The corrosion of UO$_2$ versus ThO$_2$: a quantum mechanical investigation

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Quantum mechanical surface energy calculations have been performed on both uranium dioxide (UO$_2$) and thorium dioxide (ThO$_2$) (111), (110), and (100) surfaces to determine their relative reactivities. While UO$_2$ and ThO$_2$ both have the fluorite structure $Fm\bar{3}m$, they differ in that uranium has two dominant oxidation states, U$^{4+}$ and U$^{6+}$, while thorium only has one, Th$^{4+}$. Furthermore, UO$_2$ is an intrinsically weak p-type semiconductor with a band gap of 2.14 eV (Killeen, 1980), while ThO$_2$ is an insulator. Dissolution and spectroscopic studies indicate that UO$_2$ and ThO$_2$ have different solubilities (Sunder and Miller, 2000). We use the quantum mechanical program, CASTEP (CAmbridge Scientific Total Energy Package) to perform surface and adsorption energy calculations on the (111) surface of both materials, with specific attention to O, H$_2$O, and combined adsorption cases.

UO$_2$ and ThO$_2$ bulk unit cells were optimized to find the most stable configuration of atoms. Surface slabs were "cleaved" from the relaxed bulk for each orientation, placed in a 10 Å vacuum gap in order to simulate a free surface and were optimized. Relative surface energy trends and atomic relaxation were compared between the surfaces of UO$_2$ and ThO$_2$. The (111) surface is found to have the most energetically stable configuration of atoms in both cases, although ThO$_2$ has higher surface energy values than UO$_2$ on all three surfaces.

The (111) surface slab is doubled in width in order to increase the number of surface sites, and different starting positions for adsorbates are tested in order to calculate the most energetically favorable adsorption sites. Adsorption energy results indicate that adsorption is more favorable on the UO$_2$ (111) surface than the ThO$_2$ (111) surface. Adsorption calculations are accompanied by partial density of state (PDOS) and bandstructure analyses in order to understand the role of electrons during adsorption on semi-conducting versus insulating mineral surfaces.