Peering into nanopores: XAS studies of Zn adsorption under confinement

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Nanopores (<100 nm diameter pores) contribute significantly to the total specific surface area of rocks and soils, and synthetic nanoporous substrates have been proposed as a useful material for environmental remediation. Within these nanopores, the physiochemical processes of sorption and transport differ from those within macropores. Despite the ubiquity of confined spaces in natural and industrial porous media, we lack an understanding of how the effects of nanopore confinement vary with pore size, and the molecular-scale mechanisms controlling nano-confinement phenomena in environmentally relevant systems (i.e., mineral surfaces in aqueous solutions).

We studied the simplified Zn-silica-H_2O model system to probe sorption reactions on nanopore surfaces that commonly influence the fate of contaminants in complex geologic contexts. Batch reactors containing aqueous Zn and macroporous, nanoporous, or macro-particulate silica substrates at variable pH (6-8) were equilibrated for 48 hours on a shaker table. The pore size distributions and surface areas of the silica substrates were quantified with BET and non-local density functional theory analysis of the adsorption branch of N_2 isotherms. Adsorption of Zn onto macro-particulate and macro- and nanoporous silica, normalized to surface area, is greatly enhanced in silica with 300 nm and smaller pores relative to macro-particulate silica. Shell-by-shell fitting of the EXAFS spectra reveals that Zn adsorbed at a surface coverage of ~0.2 μmol m^{-2} in silica nanopores exhibits tetrahedral coordination as opposed to octahedral coordination in silica macropores and on silica macro-particles. This difference in Zn coordination may be the result of complexation at different surface sites and/or alteration of the hydration shell of Zn under nano-confinement. Confinement effects within nanopores represent an emerging frontier in geochemistry, and pursuit of molecular-scale understanding will contribute to more accurate modeling of reactive transport in natural porous media and to the use of nanoporous materials to sequester contaminants.