

Hydro-mechanical and chemical-hydraulic behaviour of different types of shaft sealing materials (DOPAS Project)

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This paper describes research and development work on plugging and sealing repositories, an issue of fundamental importance for the rock salt option which represents one of the three European repository options, besides the clay rock and the crystalline rock options. The programme aims at providing experimental data needed for the theoretical analysis of the long-term sealing capacity of concrete-based sealing materials, excavated claystone material and mixtures with bentonite. In order to demonstrate hydro-mechanical material stability under representative load scenarios, a comprehensive laboratory testing programme is carried out. This comprises investigation of the sealing capacity of the combined seal system and impact of the so-called excavation-damaged zones (EDZ) as well as investigation of the hydro-chemical long-term stability of the seal in contact with different brines under diffusive and advective conditions. This paper presents experimental approaches and preliminary results from laboratory investigations on salt concrete and combined systems as obtained to date.

1 Introduction

The investigation programme of GRS (which is undertaken within the auspices of the LASA, LAVA and THM-Ton Projects) addresses sealing materials planned to be utilised in the shaft seals. The data acquired in the LASA, LAVA and THM-Ton projects will be used to assess the long-term performance of the seals with respect to the required hydraulic conductivity.

2 Results and discussion

This paper provides a short overview of the studies undertaken in DOPAS that are part of the LASA, LAVA and THM-Ton programmes. The results are taken from the respective final technical reports, published as Deliverables D3.29 (Jantschik et al., 2016), D3.31 (Czaikowski et al., 2016) and D3.32 (Zhang, 2016).

In Section 2.1, selected experimental investigations relevant for the hydro-mechanical long-term material behaviour according to the LASA programme are summarised. In Section 2.2, selected experimental investigations relevant for the hydro-chemical long-term material behaviour according to the LAVA programme are summarised. In Section 2.3, selected experimental investigations relevant for the hydro-mechanical long-term sealing behaviour according to the THM-Ton programme are summarised.

2.1 LASA programme

The LASA programme focuses on the hydro-mechanical properties of candidate seal materials in a salt rock such as MgO and cement-based salt concrete. The LASA programme (in conjunction with the LAVA programme, Section 2.2) aims to provide experimental data required for the theoretical analysis of the long-term behaviour of cement-based salt concrete and MgO concrete including the interaction with the host rock and formation water. The data gained will underpin the understanding of the long-term evolution of the hydraulic conductivity of the seals. Samples for experimental investigations were drilled from an *in situ* construction in a former salt mine. The drift sealing element was constructed at the 945 m level of the mine in January 1992. The samples were taken from two different boreholes. The salt concrete is a mass concrete consisting of a cement matrix with crushed salt filler. At the time of sampling the seal had been subjected to convergence of the surrounding rock salt for approximately ten years.

2.1.1 Long-term deformation behaviour

The tests aim at determining the deformation of the samples in terms of strains and strain rates in order to describe the time-dependent uniaxial creep behaviour of salt concrete at different stress states. Uniaxial creep tests were performed in a rig in an air-controlled room at approximately 25°C. The results of the uniaxial creep test show that material behaviour is different at lower stress levels of 5 MPa and 10 MPa and at a stress level of 20 MPa. While strains are small at lower stresses, a distinct creep deformation occurs at a stress level of 20 MPa. The reason for the different deformation behaviour at various stress levels might be that the cement structure of the salt concrete bears at uniaxial stresses up to 10 MPa. Cement is expected to have an elastic material behaviour without viscoplastic deformations after the water curing process has finished. Therefore, no stable creep rates could be derived at lower stress. When the stress level was increased up to 20 MPa, the cement structure of the salt concrete was damaged. Consequently, the salt grit structure of the salt concrete was subjected to the load, and because of the viscoplastic material behaviour of salt grit, the specimens exhibited explicit creep behaviour.

2.1.2 Material stability

Triaxial compressions tests (TC-Tests) were performed in order to investigate the mechanical stability of salt concrete. Onset of dilatancy, start of gas flux and failure of the specimens were determined under different radial stresses. The objective of the TC-Tests was to develop a greater understanding of the deformation behaviour of salt concrete than developed through the uniaxial creep testing described previously. Damage tests were carried out on three salt concrete samples in a triaxial apparatus, and deformation and gas permeabilities were measured under various stress conditions. The results of the triaxial compression tests show that salt concrete exhibits reversible (elastic) and irreversible (plastic) material behaviour during the compaction phase. The compaction test phase was identical for all three specimens. During the deviatoric stress phase, the results of the tests are different due to different confining stresses. It is possible to identify the onset of dilatancy by the evolution of volumetric strains. In all three tests, the onset of gas flux is measured at higher deviatoric stress levels than the onset of dilatancy. The boundary for the failure of the specimen increases with higher confining stress, analogue to the onset of dilatancy. The onset of gas flux and the failure of the specimens occurred nearly at the same deviatoric stress level. Consequently, the test results show that the investigated salt concrete samples were gas-tight until the load limit was reached. Generally, no damage is expected in the salt concrete specimens below deviatoric stresses of 30 MPa.

2.2 LAVA programme

The LAVA programme focuses on the hydro-chemical properties of candidate seal materials in a salt rock. The chemical stability of cement-based sealing materials is of vital importance for the longevity of sealing elements. In scenarios where there is a permanent contact between an aqueous solution and the sealing element, dissolution and precipitation processes can occur which eventually might result in changes of porosity and subsequently mechanical stability. Two evolutions are conceivable: firstly, porosity and consequently permeability increase. This may lead to a loss of mechanical stability. Secondly, porosity could decrease due to a net increase of solid phase volume. This would result in a decrease of permeability (Meyer *et al.*, 2003).

The composition of the aqueous solution depends on the ambient host rock formation. For the present considerations, the most important mineral phases in salt rock are halite (NaCl), anhydrite (CaSO₄), gypsum (CaSO₄*2H₂O), sylvite (KCl), kieserite (MgSO₄*H₂O), polyhalite (K₂Ca₂Mg[SO₄]₄*2H₂O), carnallite (KMgCl₃*6H₂O) and kainite (K₄Mg₄[Cl₄SO₄]₄*11H₂O). Naturally occurring brines in equilibrium with rock salt are always saturated with respect to halite. Equilibration with other mineral phases leads to quinary (without Ca) or hexary solutions (with Ca), with the composition specific to the particular set of mineral phases with which the solutions have equilibrated. For example, equilibration with potash salts results in brines that are dominated by Mg²⁺ and Cl⁻ (Herbert, 2000).

The corrosion mechanism of sealing elements depends significantly on the construction material and the solution composition. NaCl-based salt concrete is stable against NaCl-saturated brine (hereafter referred to as “NaCl-solution”) but corrodes in the presence of high MgCl₂-concentrations. A specific MgCl₂-rich solution in equilibrium with halite, sylvite, carnallite, kainite, and polyhalite is of particular interest and hereafter is referred to as “Mg-rich-solution”. MgCl₂-based sorel cement shows an opposite behaviour to salt concrete: it is stable in Mg-rich-solution and corrodes in NaCl-solutions containing small amounts of MgCl₂ only (Krauke and Fliß, 2008).

The objective of laboratory tests executed by GRS was to investigate the reaction path and diffusive and advective transport mechanisms in salt and sorel concrete in contact with Mg-rich- and NaCl-solution. The experiments described below were performed in the GRS laboratory and are ongoing.

2.2.1 Batch- and cascade experiments

The “Cascade experiments” are executed to investigate the reaction path between sealing material and solution. The cascade experiment is a sequence of batch experiments and has to be performed in air-tight vessels for the elimination of carbon dioxide. In any batch experiment, powdered concrete is exposed to solution in a defined solid-solution-ratio. Vessels are shaken in an overhead-shaker during the whole reaction time. If equilibrium is reached between concrete and solution, the solution is separated from solid and is exposed to new powdered concrete for the next cascade in the same solid-solution-ratio as before. This process is repeated until no free aqueous solution can be regained anymore after an equilibration step. Solution and solid phases are analyzed at the end of each cascade.

Before starting cascade experiments singular batch experiments were executed in each system (Sorel concrete / Mg-rich-solution, Sorel concrete / NaCl-solution, Salt concrete / Mg-rich-solution, Salt concrete / NaCl-solution). On basis of development of solution- and solid phase composition the reaction time between powdered concrete and solution until the equilibrium is reached was determined. Determined reaction times appoint the duration of each cascade in the following cascade experiments.

Sorel concrete A1 consists of characteristic Sorel phases (3-1-8-phases), anhydrite (CaSO) and some halite (NaCl). Batch experiments have shown that Sorel concrete typical 3-1-8-phases dissolve in contact with NaCl solution. After 11 days a further change in phase composition has not been observed. The analysis of the solution has revealed no significant change in its composition over total testing time. Consequently, each cascade in the cascade experiment in system Sorel concrete / NaCl-solution needs minimum 11 days. In batch-experiments with salt concrete and Mg-rich-solution the dissolution of typical CSH-phases (calcium-silicate-hydrate) could be observed by the increase of Ca-content in solution as result of Mg-attack. Equilibrium has been reached after circa 15 days. Equilibration time between concrete and NaCl-solution is only valid for a system with powdered concrete, for solid samples a longer equilibration time is expected because of the smaller specific surface.

The total chemical reaction path of a solution penetrating a geotechnical barrier can be reproduced by the cascade experiment until thermodynamic equilibrium between the original solution and the solid material is attained. In this way, chemical reactions which may occur by an intrusion of brine to a sealing element can be simulated in a short time (Niemeyer *et al.*, 2014).

2.2.2 In-diffusion and through-diffusion experiments

In-diffusion and through-diffusion experiments have also been undertaken. For in-diffusion experiments, Sorel concrete samples, coated with Araldite on generate surface and one front side, were placed in tracer-spiked magnesium-rich NaCl-solutions. Literature research and calculations, which were undertaken to derive diffusions coefficients, had shown that the diffusion coefficient in concrete is small (1×10^{-13} to 1×10^{-15} m²/s) (Mattigod *et al.*, 2012). Hence, all samples are still being tested to gather more robust intrusion profiles.

Through-diffusion-experiments are executed in special diffusion cells. The concrete sample is installed in the diffusion cell and tracer-spiked brine is passed across the bottom of the sample. A second, non-spiked brine is passed across the top of the sample and is analysed with regard to its development of tracer concentration over time. Because of the concentration difference between brine 1 (spiked) and brine 2 (non-spiked), a diffusional transport of tracer molecules from the bottom to the top of the sample is expected. The diffusion coefficient can be calculated on the basis of these experimental data. The thickness of samples and the duration necessary for saturation prior to starting diffusion experiments is determined in preparatory experiments. Through-diffusion experiments aim furthermore at investigating the kinetics of chemical reactions by diffusive corrosion processes. In principle, two scenarios are conceivable: on one hand a parallel progression of diffusion and corrosion may occur, on the other hand diffusion may occur faster than the process of corrosion. This circumstance will be investigated by analyses of the solid sample using x-ray diffraction.

2.2.3 Advective corrosion experiments

Advective transport is another transport mechanism in porous media which may affect corrosion of sealing elements. Corrosion as a result of advective transport and its consequences for the long-term sealing capacity will be investigated in two types of advection experiments: advection experiments which aim at reaction kinetics similar to diffusion experiments and experiments for investigating the influence of corrosion on porosity and permeability of the sealing material. A concrete sample was loaded with fluid pressure (NaCl- / Mg-rich-solution) on one face in the first type of advection experiments. The effluent brine is collected on the other face. The sample surface is pressure-less cast in araldite in an advection cell. In regular intervals, permeability is

measured and vessels for collecting brine are substituted. The individual brine samples will be analysed with regard to their composition. Additionally, the composition of each concrete sample will be investigated by decomposition and x-ray-diffraction. A conclusion and better understanding of corrosion mechanisms affected by advection processes in concrete is expected from these experiments.

The installation of the second advection experiment is very similar to the first experiment. The main difference is that the cylindrical concrete samples are surrounded by rock salt, thus exhibiting a circular contact zone. It is assumed that the contact zone is the primary pathway for brine and for the migration of nuclides. For these tests samples of the hollow rock salt cylinders with a salt concrete core described in Section 2.1.3 are used. The samples are exposed to a confining pressure until permeability is minimized. This process simulates salt creep onto an *in situ* sealing element. Afterwards, samples are placed in advective cells in the same manner as described before for concrete samples.

A further experiment on combined samples is in progress. The sample was tested with a NaCl-solution in the beginning of test. A radial pressure of 5 MPa in the beginning and 10 MPa in further process were brought to the sample. After the contact zone was closed up to a permeability of 10^{-18} m²/s, radial pressure was reduced to 2 MPa for relaxing the sample. In the next step, NaCl-solution was changed to a Mg-rich-solution. Permeability increases in the beginning because of the high injection pressure and decreases after pressure was reduced. After two month of contact to Mg-rich-solution, permeability starts to increase again. This phenomenon results from chemical processes in the salt concrete as former investigations at GRS have shown: If the Mg-rich-solutions is brought in contact to salt concrete, free hydroxide (OH⁻) is fixed by magnesium and brucite (Mg(OH)₂) is precipitated. As a result, pores are clogged by brucite and pH decreases to 8-9 (Phase 1). As result of the pH decrease, Portlandite (CaO)₂ becomes unstable and decomposes into Ca- and hydroxide ions. After consumption of all Portlandite, the pH decreases further and stabilizing CSH-phases are dissolved. Now concrete loses its stability and permeability starts to increase (Phase 2) (Niemeyer *et al.*, 2014).

Hence, the dissolution of CSH-phases is also to observe in this experiment composition. But dissolution needs more time compared to the batch- and cascade-experiments with powdered concrete.

2.3 THM-Ton programme

Crushed claystone produced by excavation of repository openings is considered a favourable backfill and seal material for disposal of radioactive waste in clay formations, because of its many advantages such as chemical-mineralogical compatibility with the host rock, availability in sufficient amounts, low costs of material preparation and transport, and no or less occupancy of the ground surface for the excavated claystone. The crushed raw claystone shall be used for backfilling the repository openings and, mixed with bentonite, for sealing boreholes, drifts, and shafts. In the frame of THM-Ton Experimental Programme, GRS has characterised the excavated COX claystone and mixtures with bentonite with regard to the following important properties:

- Compressibility which controls the mechanical stability, interactions with the surrounding rock, and the hydraulic conductivity.
- Water adsorption capacity which determines the water saturation, retardation and the resulting swelling pressure.
- Swelling capacity which is required for sealing gaps between rock wall and seal, for supporting the surrounding EDZ against damage propagation and enhancing the sealing of the EDZ.

- Hydraulic conductivity which dominates water transport and radionuclide migration in the seal.
- Gas migration properties which control development of gas pressure in the repository to prevent the whole multi-barrier system from gas fracturing.

The geotechnical properties of the crushed claystone and mixtures with bentonite were determined also from the previous experiments, e.g., (Zhang, 2014). The most important results are reviewed briefly below.

Crushed claystone (COX) produced by excavation of the Andra's Bure URL drifts was used in the experiments. It is convenient to use the excavated material immediately for backfilling the repository openings without further treatment. Therefore, raw crushed claystone with grain sizes up to a diameter of 10, 20 and 32 mm was tested for its suitability for use as a backfill material. In addition, fine-grained claystone powder with grain sizes of $d < 0.5$ mm was mixed with the MX-80 bentonite of $d < 0.5$ mm in different ratios. The claystone-bentonite mixture is considered to be used as seal material.

2.3.1 Compaction and permeability of crushed claystone backfill

Large-scale samples of 280 mm diameter and 640-680 mm lengths were prepared with the coarse crushed claystone of grain sizes of $d < 32$ mm and $d < 20$ mm. The initial dry densities reached by hand stamp, vibration and slight compression respectively vary in a range of 1.45-1.82 g/cm³. The samples were compacted in the GRS big triaxial apparatus with measurement of gas permeability.

The compressibility of the material is relatively high, i.e., its resistance against external load is relatively low. At stresses of 12–16 MPa, corresponding to the overburden pressures at depths of 500–600 m, the backfill can be compacted to a low porosity of 20% which is close to the rock porosities of 14–18%. The compaction leads to a decrease in permeability. The permeability of the coarse-grained backfill is higher than that of the fine-grained material at a given porosity. It is interesting that the permeability measured by flowing water through a sample ($d < 10$ mm) is much lower than the permeability to gas. The low water permeability is attributed to the effects of water-induced swelling and slaking of the clay grains into the pores. The compacted samples exhibited very low water permeability of 10-19 m² at a porosity of 30%, while such low gas permeability was observed at lower porosities of 20–25%, depending on the grain size.

2.3.2 Sealing properties of compacted claystone-bentonite mixture

As seal material, crushed claystone shall be mixed with bentonite and compacted to certain densities to meet specific requirements for sealing boreholes, drifts, and shafts. Commonly, the seals must have a sufficient supporting capacity against damage propagation of the surrounding rock, a certain swelling capacity for sealing of gaps and interfaces between compacted blocks and the surrounding rock, and a low hydraulic conductivity against migration of radionuclides with fluids.

Fine-grained COX claystone powder ($d < 0.5$ mm) and coarse-grained claystone ($d < 10$ mm) were mixed with MX-80 bentonite ($d < 0.5$ mm) in different ratios of COX/MX-80 = 100/0, 40/60, 50/50, 60/40, 80/20 and 0/100. The claystone-bentonite mixtures were compacted in Oedometer cell to a maximum load of 30 MPa. This leads to different dry densities of the mixtures from 1.56 kg/m³ at the pure bentonite to 2 kg/m³ at the pure claystone. The higher the fraction of the crushed claystone in the mixture, the higher density can be achieved by application of the same load.

The water content of each mixture increases with decreasing suction or increasing humidity. The moisture uptake at a given suction is proportional to the bentonite content of the mixture. In the wet environment at zero suction or 100% relative humidity, all the mixtures can take up large amounts

of water up to 12% for the crushed claystone and 48% for the bentonite. The increase in water content is accompanied by volume expansion. At the high humidity of 96-100%, the compacted claystone can expand to a volume increase of 12%, while the other mixtures expand even more up to 20-40% due to more bentonite content.

The swelling capacity of the compacted mixtures was measured in semi-confined conditions. The annulus between sample and cell was filled with fine-grained quartz sand. The samples were pre-loaded to an axial load of 5 MPa and then fixed. Response of the axial stress was recorded to drying and wetting. The measurement shows that drying leads the axial stress dropping down to zero and wetting contrary causes a rapid increase in the stress to high levels: 3 MPa in the compacted pure claystone; 4.5–4.7 MPa in COX/MX-80 mixture in ratios of 60/40 and 40/60, and 7.6 MPa in the compacted pure bentonite. Flooding the compacted mixtures with synthetic pore water can increase the swelling pressure further to higher levels of 6–7 MPa. The observations suggest high swelling capacities of the compacted claystone-bentonite mixtures.

The water permeability of the compacted claystone-bentonite mixtures was determined by flowing synthetic clay water through the samples in Oedometer cells. It is obvious that all the compacted mixtures exhibited very low water permeabilities: $K_w = 2 \times 10^{-19} \text{ m}^2$ at 80COX+20MX-80, $K_w = 3 \times 10^{-20} \text{ m}^2$ at 60COX+40MX80, and $K_w = 2 \times 10^{-20} \text{ m}^2$ at 40COX+60MX-80. In case of the crushed claystone with grains of $d < 10 \text{ mm}$, the water permeability becomes very low, too, $K_w < 1 \times 10^{-19} \text{ m}^2$, as the porosity is below 30%. The very low water permeabilities of the compacted mixtures are close to that of intact rock ($K_w < 10^{-20} \text{ m}^2$). Excavated raw claystone as backfill material and compacted claystone-bentonite mixtures as seal material have been comprehensively investigated. All the materials exhibit favourable geotechnical properties with respect to their barrier functions to prevent the release of radionuclides from a repository into the biosphere.

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