

Np Incorporation into Uranyl Alteration Phases: A Quantum Mechanical Approach**L.C. Shuller¹, R.C. Ewing^{1,2}, U. Becker²**

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Neptunium is a major contributor to the long-term radioactivity in a geologic repository for spent nuclear fuel (SNF) due to its long half-life (2.1 million years). The mobility of Np may be decreased by incorporation into the U^{6+} phases that form during the corrosion of SNF. The ionic radii of Np (0.089nm) and U (0.087nm) are similar, as is their chemistry. Experimental studies have shown Np can be incorporated into uranyl phases at concentrations of ~ 100 ppm. The low concentration of Np in the uranyl phases complicates experimental detection and presents a significant challenge for determining the incorporation mechanism. Therefore, we have used quantum mechanical calculations to investigate incorporation mechanisms and evaluate the energetics of Np substituting for U.

CASTEP, a density functional theory based code that uses plane waves and pseudo-potentials, was used to calculate optimal H positions, relaxed geometry, and energy of different uranyl phases. The incorporation energy for Np in uranyl alteration phases was calculated for studtite, $[(UO_2)O_2(H_2O)_2](H_2O)_2$, and boltwoodite, $HK(UO_2)(SiO_4) \cdot 1.5(H_2O)$. Studtite is the rare case of a stable uranyl hydroxyl-peroxide mineral that forms in the presence of H_2O_2 from the radiolysis of H_2O . For studtite, two incorporation mechanisms were evaluated: (1) charge-balanced substitution of Np^{5+} and H^+ for one U^{6+} , and (2) direct substitution of Np^{6+} for U^{6+} . For boltwoodite, the H atomic positions prior to Np incorporation were determined, as well as the Np incorporation mechanisms and the corresponding substitution energies. The preferential incorporation of Np into different structure types of U^{6+} minerals was also investigated. Quantum mechanical substitution energies have to be derived at Np concentrations higher than the ones found in experiments or expected in a repository. However, the quantum mechanical results are crucial for subsequent empirical force-field and Monte-Carlo simulations to determine the thermodynamically stable limit of Np incorporation into these uranyl phases.