

Interactions of U(VI) with cement alteration products in brines

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The retention of radionuclides in a nuclear waste repository strongly depends on near-field materials, e.g. waste packages, backfill and the geochemical environment. Upon intrusion of groundwater, the present solid and liquid phases will define the geochemical conditions and, thus, the mobility of radionuclides in the near-field. In order to study the near-field processes relevant to a low/intermediate level waste repository in rock salt, experiments are conducted with simulated full-scale waste products and laboratory scale samples. The evolution of the measured concentration of major solution components, dissolved uranium and the secondary solid phases, are compared to geochemical equilibrium calculations.

On the laboratory-scale, systems with different ratios of cement to MgCl_2 -rich brine are studied to gain understanding of the corrosion progress ($0.01 \leq m/V \leq 1.0 \text{ kg cement (L solution)}^{-1}$). Static full-scale experiments are conducted with 336 kg of cement forms doped with 951 g U_{nat} and exposed to 135 liters of MgCl_2 -rich brine. Geochemical calculations are done with the use of the computer codes "The Geochemist's Workbench" and "EQ3/6", which apply the Pitzer approach for the activity corrections required due to the high ionic strengths of the salt brines.

The results of the thermodynamic simulations are in good agreement with the measured concentrations of major solution components and the pH. In the laboratory experiments with a low amount of cement compared to the available solution ($m/V < 0.2$), pH_m (i.e. $-\log m_{\text{H}^+}$) is found to be in the range of ~ 8.5 -9. This corresponds to the calculated pH_m , which is controlled by the formation of Mg-oxychloride (Fig. 1). The results are found to be in agreement with those of the full-scale experiments within the first 10 years (Fig. 2). In the systems with a higher ratio of cement to brine, dissolved Mg in the solutions is observed to be significantly exchanged against Ca from the solid phase. The reactions lead to an increase in the measured pH_m to values between 11 and 12 at ratios of $m/V > 0.5 \text{ kg cement (kg H}_2\text{O)}^{-1}$. These high pH_m values correspond to the results of the full-scale experiments after ~ 15 years. The changes in solution composition from a near neutral MgCl_2 - to an alkaline CaCl_2 -dominated solution strongly affect the U(VI) concentration. While the U(VI)-concentration in solution was $< 5 \times 10^{-8} \text{ mol L}^{-1}$ within the first 10 years, it approached concentrations of $\leq 5 \times 10^{-7} \text{ mol L}^{-1}$ after 17 to 18 years. Considering the high inventory of uranium in the waste product, the low concentrations in the aqueous phase indicate that the uranium concentration is controlled by solubility phenomena. XRD, TRLFS and U L3-XAFS analyses of powdered samples of the corroded cement monoliths suggest uranophane ($\text{Ca}(\text{UO}_2)_2(\text{SiO}_3\text{OH})_2 \cdot 5\text{H}_2\text{O}$) as the dominant uranium bearing solid phase (Kienzler et al., 2010). Recent μ -XAFS and Raman spectroscopy analyses of various U-bearing particles in the corroded cement monoliths corroborate these results.

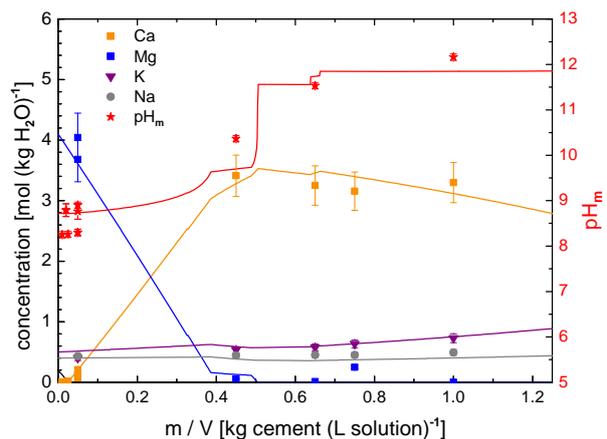


Fig. 1. Cement corrosion in MgCl_2 -rich brine; symbols denote experimental data points, lines denote calculated concentrations and pH_m values.

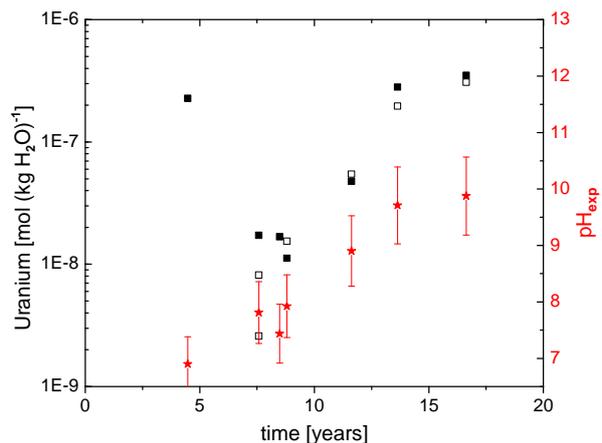


Fig. 2. Evolution of the Uranium concentration (black squares) and pH_{exp} (red stars) in two different full-scale leach tests (Kienzler et al. 2010).

Reference:

Kienzler, B., Metz, V., Brendebach, B., Finck, N., Plaschke, M., Rabung, T., and Schild, D. (2010). Retention of U(VI) in cemented waste forms under saline conditions. *Radiochimica Acta* 98, 675-684