

Quantum Mechanical Determination of the Incorporation of Pentavalent Plutonium into Carbonate and Sulfate Minerals

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Pentavalent plutonium is the most abundant form of soluble, mobile, and oxidized Pu in natural systems. The incorporation of Pu into environmentally abundant mineral hosts can strongly influence the transport and concentration of contaminants in both aqueous environments and the subsurface. This study concerns the adsorption of Pu in the pentavalent state onto carbonate and sulfate surfaces, and its subsequent incorporation into the uppermost surface layer and bulk structures using ab initio computational methods.

While previous studies have used a similar methodology for calculating the thermodynamics of incorporation, what is new in this study is that the method was extended to observe the rate-controlling steps from a species in solution (e.g., PuO_2^+ and HSO_4^- or HCO_3^-), to their co-adsorbed state on their respective carbonate or sulfate surface, followed by their co-incorporation (by replacing divalent cations and anions from the surface of the host mineral), and finally being incorporated into the bulk, mimicking the stability of co-precipitated or overgrown plutonyl defects.

Through the use of a novel method including the effects of hydration, cluster models, surface energy, and Hubbard U parameters, our findings closely approximate real-world conditions. Results suggest that barite group and aragonite mineral structures with orthorhombic symmetry, high coordination number, and large ionic radii have greater interstitial cell space and are therefore more favorable for PuO_2^+ incorporation than other host minerals.

In general, thermodynamic trends of adsorption and surface incorporation are consistent in that the adsorption is an exothermic process and the highest endothermic step is the incorporation into the surface layer, while relatively insignificant gains or losses are observed when going from surface to bulk incorporation.

These findings, and the environmentally-relevant approach that considers both hydration and mineral surfaces, have substantial implications for the long-term sequestration of mobile actinide contaminants.