# 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-3m*, 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 Serial Total Energy Package) to perform surface and adsorption energy calculations on the (111) surface of both materials, 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. Adsortpion 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.

## References

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Sunder, S. & Miller, N.H. (2000) J. Nucl. Mat. 279, 118-126.

# Standard thermodynamic properties of aqueous lanthanides and solubility of synthetic pure Nd monazite

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Study of lanthanides ($Ln^{3+}$) as analogs of actinides and as major products of radioelement fission, is necessary for prediction of their solubility, reactivity and transport in hydrothermal fluids. Monazite is considered as a potential confining matrix. Previous studies concluded that the standard thermodynamic properties based on experimental data, obtained at low temperature and pressure, fail to predict the behaviour of $Ln^{3+}$ in hydrothermal systems.

In order to obtain more realistic values, apparent molar volumes and heat capacities of ($La^{3+}$, $Nd^{3+}$, $Gd^{3+}$, $Yb^{3+}$) triflates solutions are determined up to 300°C and 300 bars, using a vibrating tube flow densimeter and a differential flow calorimeter. The univalent triflate anion of a large size is stable at high temperature and doesn't form complexes with $Ln^{3+}$. Properties of triflic acid and sodium triflate are also measured to obtain the properties of triflate anion. Our new data will be used to readjust the $Ln^{3+}$ parameters in the revised H.K.F. model.

Our solubility measurements of synthetic pure Nd monazite based on isotope dilution suggest that $Nd(OH)_3°$ is the major species that is present at high temperature and pressure in $H_2O$-NaCl-HCl and $H_2O$-$H_3PO_4$-NaCl-HCl solutions, at pH close to neutrality.

The reaction is: $NdPO_{4(s)} + 3\,H_2O \leftrightarrow Nd(OH)_3° + H_3PO_4°$, with $\Delta_fG(NdPO_{4(s)})_{25°C} = -1817.7\ J.mol^{-1}$. The temperature dependance of $\log K_R$ for this reaction is shown below.
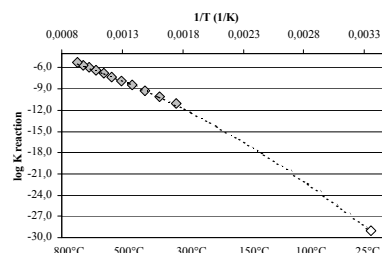


At temperature close to 300°C, experiments with Cl-rich solutions show the presence of charged species, their nature remaining to be specified.