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# *Ab initio* modeling of magnetite surfaces for radionuclide retention

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In many European countries (e.g., France, Switzerland), thick steel casks are foreseen 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 ($Fe_3O_4$). After tens of thousands of years, casks may breach allowing for leaching of the radionuclides (e.g., Tc and Pu) into pore-water. The radionuclides can be retarded by corrosion products either by adsorption or via structural incorporation [1,2]. The molecular scale mechanisms of these phenomena are investigated by *ab initio* simulations and X-ray absorption spectroscopy (XAS).

The dominant low-index surfaces of magnetite particles and their termination at the relevant conditions were identified based on Kohn-Sham density functional theory (DFT), using the open-source CP2K code [3]. The DFT+*U* method was employed for the strongly correlated *3d*, *4d* and *5f* electrons of Fe, Tc, and Pu, respectively. After benchmarking the model setup, the surface energies of the (111) facet with different surface terminations and water coverage were analyzed as function of redox conditions and pH. The Eh and pH predominance diagram (cf. fig. 1) could be predicted for the most stable surfaces under real repository conditions. Subsequently, we used ab initio molecular dynamics (MD) to simulate sorption structures of radionuclides on the expected magnetite (111) surfaces based on experimental findings [2,4].

[1] R. Kirsch et al. (2011), *Environ, Sci. Technol. 45*, 7267–7274.

[2] E. Yalçintaş et al. (2016), *Dalton Trans. 45*, 17874-17885.

[3] T. D. Kühne et al. (2020), *J. Chem. Phys. 152*, 194103.

[4] T. Dumas et al. (2019), *ACS Earth Space Chem*. 3, 2197-2206.

Figure 1: Surface stability plot of different magnetite (111) surfaces as function of Eh and pH at 298 K. oct1 and tet2 refer to certain octahedral (oct) or tetrahedral (tet) terminations, further, the charge of the outmost iron layer is denoted.

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