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Quantum mechanical versus empirical potential modeling of UO_2 surface-water interactions

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The interaction of uranium dioxide (UO_2) surfaces with water and oxygen is of interest from a mineralogical and a nuclear waste management perspective. Spectroscopic analyses are often used to investigate mineral surface-water interactions involving UO_2, however, questions remain regarding the form of oxygen and water on different crytallographic faces. Therefore, we are using a graphical computer modeling program (Cerius^2) that contains a quantum mechanical total energy calculation package (CASTEP) in order to calculate the relative energies of different UO_2 crystal faces, and ultimately the stability of water and oxygen on these faces. The results from quantum mechancial calculations are compared with empirical potential modeling results.

In order to model the different UO_2 surfaces, a bulk UO_2 structure is generated and allowed to relax in order to find the minimum energy configuration of atoms. Then, a series of surface slabs: (111), (110), and (100), is created from the bulk model and each slab is placed in a vacuum gap. The slabs range from 2 to 5 unit cells thick. The energy of each slab is minimized under conservative conditions (*e.g.*, fixed cell parameters) and under less restrictive conditions (*e.g.*, P1 symmetry, a,b, and γ variable). We find that the conservative surface energy calculations do not reflect the expected relative surface energies proposed by empirical potential models. However, when the cell parameters are allowed to vary, the relative surface energies of the three faces suggest that the (111) face has the lowest surface energy, while the (100) face has the highest. These results are in agreement with trends in empirical energy calculations [1] and with what is expected based on the structural termination of each slab.

One main difference in the calculated results is that the quantum mechanically derived surface energies are consistently lower than the empirical potential energies. This discrepancy may be due to the use of first principle calculations that reflect the behavior of atoms and electronic changes on the surface and in the near-surface region more closely than the use of empirical potentials, which are derived from bulk UO_2 properties. Calculations of hydroxylated and oxidized surfaces aid in the interpretation of the dissolution behavior of these crystal faces.

Reference

[1] Abramowski, M., Redfern, S.E., Grimes, R.W., and Owens, S. (2001) *Surf. Sci.* **490** (3), 415-420.

2.1.21

Surface properties of manganite (γ-MnOOH)

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Minerals play an important role in the biogeochemical cycling of different elements and substances in the environment. In order to understand and predict this cycling, the knowledge of surface properties of minerals, such as acid-base characteristics, is very important. In this context, the secondary (hydr)oxo minierals of iron, aluminium and manganese are the most important. Here, the acid-base characteristics of the manganite (γ-MnOOH) surface is described at pH > 6 where the dissolution of the mineral is negligible. Synthetic manganite was used in the experiments. From x-ray photoelectron spectroscopy [1], electrokinetic mobility measurements, and potentiometric titrations, a one-pK_a model was constructed that explains the observations from the different techniques. The data show no ionic strength effect at pH < 8.2, which is the pH of the iso electric point (pH(iep)): but this ionic strength effect was visible above pH 8.2. To explain this, Na^+ -ions were suggested to form surface complexes. The following equilibria were established:

$$=MnOH_2^{+½} \leftrightarrow =MnOH^{-½} + H^+$$
$$\log \beta_{(intr.)} = -8.20$$

$$=MnOH_2^{+½} + Na^+ \leftrightarrow =MnOH^{-½}\ Na^+ + H^+$$
$$\log \beta_{(intr.)} = -9.64$$

The excess of Na^+ at the surface at high pH was supported by XPS measurements. The concentrations obtained from XPS and the theoretical calculations, although not directly comparable, are in the same order of magnitude. In the XPS measurements, approximatelly 5 atomic % of excess Na^+ was observed at the surface and the model predicts that 1-2 % of the surface sites would be occupied by Na^+ ions in manganite suspensions with 10 mM NaCl.

References

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