

Ab initio modeling of magnetite surfaces for plutonium retention

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UNIVERSITY OF BERN

Anita Katheras^{a*}, Konstantinos Karalis^a, Matthias Krack^b, Andreas C. Scheinost^c, Sergey V. Churakov^{a,b}

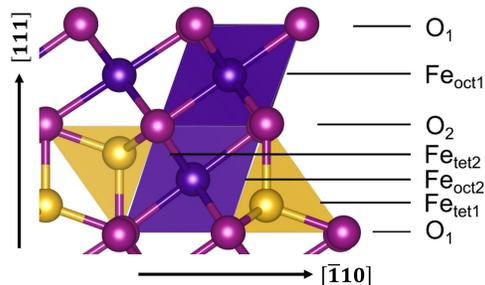
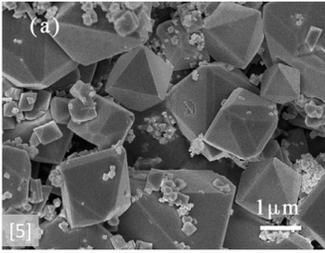
^a University of Bern, Switzerland; ^b Paul Scherrer Institute, Switzerland; ^c Helmholtz-Zentrum Dresden-Rossendorf, Germany.

* Corresponding author: anita.katheras@geo.unibe.ch.

Abstract

In many countries, thick steel casks are used for the containment of high-level radioactive waste in deep geological repositories. In contact with pore-water, steel corrodes forming mixed iron oxides, mainly magnetite (Fe₃O₄). After tens of thousands of years, casks may breach allowing leaching of the radionuclides by pore-water. The magnetite can retard radionuclides either by adsorption or structural incorporation as concluded from X-ray absorption spectroscopy (XAS) [1,2]. Our goal is to better understand these interaction mechanisms by using computer simulations alongside experiments [3]. Energetically favourable termination and stoichiometry of possible (111) Fe₃O₄ surfaces at repository relevant conditions are revealed based on Kohn-Sham density functional theory with Hubbard correction (DFT+U) for Fe 3d electrons [4]. The U value to describe Pu 5f electrons is determined allowing for subsequent investigations of the Pu uptake mechanisms on expected magnetite (111) surfaces with *ab initio* molecular dynamic simulations (AIMD).

Magnetite (111) surfaces



Various stoichiometries of oct1/oct2/tet1/tet2 terminations of {111} facet were investigated with the CP2K code (QUICKSTEP module) keeping overall charge neutrality (adsorbed H) and slab symmetry avoiding dipole moment. The system energy derived from these self-consistent field (SCF) simulations is used to determine the surface stability.

$$\mu_{molecular} = E_{SCF} + E_{ZPE} + \Delta G_{0K \rightarrow T}$$

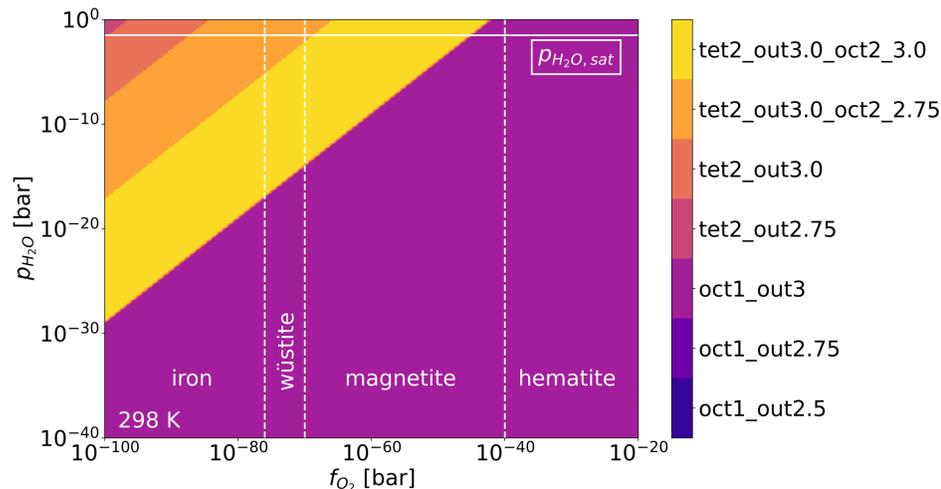
$$G_{slab} = E_{SCF,slab} - \frac{1}{2}N_H\mu_{H_2} - \frac{1}{2}N_O\mu_{O_2} - N_{Fe}E_{SCF,Fe} + F_{vib}$$



Surface stability evaluating the surface energy as function of...

... water and oxygen fugacity:

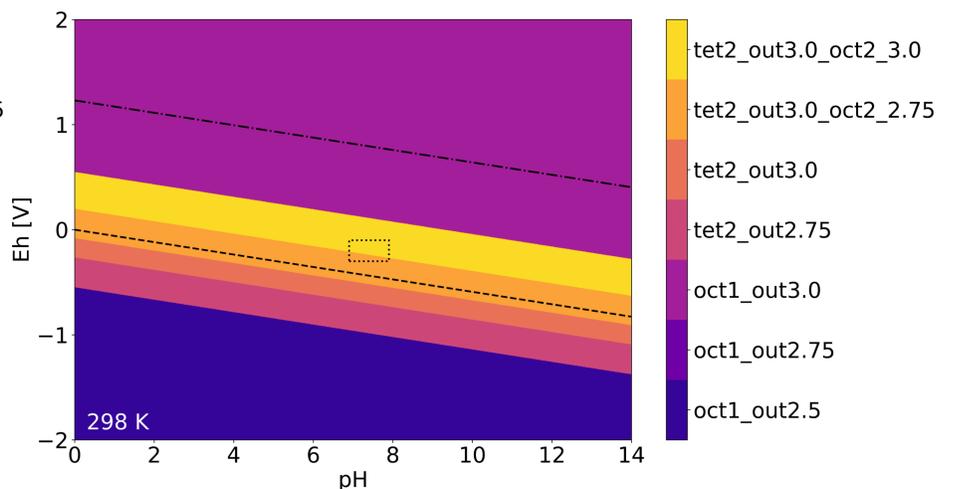
$$\gamma = \frac{1}{2A} \left(G_{slab} - N_{Fe_3O_4}\mu_{Fe_3O_4} - N_{O_2}\mu_{O_2} - N_{H_2O}\mu_{H_2O} - k_B T \ln \left(\frac{p_{H_2O} f_{O_2}}{p_{H_2O}^0 p_{O_2}^0} \right) \right)$$



... Eh and pH:

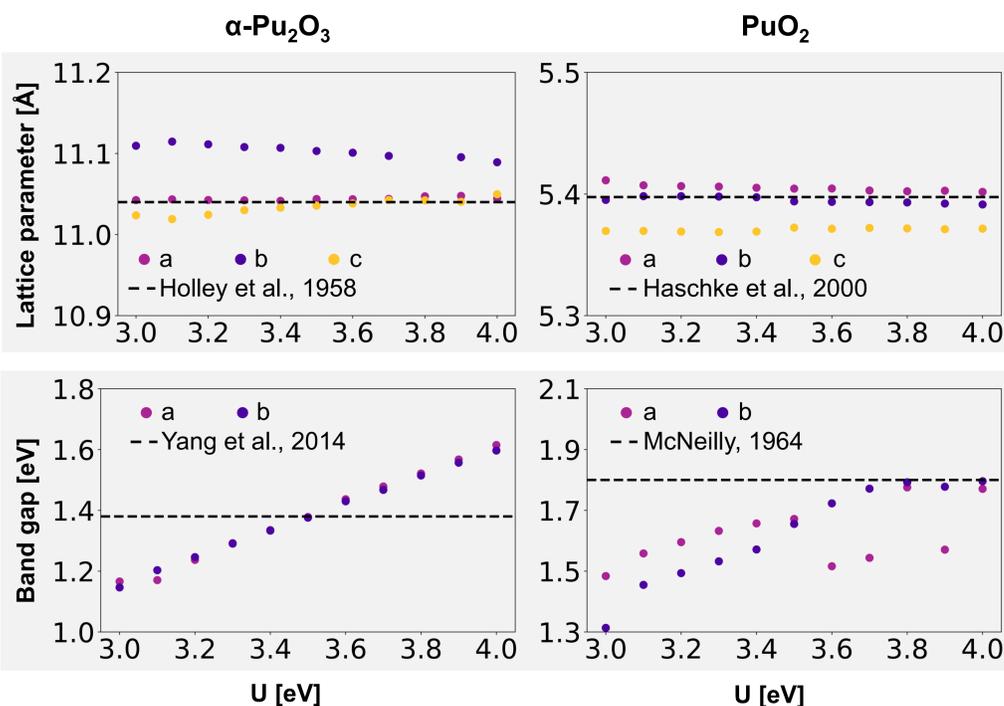
$$\gamma = \frac{1}{2A} \left(G_{slab} - N_{Fe_3O_4}\mu_{Fe_3O_4} - N_O\mu_{H_2O} - E_h(Q + 2N_O - N_H) - RT(2N_O - N_H) \ln(10) \text{pH} \right)$$

Expected long-term repository conditions: Eh -0.3 V ... -0.1 V, pH 6.9 ... 7.9 [6]



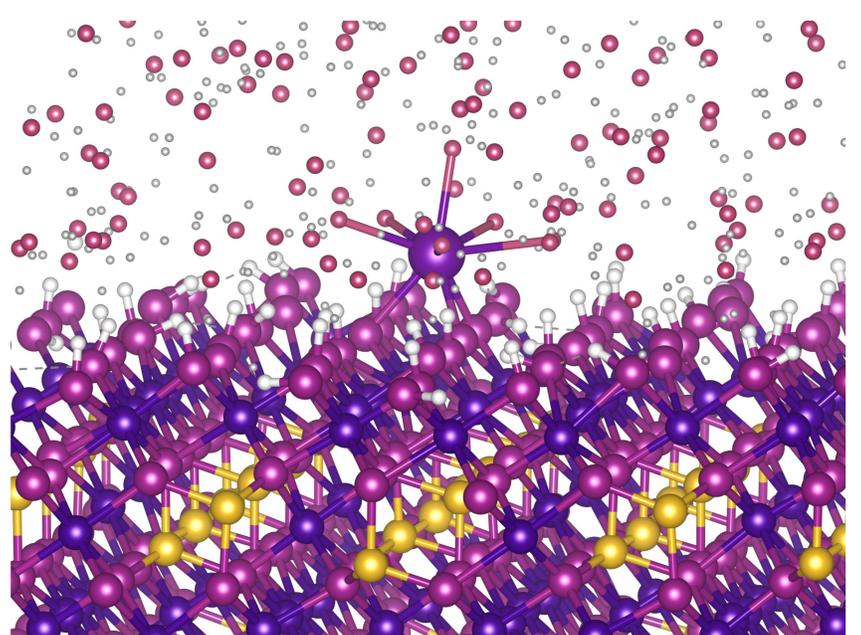
Interaction with H₂O and Pu

Hubbard U parameter for Pu(III,IV)



Adsorption of Pu(III) at magnetite (111) surface

XAS: tri-dentate complex at oct1, R(Pu-O) = 2.45 Å, CN = 9 [1,2]
AIMD (ionic radii adapted for visualization): plausible



Key findings and outlook

We examined the magnetite (111) surfaces expected under geological repository conditions. Using DFT+U, we can predict the most stable and, hence, most likely occurring surfaces to be oct1 and tet2 close to water saturation and the expected redox conditions. The obtained surface stoichiometry at relevant redox conditions is used to investigate the surface uptake of Pu³⁺ including the description of Pu 5f electrons based on our successful DFT+U study. These results will be used to obtain theoretical EXAFS spectra and compared to experimental findings.

References

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