

Roles of Nanopores in Enhancing Adsorption of Dissolved Mo and Uranium Anions / Metal-Complexes

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Nanopores are ubiquitous in porous geologic media and constitute an integral part of the overall porosity of rocks, especially in the “critical zone” where land meets the fluid envelopes of the Earth. Existing data indicate that contribution of nanopores to the total surface area in geologic materials could be very significant. It has been found that in B-horizon soils, pores with diameters smaller than 100 nm account for 10 to 40% of the total porosity, whereas the pores with diameters larger than 1 nm contribute > 60% of it.

It is generally known that a condensed phase may exhibit different physical and chemical properties as its dimension is reduced from macroscopic to nanometer scale, due to the effects of quantum confinement. For a given nanoporous material, two factors are expected to control the enrichment of trace metals in nanopores: the accessible pore surface area and the effect on solution and mineral reactivity induced by nanopore confinement. Nanopore confinement can modify the water properties and dissolved species, including metal complexes like uranyl-carbonates and molybdate. FTIR study shows that vibration modes at the range of ~1620 to ~1640 cm^{-1} from nanopore water (1625 cm^{-1} for water in 2 nm pores, and 1635 cm^{-1} for water in 3 nm pores) are different from that from bulk water (1643 cm^{-1}). Both goethite and alumina-based nanopore surfaces enhance adsorption of uranyl-carbonate complexes dramatically and also stabilize the adsorbed complexes. Adsorption experiment based on Ti-oxide nanotube and molybdate anion also proves that nanotube inner surface preferentially adsorbs molybdate anions than outer surface. Low dielectric constant of confined water in the nanotubes and nanopores is a factor for promoting adsorption and increasing stability of the adsorbed species. The adsorbed U and Mo in nanopores and nanotubes are difficult to be reduced and desorbed. Nanoporous alumina or Al-hydroxide may be used as sinker of uranyl for in-situ immobilization of uranium in groundwater aquifers.

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