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Interaction of hydrogen with radiolysis products in NaCl solution – comparing pulse radiolysis experiments with simulations

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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. A recent international benchmark study on modeling of spent nuclear fuel corrosion shows that model uncertainties are still very large, especially regarding the effect of hydrogen as well as the respective parameters of the radiolytic reactions.

In pulse radiolysis experiments at 22 °C production and decay of $Cl_2^{\bullet-}$ radicals are studied in 0.1 and 1.0 molar NaCl solutions by observing its optical absorption over a time span of 20 ms. In addition to experiments with NaCl solutions equilibrated with N_2O at ambient pressure, a series of experiments are conducted with NaCl solutions equilibrated at 10 MPa hydrogen partial pressure and 0.1 MPa N_2O partial pressure. In the presence of hydrogen, the $Cl_2^{\bullet-}$ yield is significantly reduced compared to that in hydrogen free experiments. The effect of hydrogen on the radiolytic yield is more pronounced in 0.1 molar NaCl solution than in the relatively concentrated NaCl solution. In parallel to the experiments the evolution of the $Cl_2^{\bullet-}$ concentration is simulated using a kinetic model. Based on the comparison between measured and simulated optical absorption, which is mainly caused by the $Cl_2^{\bullet-}$ radical, the rate constant of reaction $Cl_2^{\bullet-} + Cl_2^{\bullet-} = Cl^- + Cl_3^-$ is determined as $5.2(\pm0.8)\cdot10^8$ L mol^{-1} s^{-1} at zero ionic strength. This value is within the range of published rate constants for the $Cl_2^{\bullet-}$ disproportionation reaction.