

## Aqueous surface chemistry of $\alpha$ -uranophane

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Hexavalent U (VI) solid phases form in uranium mill tailings and spent nuclear fuel (SNF) under oxidizing conditions. While SNF is primarily  $\text{UO}_2$  (tetravalent), it also contains fission products and transuranium actinides. These species make up only 1-5 wt. % of the waste, but are responsible for the majority of its ionizing radiation. Given the eventual rupture of SNF packages stored underground and the formation of U (VI) solids, it is possible for these secondary phases to act as barriers for radionuclide migration through fission product adsorption events. It is thus imperative that the pH stability and surface reactivity of U (VI) solids be understood.

In this paper we seek to shed light on the pH induced dissolution mechanisms and surface reactivity of the U (VI) silicate,  $\alpha$ -uranophane using combined quantum mechanical and classical molecular dynamics methods. Within the pH studies, valence bond techniques were first used based upon the crystal structure, then combined with structural information from density functional theory (DFT). Finally, the pKa of the relevant protonation sites was determined from explicit periodic boundary DFT calculations using a complete surface hydration layer. These data compare well to recent experimental work by collaborators.

The ability of  $\alpha$ -uranophane to sorb metal ions was first examined by investigating the organizational structure of surface waters, where very strong hydrogen bonding networks were observed that involved not only the uranyl sites, but also bridging silica tetrahedra. The sorption of  $\text{UO}_2^{2+}$  was examined using a constrained molecular dynamics approach, yielding a free energy profile for the event, and indicating the preference of inner- vs. outer-sphere sorbed species.

## Geochemical and isotope tracers in pore waters from low permeability Paleozoic strata of the Michigan Basin of Southwest Ontario

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Hydrogeochemical investigations of groundwaters and porewaters in the Paleozoic formations of the Michigan Basin were carried out to address the far-field integrity of the geological system for solute migration from the Canadian Nuclear Waste Management Organization's proposed Deep Geological Repository for low and intermediate level waste. Three holes were drilled through the Paleozoic basin to the basement, providing core for pore fluid extraction and analysis a suite of geochemical species and isotopes. Water and  $\text{CO}_2$  were extracted from these low permeability shales and limestones ( $K_p < 10^{-12} \text{ m s}^{-1}$ ) by vacuum distillation of crushed rock (2 to 4 mm fraction) at 150 °C for 6 hours with volatile trapping in exetainers with liquid  $\text{N}_2$ . Pore water geochemistry was reconstructed by solute leaching of the dried rock sample normalization to gravimetric water loss. Good correlation between pore waters and groundwaters collected from three permeable zones for both isotopes and geochemistry suggests that the extraction method faithfully represents *in situ* conditions. Further confidence is provided by the coherent tracer profiles reproduced for all three core holes from which the history of brine migration can be reconstructed.