Interfacial chemistry under nanoconfinement

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We use a combination of molecular modelling and experimental techniques to investigate the role of nanoscale confinement on interfacial geochemistry. Nanopores are widespread in geologic systems, and fluids in these pores exhibit structural and dynamic properties different from bulk fluids or ideal bulk fluid-mineral interfaces. We investigate changes in water structure in nanopores and their effects on the coordination chemistry, uptake and kinetics of metal adsorption.

Our experimental studies use well characterized synthetic mesoporous silica and alumina with fixed pore sizes ranging from 2 to 8 nm, for straightforward comparison with classical molecular dynamics (MD) simulations of silica and alumina using slit-pore, cylindrical nanopore, and nanoparticle aggregate models. We have created model silica and alumina surfaces based on simulated annealing and surface protonation that result in more realistic (less flat) quenched surfaces with surface hydroxyl densities comparable to the mesoporous materials. Accompanying *ab initio* molecular dynamics (AIMD) simulations provide details of the energetics and local ion coordination environments as ions adsorb onto surfaces.

Initial experimental batch adsorption results indicate that both uptake and kinetics of Cu^{2+} adsorption on silica increase with decreasing pore size. AIMD simulations suggest that as Cu^{2+} desorbs from a partially deprotonated silica surface, it hydrolyzes one of the H_2O molecules in its first solvation shell, becoming $CuOH(H_2O)_3$. Future research will include both experiments and modelling to investigate both solution and surface speciation of Cu^{2+} in silica nanopores.

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