool to room temperature. All products were washed using boiling H_2O and analyzed by powder XRD to verify phase purity. Np in the products was quantified by inductively coupled plasma-mass spectrometry (ICP-MS) with a VG Elemental Plasma Quad II Plus system.

Discussion of Results

Initial results show incorporation of significant quantities of Np into the powders of synthetic uranyl minerals. The quantity of Np is related to the temperature and pH under which the phases are found. Additional experiments are being conducted to explore these trends.