# The corrosion of $UO_2$ versus $ThO_2$: a quantum mechanical investigation

F. N. Skomurski[1], L. C. Shuller[2], U. Becker[1], and R. C. Ewing[1,2]

[1]University of Michigan, Dept. of Geological Sciences, Ann Arbor, MI USA. fskomurs@mich.edu, ubecker@umich.edu, rodewing@umich.edu
[2]University of Michigan, Dept. of Materials Science and Engineering, Ann Arbor, MI USA. lshuller@umich.edu

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 $ThO_2$ have the fluorite structure *Fm3m*, 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 semi-conductor 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 minerals, with specific attention to O, $H_2O$, 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 analysis in order to understand the role of electrons during adsorption on semi-conducting versus insulating mineral surfaces.

Killeen, J. C. (1980) *J. Nucl. Mat.* 88, 185-192.
Sunder, S. & Miller, N. H. (2000) *J. Nucl. Mat.* 279, 118-126.