

## Quantum-mechanical evaluation of Np-incorporation into studtite

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### ABSTRACT

Radionuclide incorporation into the alteration products of corroded UO<sub>2</sub> in used nuclear fuel may control the release and mobility of key radionuclides, such as the very long-lived minor actinide, <sup>237</sup>Np ( $\tau_{1/2} = 2.1$  Ma). Studtite, [UO<sub>2</sub>(O<sub>2</sub>)(H<sub>2</sub>O)<sub>2</sub>](H<sub>2</sub>O)<sub>2</sub>, may form in the presence of peroxide produced by radiolysis of water in contact with the spent fuel. Experiments have indicated that the studtite structure can incorporate Np; however, due to the low concentrations in the solid, the incorporation mechanism could not be determined. In this study, density functional theory is used to calculate an optimized structure, determine the electronic density of states, and calculate the energetics of the incorporation of Np<sup>6+</sup> vs. Np<sup>5+</sup>+H<sup>+</sup> into the studtite structure. The definition of the source/sink phase (reference phase) for the cations involved in the incorporation process greatly affects the final incorporation energy. The incorporation energy of Np into studtite based on the 4<sup>+</sup> oxide reference phases (e.g., source/sink = NpO<sub>2</sub>/UO<sub>2</sub>) results in lower incorporation energies (−0.07 and 0.63 eV for Np<sup>6+</sup> and Np<sup>5+</sup> incorporation, respectively) than the incorporation energy calculated using higher-oxide reference phases (e.g., Np<sub>2</sub>O<sub>5</sub>/UO<sub>3</sub>), where the incorporation energies for Np<sup>6+</sup> and Np<sup>5+</sup> into studtite are 0.42 and 1.12 eV, respectively. In addition, Np<sup>6+</sup>-incorporation into studtite is energetically more favorable than Np<sup>5+</sup>-incorporation as assessed from the lower incorporation energy. Estimates of the solid-solution behavior from a combination of quantum-mechanical calculations and Monte-Carlo simulations indicate that the Np<sup>6+</sup>- and U<sup>6+</sup>-studtite solid solution is completely miscible at room temperature with respect to a hypothetical Np<sup>6+</sup>-studtite structure. The Np-studtite structure was calculated to be stable with respect to the corresponding oxides, but its formation may be kinetically hindered. Knowledge of the electronic structure provides insight into Np-bonding in the studtite structure. The Np 5f orbitals are within the band gap of studtite, which results in the narrow band gap of Np-incorporated studtite (1.09 eV), as compared with the band gap of studtite alone (2.29 eV).

**Keywords:** Studtite, Np-incorporation, density functional theory (DFT), quantum-mechanical calculations, electronic structure