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Spent fuel corrosion under hydrogen

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Radiolysis studies and leaching experiments with spent nuclear fuel and UO_2(s) indicate that molecular hydrogen both impedes radiolytic decomposition of the studied formation water simulates and considerably inhibits corrosion of the UO_2(s) matrix. Still, there is insufficient knowledge about the molecular mechanisms of the protective hydrogen effect on SNF corrosion.

Radiation induced UO_2(s) corrosion was studied with spent nuclear fuel (SNF) pellets and depleted UO_2(s) at elevated hydrogen pressure in NaCl brine. Some of the SNF leaching experiments were conducted in presence of Fe-bearing phases (metallic iron and magnetite). Currently, two SNF leaching experiments are conducted in NaCl brine containing traces of bromide. For comparison, depleted UO_2(s) pellets were γ-irradiated in NaCl brine at 10^{-3} mol H_2 (kg H_2O)$^{-1}$ and 0 - 10^{-4} mol Br^- (kg H_2O)$^{-1}$, respectively. In the γ-radiolysis experiments a significant increase in the yield of radiolytic products due to Br^- is observed. Both, in the γ-radiolysis experiment with Br^- and in that without Br^-, the UO_2(s) sample was oxidized, and the concentration of dissolved uranium was controlled by precipitation of meta-schoepite and clarkeite. In the spent nuclear fuel corrosion experiment under H_2 overpressure, aqueous concentrations of Tc and Np were in the range of solubilities of Tc(IV) and Np(IV) hydroxides, whereas measured U concentrations were between solubilities of U(VI) and U(IV) phases. The release rate of Sr was significantly increased in the presence of Br^- traces. Results of the complementary spent nuclear fuel corrosion and γ-radiolysis experiments allow the conclusion that Br^- traces reduce significantly the protective hydrogen effect with respect to the release of certain radionuclides and the yield of radiolytic products. Since bromide affects the radiolytic reactions between hydrogen and oxidizing radiolysis species, the observed bromide effect on the radionuclide release from spent nuclear fuel emphasizes the relevance of the radiolytic interaction of hydrogen with respect to the overall hydrogen effect on SFS dissolution.