

Uranyl-calcium coordination in calcium carbonate systems

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The interaction of U-carbonate complexes with calcium in both aqueous and solid phases has implications for the fate and transport of U in the subsurface. The ages of calcite deposits are commonly determined by using U isotope ratios, assuming that U is not mobile in the sediment. Remediation efforts for U-contaminated subsurface environments now focus on reducing relatively mobile U(VI) to insoluble U(IV). Environmentally relevant concentrations of Ca²⁺ in calcareous groundwater were recently shown to have negative effects on bioreduction of U(VI), hence affecting the fate and transport of U.

X-ray absorption fine structure (XAFS) measurements are ideally suited for investigating incorporation of dilute concentrations of U into calcium carbonate aqueous solutions and solid phases. Our U LIII edge XAFS, micro-x-ray fluorescence, and micro-XAFS measurements on natural and synthetic samples have revealed U incorporation into natural calcite, as well as Ca²⁺ counterions associated with uranyl-triscarbonate moieties in solution. These results on the local chemical environment of U directly address the geologic dating of calcite deposits and the feasibility of bioremediation of U in calcium- and carbonate-rich environments.

Spent nuclear fuel: Research needs

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In 2005, the global inventory of spent nuclear fuel (SNF) is approximately 175,000 metric tonnes (slightly less than one third is in the USA) (Ewing, 2004). Most of this SNF is still at 236 nuclear power stations where it was originally generated in 36 different countries. In the USA, the inventory in 2010 will be 61,800 metric tonnes of heavy metal (tHM) with a total activity of 32.6 GCi. The USA presently has an open nuclear fuel cycle (without reprocessing) with SNF planned for ultimate disposal at Yucca Mountain, Nevada. The SNF represents >95% of the radioactivity. Thus, a major challenge of successful geologic disposal of radioactive waste is to understand the long-term behavior of SNF.

SNF is essentially UO₂ with minor impurities, mainly the fission product (3%) and transuranium elements (1%). The precise radionuclide inventory and physical state of the fuel depend on its irradiation and thermal history. Three critical parameters change dramatically during the first 10,000 years in the repository: 1.) the thermal output will decrease to < 0.1%; 2.) the radioactivity will decrease to < 0.01%; 3.) the inventory of radiotoxic nuclides will change. Radionuclides of major importance under oxidizing conditions include: ²³⁹Pu, ²³⁷Np, ¹²⁹I and ⁹⁹Tc. Less problematic elements include: ²⁴¹Am, ⁷⁹Se and ³⁶Cl. These elements exist in a variety of chemical forms: incorporated into the UO₂ structure, as separate phases in inclusions and at grain boundaries. Corrosion under oxidizing conditions leads to the formation of a variety of U(VI)-phases. An understanding of their long-term behavior requires an improved knowledge of their structures, thermochemical parameters, solubilities, substitution mechanisms for trace radionuclides, surface properties and the kinetics of dissolution/precipitation reactions. Natural uranium deposits, such as the Oklo natural reactors, also provide important data. This paper reviews recent research on these topics, and its relation to the properties of SNF.

Reference

Ewing, R.C. (2004) Environmental impact of the nuclear fuel cycle. In *Energy, Waste, and the Environment: A Geochemical Perspective*, Geological Society, London, Special Publications, 236, 7-23.