Crystal growth of the barite (001)-surface in aqueous solution via a hybrid DFT-continuum solvation approach

STEFAN RUDIN1, PIOTR KOWALSKI1, MARTINA KLINKENBERG1, DIRK BOSBACH2 AND FELIX BRANDT1

1Forschungszentrum Jülich
2Institute of Energy and Climate Research (IEK-6), Forschungszentrum Jülich GmbH

Presenting Author: s.rudin@fz-juelich.de

226Ra is a major constituent of naturally occurring radioactive materials (NORM) and readily forms solid solutions with barite. In some scenarios for the direct disposal of spent nuclear fuel, 226Ra dominates the dose after 100,000 years. Several studies have shown that upon contact with 226Ra, original pure barite is replaced by the (Ba,Ra)SO4 solid solution, which lowers the radium aqueous solubility by several orders of magnitude [1]. Recrystallization experiments indicate a wide range of 3 to 16,900 years until full equilibration [2]. While the thermodynamic aspects of the (Ba,Ra)SO4 solid-solution have been extensively studied, the details of the molecular scale mechanisms controlling the Ra-uptake kinetics are not well understood.

Here we harness advanced methods of computational quantum mechanics: a hybrid Density Functional Theory (DFT) and Self Consistent Continuum Solvation (SCCS) approach for computation of barite-aqueous phase interface, and a Nudged Elastic Band (NEB) approach for computation of activation energies, to shed the light on the barite crystal growth process. The applied first principles-based approach represents an advancement comparing to previous atomistic modelling studies of Stack et al. [3], which apply a simplified, force-field-based description of interatomic interactions. We computed the activation energies for Ba2+, Ra2+ and SO42- attachment and incorporation into barite at relevant surface sites, allowing for a detailed understanding of the structural and kinetic aspects of barite crystal growth. In particular we characterized the Ba2+, Ra2+ and SO42- attachment on the barite (001) surface and the role of the aqueous phase in the process, focusing on “Kink-site-nucleation” [3]. The obtained results are compared to existing experimental data [4] and results of previous computational studies [3]. Similarities and differences between Ra and Ba uptake will be highlighted. In addition, we will discuss the stability of the nine most relevant barite-surface terminations. We will elucidate the challenges associated with applying atomistic simulations for understanding the details of crystal growth.