

Dissolution of mixed uranium, thorium dioxide in groundwater under anoxic conditions with hydrogen peroxide additions.

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Geological disposal is internationally recognised as the safest long-term disposal solution for spent nuclear fuel. A significant amount of research has focused on how uranium-based fuels will dissolve in a breach of containment scenario. It has been found that U(VI) is much more soluble than U(IV) so the redox conditions underground are hugely significant. Groundwaters are naturally reducing but the oxidising potential is increased by the formation of radiolytic oxidants in the water by alpha radiation from spent nuclear fuel. Hydrogen peroxide can be used to simulate radiolytic effects since it is the most long-lived of the oxidants produced during radiolysis. Hydrogen peroxide is consumed in both the oxidative dissolution of uranium and in autocatalytic decomposition at the actinide oxide surface.

This research anticipates the geological disposal of spent mixed-oxide nuclear fuels containing uranium and plutonium dioxides. The ultimate aim is to understand the effect on the dissolution of an additional actinide in the uranium dioxide matrix. Mixed-oxide fuels are more radioactive so the production of radiolytic oxidants will be larger. At the same time, plutonium dioxide is much less soluble than uranium dioxide. After an initial uranium dissolution, a plutonium rich layer could form a protective layer at the surface. By using lower activity samples of mixed uranium thorium dioxide, it is possible to model the presence of an additional actinide whilst separating the competing factors of radiolytic production and consumption.

In this dissolution study groundwater doped with hydrogen peroxide is added at a flow rate of 6.5 nL/s by a syringe pump into groundwater solutions containing pellets of U_{0.72}Th_{0.28}O₂. The leachant volume is returned to 50 ml by sampling every 5 days. The aim was to simulate the production of radiolytic oxidants more realistically than in simple batch experiments. Sedimentary rock groundwater has been simulated by synthetic Callovo-Oxfordian groundwater, typical of the French disposal site at Bure. The ion concentrations were followed through the study by ICP-MS and the hydrogen peroxide concentrations by UV/vis spectroscopy.