

## Investigation of the Thermal Stability of Materials to be used in a High-Level Nuclear Waste Repository

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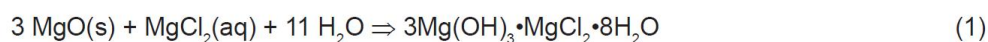
The decay heat of nuclear waste stored in an underground repository, results in a temperature rise of the host formation as well as of the materials used for the construction of drift seals and borehole plugs. Elevated temperatures induce structural and mineralogical changes of the materials influencing the permeability of engineered barriers. Flow paths can occur due to the formation of cracks and a loss of the bond between the sealing material and the adjacent rock. In addition, thermal dehydration creates pores and with the grade of connectivity the material permeability.

Comprehensive investigations were performed to determine temperature limits for the host rocks, which were used as design criteria of repositories and to specify maximum temperatures of the waste packages. Thus, the surface temperature of heat-generating waste stored in rock salt is limited to 200°C and the temperature of carnallite must not exceed 167°C. However, less attention was paid to the thermal stability of sealing materials considering the pressure dependence of dehydration processes.

Investigations of cement paste at low pressures show with increasing temperature a loss of physically bound water, a mobilization of interlayer water of the hydration products, and a thermal degradation of ettringite. At temperatures above 105°C, most important is the conversion of primary calcium-silicate-hydrates (C-S-H) to crystalline  $\alpha$ -dicalcium silicate hydrate ( $\alpha$ -C<sub>2</sub>SH), as the crystallization causes a reduction in solid volume and is accompanied by an increase in permeability and strength retrogression (e. g. MELLER et al. 2007, PETERSON 1962). For this silica fume is often added to the cement mixtures to reduce the CaO-SiO<sub>2</sub>-ratio. This reduces or prevents the formation of  $\alpha$ -C<sub>2</sub>SH.

In rock salt and potash mines the most common material used for plugging boreholes is magnesia binder, satisfying the essential criteria of an adequate plug. Magnesia binders containing magnesium oxide (MgO) or magnesium hydroxide (Mg(OH)<sub>2</sub>) can be distinguished. MgO-type mixtures contain admixtures or aggregate to reduce the temperature rise during hardening. The raw material of the MgO and Mg(OH)<sub>2</sub> was dense or cryptocrystalline magnesite. In addition, a mixture with MgO was investigated, which was produced in Styria (Austria) by burning macrocrystalline magnesite, also referred to as spar magnesite. The MgCl<sub>2</sub> concentration of the mix solution ranges between 30 and 33 wt.-%.

The MgO-type material contains halite powder. For this reason, only the integrity of hardened specimens and the thermal stability of the magnesium oxichloride (MOC) must be investigated, which are the reaction products of MgO and Mg(OH)<sub>2</sub> with the MgCl<sub>2</sub>-rich mix solution. In the range of the rock temperature (< 40°C) the so-called 3-1-8-phase (F3) and the 5-1-8-phase (F5) are reaction products (e.g. KARIMI & MONSHI 2012). The F5-phase is metastable and converts to the F3-phase as X-ray-diffraction analyses of specimens stored several months in MgCl<sub>2</sub>-solution showed. The equation 1 describes the formation of the F3-phase (korshunovskite). The amount of crystal water of the F3-phase is about 34.8 wt.-%.



The influence of thermal stresses was investigated on cylindrical specimens (diameter 5 to 10 cm) stored in a heat-cabinet several months at temperatures up to 180°C. At the end of this heat treatment the specimens were slowly cooled down to room temperature. Visual inspections of the samples prove the integrity of the material, regardless the material were stored in closed moulds or unprotected to enable an evaporation of water. Due to the loss of water occurred a drying shrinkage of the specimens. Figure 1 shows a borehole in rock salt, which is filled with Sorel concrete to proof the strength of the contact zone.

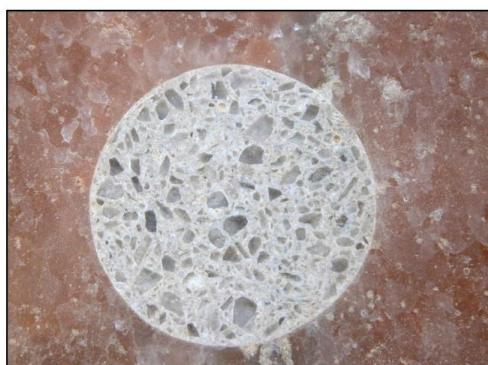


Fig.1

X-ray diffraction analysis of the dried solids showed phase transformations, in particular the formation of oxichlorides, which are characterized by low crystal water contents. The following results can be pointed out:

- The dehydration of the primary oxichlorides began at a temperature of approx. 70°C.
- With increasing temperature develop a sequence of mineral assemblages.

- First of all, the F3- and F5-phases are replaced by a 2-1-4- (25.4 wt.-% H<sub>2</sub>O) and a 3-1-4-phase (21.1 wt.-% H<sub>2</sub>O). In comparison, investigations of pure mineral showed a formation of the 2-1-4-phase above 100°C (e. g. DINNEBIER et al. 2010, DINNEBIER et al. 2012).
- A 9-1-4-phase (10.4 wt.-%) was detected after the storage at temperature 80°C and above.
- At temperatures in excess of approx. 110°C occurs the anhydrous 3-1-0-phase.
- A further rise in temperature resulted in a formation of a 2-1-0-phase.
- The samples produced by using magnesium oxide from Styria contain additionally a 7-1-12-phase, which is called nepskoeite.

In comparison to analysis performed on pure minerals the onset of mineral dehydration was comparable or slightly lower (cf. BALL 1977). Some phases described by XIA et al. (1991), such as a 3-1-6-phase and the dehydration products of the F5-phase could not be detected. It is possible, that these findings are a result of the different origin and processing of the binding agents.

In a borehole the pressure increases due to the convergence of the host rock formation. Dehydration reactions are coupled with a volume increase. According to the Le Châtelier principle, increased pressure inhibits mineral dehydration. This effect can be demonstrated by experimental results of C-S-H-phases or of the salt carnallite (KCl·MgCl<sub>2</sub>·6H<sub>2</sub>O, cf. KERN & FRANKE 1986), which is chemically related to magnesium oxichlorides (xMg(OH)<sub>2</sub>·yMgCl<sub>2</sub>·zH<sub>2</sub>O). At atmospheric pressure the mobilization of carnallite crystal water begins between 80°C and 90°C. In a plot of ln P versus 1/T (absolute temperature) the pressure-temperature relationship has the form of a nearly straight line (Figure 2). Accordingly, the dehydration temperature was extrapolated to high pressures using the Clausius-Clapeyron-equation.

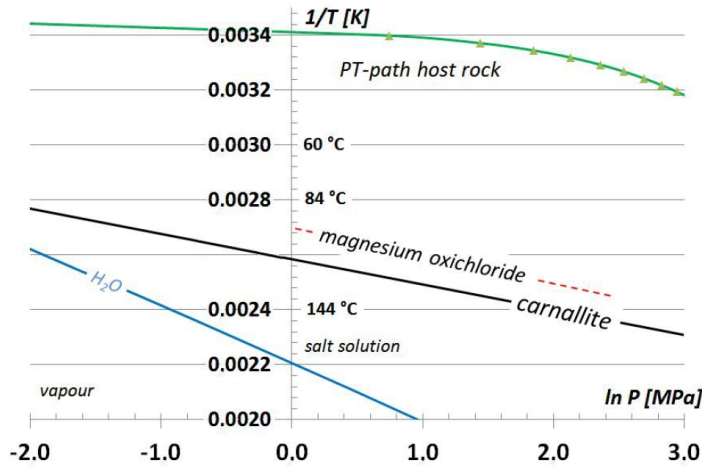


Fig. 2

The boreholes, which were considered, are located at a minimum depth of 840 m below the earth surface, corresponding to a minimum pressure of 17.3 MPa and an initial rock temperature of approx. 40°C. Assuming a comparable heat of vaporization, the dehydration of the F3-phase begins in this pressure range at a temperature > 145°C. Differential thermal analysis as well as X-ray diffraction analysis of samples showed that the dehydration process of the magnesium oxichlorides begins at approx. 130°C. Figure 3 shows the heat flow due to the endothermic reaction of the mineral degradation. It can be concluded that magnesia binders, which contain MgO produced by burning cryptocrystalline magnesite and thermally stable admixtures (e. g. halite) can be used as a backfill and sealing material if the temperature development does not exceed 130°C. In deep boreholes occur salt solutions due to thermal dehydration processes. The dissolution of minerals will significantly affect the composition of backfill materials.

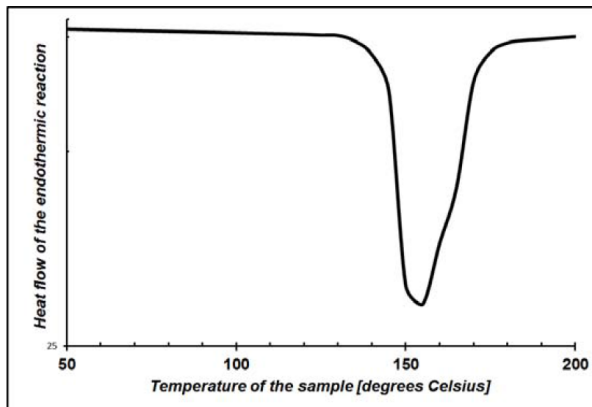


Fig. 3

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