

Atomistic computational modeling of contaminant cation adsorption at the edge surfaces of clays

BRICE F. NGOUANA-WAKOU¹, IULIA ANDRONIUK¹,
ANDREY G. KALINICHEV^{1,2}

¹ Laboratoire SUBATECH (UMR 6457 - Institut Mines-
Telecom Atlantique), 44307, Nantes, France
(*correspondence: kalinich@subatech.in2p3.fr)

² International Laboratory for Supercomputer Atomistic
Modeling and Multi-Scale Analysis, National Research
University Higher School of Economics, Moscow, Russia

Quantitative nanoscale understanding of the structure, dynamics, and reactivity of hydrated clay interfaces is extremely important for many energy, environmental, and geochemical applications: geological disposal of radioactive waste, shale gas exploration and exploitation, geological carbon sequestration, etc. Experimental studies of such systems are extremely challenging, and their results often require extensive interpretation in order to extract quantitative interface-specific information from the measurements.

Atomistic computer simulations have already significantly complemented such efforts in recent years by providing detailed molecular-scale picture of the specific effects of the mineral substrate structure and composition on the structure, dynamics and reactivity of the interfacial aqueous species. However, in such simulations, clay particles are usually represented by infinite layers, i.e., only the interaction of H₂O molecules and ions with the basal (001) surfaces of clays can be investigated.

Here we extend these simulation studies to include (010) and (110) edge surfaces of finite size clay nano-particles using the recently developed upgrades of the ClayFF force field which now allows to accurately model the hydrated edge surfaces of clay minerals in classical molecular dynamics (MD) simulations. The structure of aqueous solutions and ion adsorption at the edge surfaces of kaolinite, montmorillonite, and muscovite is investigated in detail for a number of divalent cations - Sr²⁺, Ba²⁺, and Ra²⁺ - relevant for the problems of geological nuclear waste disposal and shale gas exploration, where they may have a negative environmental impact as potentially mobile naturally occurring radioactive materials (NORMs). Selected surface adsorption sites identified on the basis of unconstrained MD simulations are then probed in more detail using the potential of mean force calculations, thus providing unique site-specific quantitative information on the free energies of adsorption and the thermodynamics of interfacial cation exchange.