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Long-term cement corrosion in chloride-rich solutions relevant to radioactive waste disposal in rock salt – Leaching experiments and thermodynamic simulations

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ARTICLE INFO

ABSTRACT

Low- and intermediate-level radioactive wastes are frequently solidified in a cement matrix. In a potential repository for nuclear wastes, the cementitious matrix is altered upon contact with solution and the resulting secondary phases may provide for significant retention of the radionuclides incorporated in the wastes. In order to assess the secondary phases formed upon corrosion in chloride-rich solutions, which are relevant for nuclear waste disposal in rock salt, leaching experiments were performed. Conventional laboratory batch experiments using powdered hardened cement paste in $MgCl_2$-rich solutions were left to equilibrate for up to three years and full-scale cemented waste products were exposed to NaCl-rich and $MgCl_2$-rich solutions for more than twenty years, respectively. Solid phase analyses revealed that corrosion of hardened cement in $MgCl_2$-rich solutions advanced faster than in NaCl-rich solutions due to the extensive exchange of Mg from solution against Ca from the cementitious solid. Thermodynamic equilibrium simulations compared well to results at the final stages of the respective experiments indicating that close to equilibrium conditions were reached. At high cement product to brine ratios (>0.65 g mL^{-1}), the solution composition in the laboratory-scale experiments was close to that of the full-scale experiments (cement to brine ratio of 2.5 g mL^{-1}) in the $MgCl_2$ systems. The present study demonstrates the applicability of thermodynamic methods used in this approach to adequately describe full-scale long-term experiments with cemented waste simulates.

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1. Introduction

The safety of nuclear waste repositories depends mainly on interactions of near-field and waste components with potentially contacting aqueous solutions. As a part of safety assessment considerations it needs to be accounted for the consequences of such interactions concerning retention or release of radionuclides. For low- and intermediate level radioactive wastes (L/ILW), a cement matrix is frequently used to solidify the waste components. Various studies are available that examine the alteration of cementitious materials upon contact with dilute aqueous solutions (e.g. Berner, 1992; Ewart et al., 1992; Pointeau et al., 2004; Ritherdon et al., 2003; Wieland et al., 2010). In the case of concentrated chloride solutions, which might occur in a repository in rock salt, the composition of secondary phases in the altered cement matrix differs from the dilute systems. The initial composition of the contacting solution has a strong influence on the resulting pH values and the formation of secondary phases.

Safety assessments for the behaviour of L/ILW (especially long-lived L/ILW) under repository conditions rely on a fundamental thermodynamic description of the co-existing liquid and solid phases over long time scales. Most experiments on interactions of cementitious material and cemented L/ILW simulates in particular were conducted for several weeks, in some cases for few months. Some studies even rely on the application of aggressive reactants, e.g. NH_4NO_3, to accelerate corrosion and try to imitate long-term effects (Le Bellégo et al., 2000; Schneider et al., 1986). Very few experiments are available that confirm the results on longer time-scales and reassure that equilibrium will be approached on the long term.

This work aims at understanding the evolution of cemented L/ILW simulates in contact with chloride-rich solutions by considering conventional laboratory batch experiments and long-term full-scale experiments, as well as thermodynamic simulations. Laboratory batch experiments were performed with powdered hydrated cement paste for about 3 years. Full-scale experiments were conducted in the Asse II salt mine (Lower Saxony, Germany) for several decades using uranium doped cemented L/ILW simulates (200 L sized monoliths). The thermody-

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namic description of co-existing phases in solid/brine systems can be done using the semi-empirical Pitzer formalism (Pitzer, 1973), which is regarded as the most accurate approach to describe activity coefficients of aquatic species in high ionic strength solutions (Clegg and Whitfield, 1991; Harvie et al., 1984). We compare results of laboratory and full-scale experiments with simulations in order to test the applicability of the thermodynamic approach and database.

2. Materials and methods

In the laboratory experiments, the cementitious solid was exposed to $MgCl_2$-rich brines as leaching solutions, while the cemented full-scale L/ILW simulates were exposed to either $MgCl_2$-rich brine or concentrated NaCl brine. Solution composition and pH were measured regularly during the course of the experiments. In order to probe the presence of colloids, solution aliquots were filtered by 450 nm filters and ultrafilters of 2 nm pore sizes. After termination, solid samples from all laboratory experiments and selected full-scale experiments were recovered and mineralogically analyzed. The full-scale cement products had been doped with uranium before exposure to the leachants. The temporal evolution of dissolved uranium and detected U(VI) solids is discussed elsewhere (Bube et al., 2011; Kienzler et al., 2010).

2.1. Batch experiments with hydrated cement paste powder

Ordinary Portland Cement, OPC, (CEM I 32,5 R) had been mixed with water at a W/C ratio of 0.4 and left to hydrate for a two month period. After this hydration time, the hardened cement paste was milled to powder with a specific surface area of $1.6–3.0\ m^2\ g^{-1}$ (determined by N_2-BET method). Powdered aliquots of 1.25–200 g were leached with so called "Q-brine" at solid to brine ratios (m/V) between 0.0025 and 1.0 g mL^{-1}. The leachant contained initially 4.3 ± 0.2 molal (m) Mg^{2+}, 0.41 ± 0.05 m Na^+, 0.54 ± 0.07 m K^+, 8.9 ± 0.1 m Cl^- and 0.23 ± 0.05 m SO_4^{2-}. The experiments as well as the preparation of the hydrated cement paste were conducted in glove boxes under Ar atmosphere ($pO_2 < 5$ ppm, $pCO_2 < 5$ ppm). Solution composition and pH were monitored for up to 1327 days. Solid phases of the initial hydrated cement and of samples leached for 200 days were analyzed.

2.2. Full-scale experiments with L/ILW simulates

The cemented L/ILW simulates were produced in the 1980s. The waste concentrates were selected to represent the composition of chemical residues from reprocessing of spent nuclear fuel by the PUREX process (Vejmelka et al., 1990). A load of 11 wt.% of process chemicals was cemented with OPC (CEM I 42,5 R) in 200 L steel drums at a water cement ratio of W/C = 0.235 for monolith #11 (211 kg total weight) and W/C = 0.5 for the monoliths #31–34 (336 kg total weight each), respectively. Apart from the major component $NaNO_3$ (9 wt.%), the waste simulates contained minor amounts of $Na_2HPO_4 \cdot 12H_2O$, Na-citrate, Na-tartrate, Na-oxalate and $(NH_4)_2U_2O_7$ (see Table. 1). Upon preparation, the full-scale cement products were stirred for several minutes but inhomogeneous mixing cannot be excluded. After complete hydration the monoliths were transported to the Asse II salt mine and transferred into 400 L steel drums filled with either NaCl solution saturated with halite and anhydrite (monoliths #11, #31 and #32) or $MgCl_2$-rich Q-brine (monoliths #33 and #34). The initial composition of the NaCl leachant solution was 6.1 m Na^+, 6.21 m Cl^-, 0.04 m Mg^{2+}, 3.8×10^{-2} m K^+, 2.5×10^{-2} m Ca^{2+}, and 5×10^{-3} m SO_4^{2-}. The initial composition of the $MgCl_2$ leachant was the same as for the laboratory experiments (see section above).

The corroding solutions were removed from monoliths #31 and #33 in 2006, when the leaching experiments were terminated after 18 and 17 years, respectively. Cores were sampled from both monoliths by vertically drilling into the sample at different positions between centre and periphery of the cylindrical monoliths using a drilling device coupled to a glove box (Kienzler et al., 2010).

2.3. Analytical methods

Concentrations of dissolved Ca, Mg, Na, and K were analyzed by optical emission spectrometry using a Perkin Elmer ICP-AES PE2000. Detection limits of the Ca, Mg, Na and K analysis were 0.5, 0.8, 8.7 and 5.1 mmol L^{-1}, respectively with a precision in the range of ±4 % for Mg and Ca, ±12 % for Na and K. Dissolved Si, Al and Fe were analyzed by mass spectrometry using an ICP-MS Perkin Elmer ELAN 6100. Measured Si, Al and Fe concentrations were below the detection limits of 1.0, 3.7 and 0.3 mmol L^{-1}, respectively. Chloride, nitrate and sulphate were measured by ion chromatography (IC) using a DX300 Dionex. Detection limits of the chloride, nitrate and sulphate analyses were at 2.8, 1.6 and 1.0 mmol L^{-1}, respectively. The precision of chloride, nitrate and sulphate measurements was in the range of ±5% for chloride and ±30% for nitrate and sulphate.

ROSS semi-micro combination electrodes and ORION pH meter 720-A freshly calibrated against dilute standard buffer solutions were used for pH measurements at an estimated accuracy of ±0.1 pH units. Since the pH is only an operational value in solutions of ionic strength >0.1 m, the measured pH values, pH_{exp}, were converted into H^+ concentrations ($-\log m(H^+) = pH_m$) following the approach of Altmaier et al. (2003) and Altmaier et al. (2008). Conversion parameters ($A = pH_m - pH_{exp}$) were derived for pure and mixed $MgCl_2$, $CaCl_2$ and NaCl solutions of known H^+-concentrations. By polynomial fitting to this data, conversion parameters were related to the solution composition so that A-values could be calculated from the molal concentrations of $MgCl_2$, $CaCl_2$ and NaCl (sum of KCl and NaCl was used as proxy) measured in the batch- and full-scale experiments. The estimated accuracy for this pH_m determination is ±0.25 units due to uncertainties in measured Mg, Ca, Na and Cl and unaccounted effects of minor solutes.

Drill dust and core fragments sampled from the corroded monoliths #31 and 33, powder samples from CEM I 32,5 R, CEM I 42,5 R, hardened cement paste and samples recovered from the laboratory experiments were characterized using scanning electron microscope - energy dispersive X-ray spectrometry (SEM-EDX), X-ray diffraction (XRD), X-ray fluorescence spectroscopy (XRF), total inorganic carbon (TIC) analysis and thermal analyses (TG/DTA). SEM-EDX studies were carried out using a CamScan FE44 instrument (Obducat CamScan Ltd, Waterbeach–Cambridge, United Kingdom) equipped with a Noran Pioneer silicon drift detector. SEM-EDX measurements were made at an accelerating voltage of 20 kV and a beam current of 1 nA. Data analyses were performed using Noran Vantage software for the CamScan FE44 instrument. XRD measurements were performed using a D8 Advance diffractometer (Bruker AXS) equipped with a Cu radiation tube and Ni filter, working at an X-ray source current of 25 mA and a voltage of 40 kV. Diffractograms were recorded in the range 2–100° 2θ with steps of 0.01° 2θ, 8 s counting time and variable slit widths. Bulk chemical compositions of the solids were analyzed using XRF. Powder aliquots were analyzed under He atmosphere in the analysis chamber by WDXRF (Siemens SRS 3000, now Bruker AXS). Data were processed using the Bruker SpectraPlus software (Ver. 1.73). Carbonate contents of the samples were measured with a Shimazu TIC/TOC Analyzer 5000, having a detection limit of 1 wt.% CO_2. Thermal analyses (TG/DTA) were carried out using a Netzsch STA 449C DTA.