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Atomistic Insight Into Actinyl (UO_2^{2+}, NpO_2^{+}) Adsorption on Smectite in the Presence of Small Organic and Inorganic Ligands

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The migration of radionuclides through the environment is a topic of great concern, particularly within the context of radioactive waste. Since multiple underground repositories for high-level waste (HLW) are under construction worldwide, it is paramount that the waste is stored safely and responsibly for thousands of years. This is especially the case since, upon the eventual degradation of the waste canisters, the radioactive contents are likely to leach into the surroundings. In the planned French facility, clay mineral-rich Callovo-Oxfordian clay rock will serve as one of the barriers intended to prevent any environmental contamination.

Two radionuclides of concern are uranium(VI) and neptunium(V), particularly in their actinyl forms – UO_2^{2+} and NpO_2^{+}, respectively. Both have isotopes with very long decay half-lives, they're radiotoxic, and most must therefore be safely stored. However, their retention by the clay minerals may be limited by both organic and inorganic complexating ligands such as carboxylates and carbonate. The former are likely to be released due to canister degradation while the latter are present due to calcite minerals. We thus aim to understand the extent to which the formation of actinyl-ligand complexes may lower the effectiveness of the clay barrier and thus increase environmental actinyl mobility.

Using classical molecular dynamics computer simulations, we investigate these multi-component systems on an atomistic scale. The simulations allow us to predict the dynamic and structural properties of our systems, including identifying surface-specific adsorption mechanisms. In our simulations, we have observed different complexation and adsorption tendencies between uranyl and neptunyl, owing to the differences in their charge. Furthermore, ligand concentration was shown to influence these processes, particularly in the case of uranyl. To provide quantitative thermodynamic underpinning to the results, we also carried out "potential of mean force" (PMF) calculations to identify free energies of adsorption and complexation for the actinyls. Ongoing work will include investigations of adsorption at clay nanoparticle edge sites and the energetics of actinyl-ligand adsorption.