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Long-term cement-corrosion in chloride-rich solutions - a thermodynamic interpretation

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Nuclear waste disposal relies on safe enclosure of radionuclides over long time-scales. Most experiments on interactions of radionuclides with barrier materials are running for several months, in some cases up to a few years. Very few experiments are available that confirm the results on longer time-scales and reassure that equilibrium conditions will be approached on the long term.

This communication presents the latest results of full-scale cement corrosion experiments doped with uranium, which have been conducted for up to 22 years.

Cemented waste simulates of 200L size were doped with U_{nat} and exposed to $MgCl_2$-rich or NaCl-saturated brine in the Asse salt mine ($T = 28 \pm 1$ °C). Solution composition and pH were monitored regularly. Some of the experiments were terminated in order to sample and analyze the solid phases. A geochemical code with a Pitzer database for high ionic strength systems is used to calculate the aqueous and solid phases expected at equilibrium conditions.

In order to evaluate the thermodynamic database for the cementitious system, calculated solid phases and solution compositions were additionally compared to results of laboratory experiments on cement corrosion in $MgCl_2$-rich solutions with mass to volume ratios (m/V) between 0.025 and 1.0.

Solid and solution composition of the laboratory experiments after $\sim$3 years agree well with results predicted from the thermodynamic calculations. With increasing m/V, transformation of the initial $MgCl_2$-rich solutions into $CaCl_2$-rich solutions is observed. This exchange reaction of Mg from the solution against Ca in the cement leads to a pH_m (-log[H^+]) increase up to 12 (from initial values around 9). Major solid phases found by analytical methods are also obtained in the calculations (e.g. gypsum, calcite, hydrotalcite / friedel‘s salt, brucite). Discrepancies are caused by various amorphous phases, which cannot be represented in the database.

In the full-scale experiments (with m/V around 2.7), a similar transformation of the initially $MgCl_2$-rich solutions into $CaCl_2$-rich solutions with pH_m increasing to 12 is observed already within the first 15 years. In the NaCl systems, the pH_m increases up to 13 within the first 10 years, while the Na and Cl concentrations remain close to halite saturation. Solid phase analyses and thermodynamic calculations for the full-scale systems show similar compositions as in the laboratory-scale system with the highest m/V ratio.

U-rich particles were analyzed using μ-spectroscopic methods. Similar results are found for the $MgCl_2$ and NaCl systems. There are hints for uranophane ($Ca(UO_2)_2(SiO_3OH)_2{:}5H_2O$) and diuranate-like U-rich secondary phases, e.g. $Na_2U_2O_7{:}H_2O$ or $CaU_2O_7{:}3H_2O$. Calculations show that the measured uranium concentrations in solution are in the range of the solubilities of these three solids under the prevailing conditions.

This study shows that there is significant retention of uranium by formation of crystalline uranium solids. Calculated solid and solution compositions for different m/V compare well to experimental data. Moreover, the present study demonstrates the applicability of thermodynamic methods used in this approach to adequately describe laboratory-scale as well as full-scale long-term experiments with waste simulates.