# A NEW SELF SEALING BACKFILL MATERIAL FOR REPOSITORIES IN SALT FORMATIONS - SVV

H. Kull, H. J. Herbert

Gesellschaft für Anlagen und Reaktorsicherheit (GRS) mbH

Theodor-Heuss-Str. 4, 38122 Braunschweig, Germany

## ABSTRACT

A new self sealing and self healing backfill material, SVV, is presented in the paper. This material was developed and patented by GRS for the sealing of repositories in salt formations. The backfill is based on anhydrous magnesium sulfate and other salt minerals. This backfill material is a reactive mixture which upon contact with brine increases its volume and reduces the pore space. Due to the formation of hydrated minerals the intruding solutions loose their water content. The water consumption leads to an over saturation of the remaining solution and to the precipitation of over saturated phases. These combined effects lead to a thermodynamically stable mineral assemblage with hydraulically and mechanical properties comparable to the undisturbed rock salt. An essential advantage of the new material is the long-term stability of the resulting seal. The resulting mineral assemblages are in chemical equilibrium with the host rock and all potentially occurring brines in salt formations. Results of mineralogical analyses, geochemical modelling, and hydrological and mechanical data obtained from laboratory and in-situ experiments are presented in the paper.

## INTRODUCTION

Different backfilling and sealing concepts for radioactive and hazardous chemical waste repositories in salt formations have been developed or are under discussion in Germany. The host rock – salt – is the main barrier against radionuclide release and the release of toxic components into the biosphere. Engineered Barrier systems (EBS) are required to ensure repository stabilization and sealing against brine contact with the waste. Different materials like crushed salt, different salt concretes and bentonites have been investigated extensively. For High-Level Waste repositories in salt formations crushed salt is considered to be the main backfill and EBS material. This material minimizes and stabilizes the open voids and reduces the total permeability but does not act as a barrier against intruding brines. There for the search was extended towards a material that automatically reduces its permeability upon contact with brines. Salt mixtures based on anhydrous $MgSO_4$ with salt additives were found to be self sealing and self healing upon brine intrusion. The new backfill is called SVV, the German abbreviation of self healing (**S**elbst **V**erheilender **V**ersatz).

**MINERALOGICAL AND CHEMICAL PROPERTIES OF SVV**

Several natural materials like smectites and salt minerals have the potential to take up water and to enlarge their volume and thus to reduce the total porosity and permeability. In salt formations the use of anhydrous magnesium sulphate promises the best results with respect to volume increase, i.e. sealing capacity, and with respect to the long-term stability of the resulting mineral assemblages upon contact with brines. Addition of anhydrous magnesium sulphate to crushed salt renders the backfill material into a reactive mixture that increases dramatically its volume upon brine contact thus leading to a practically total filling of the pore space [1], [2]. The result is a tight seal without pore water that prevents the further intrusion of brine.

The water consumption due to the formation of new hydrated minerals leads to an over-saturation of the remaining solution and consequently to the precipitation of new solid phases. The volume increase of the initial material is caused by several simultaneous reactions:

- the reaction of the brine water (liquid/vapour phase) with anhydrous magnesium sulphate leads to hydrated magnesium sulphates and water consumption,
- the over-saturation of the brine is accompanied by precipitation,
- re-combination of ions in the continuously changing brine composition lead to the formation of double salts with a higher volume compared to the dissolved magnesium sulphate.

As a result of these combined processes the water is removed from the brine and incorporated in the solid phases (Fig.1). The resulting seal is brine tight when the initially unconsolidated material with a starting porosity of 50 vol. - % has been transformed into a salt matrix of negligible permeability. By this time the intruded brine which filled the initial pore space is been used up completely (Fig.2 right). Depending on the initial composition of the intruding brine, more or less of the initial anhydrous magnesium sulphate is used up in the reaction by the formation of new hydrated minerals. The reaction is completed when the intruded brine is used up entirely. After completion of the reaction, the remaining excess of anhydrous magnesium sulphate guarantees the self healing capacity of the seal. Even if later on more brine should penetrate into the seal, due to rising brine pressure or due to fracturing of the seal by deformation of the surrounding salt, the reaction will start again and seal newly created pathways, as long as un-reacted anhydrous $MgSO_4$ persists.

Some basic reactions which take place in the system NaCl-solution with anhydrous magnesium sulphate ($MgSO_4$) and sylvite (KCl) can be understood by looking at the Mg-K-$SO_4$-diagram of the 5-component seawater system (compare Figure 4.2.1 in HERBERT 2000 and Fig 2 left, this paper). In contact with $MgSO_4$, a NaCl-brine with the initial composition in the bloedite field becomes immediately over-saturated and forms the new mineral bloedite ($Na_2SO_4MgSO_4*2H_2O$). With further dissolution of $MgSO_4$, the total magnesium content of the solution increases and the reaction path enters the field of epsomite ($MgSO_4*7H_2O$), then the field of hexahydrite ($MgSO_4*7H_2O$), and finally ends up in the field of the kieserite ($MgSO_4*H_2O$).

Tools employed to understand the reactions of SVV backfill with different brines were x-ray analyses of the mineral assemblages obtained in experiments and the results of reaction path calculations with EQ3/6. The example in Fig. 1 shows the x-ray patterns of a self sealing salt backfill consisting of 80 vol.-% anhydrous magnesium sulphate, 10 vol.-% sylvite and 10 vol.-% halite and reaction products of this material with an halite-anhydrite saturated brine. Fig. 2 shows EQ3/6 modelling results of this reaction, mineral dissolution and precipitation, as well as volume changes during the reaction. A good agreement between experimental results and modelling results was obtained in all examined cases. The reaction path modelling ends always when all water is used up in the reaction. This is exactly what can be observed in all experiments. The x-ray patterns of samples from the various experiments in general identified the minerals predicted by the EQ3/6 modelling calculations (compare Fig.1 and Fig.2).
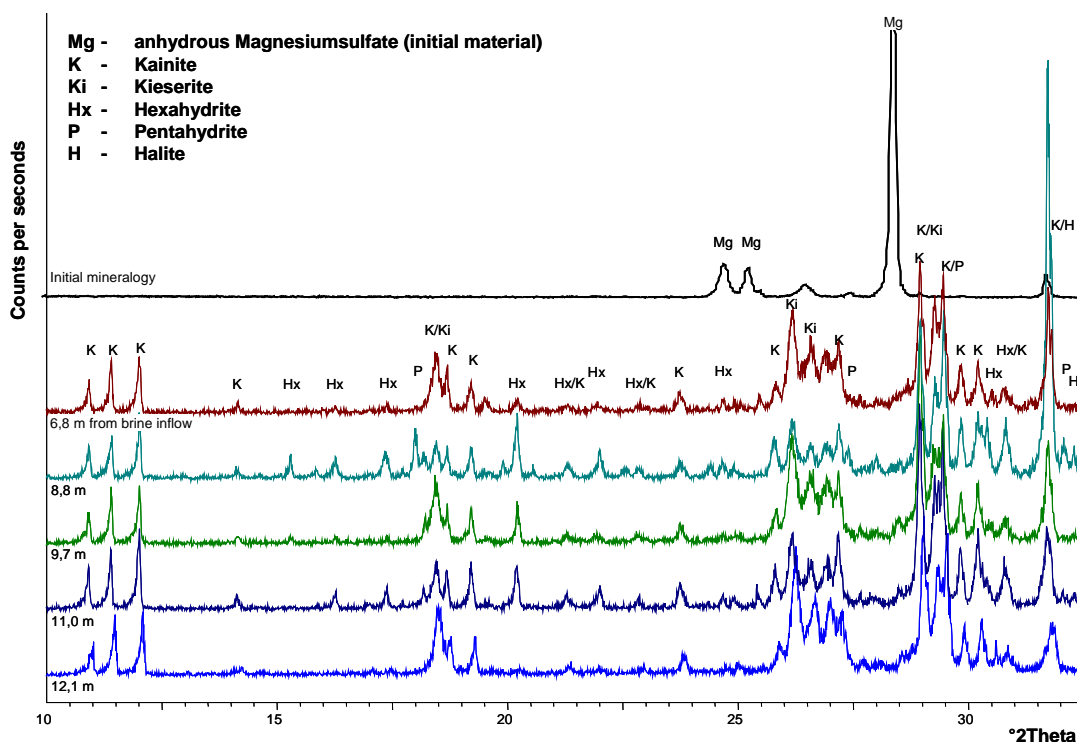


**Fig. 1. X-ray patterns of the reaction products of the self sealing salt backfill with a halite and anhydrite saturated brine – results of an in-situ experiment in the Asse salt mine.**

## EXPERIMENTS

### Laboratory Experiments

Laboratory experiments have been performed to study the reactions of different self-sealing salt mixtures [3], [5], [6]. The experiments were conducted in small pressure vessels filled loosely with fine-grained backfill. The initial pore space of these mixtures was about 50 volume-percent. This pore space was filled with salt solution using a high pressure pump and a constant flow rate. The reactions triggered by the intruding brine were most effective. Precipitation of large amounts of hydrated minerals and halite was observed. For certain initial backfill compositions the volume increase of the solid phases upon completion of the reaction was almost double.

Immediately after the first brine intrusion the reaction backfill-brine set in and leads to a sharp reduction of permeability. The brine flow decreased continuously and eventually ceased completely. In some of the small scale laboratory experiments the initial pore space disappeared almost completely. After 12 days a maximum crystallisation pressure of 100 bars was reached and a permeability of $< 10^{-20} \, m^2$ was measured.



| | Dissolved and precipitated minerals | | | Volume changes during reaction | |
|---|---|---|---|---|---|
| left | 1 = bloedite, | 2 = epsomite, | 3 = hexahydrite, | 4 = halite | 5 = kainite, |
| | 6 = starkeyite, | 7 = leonite, | 8 = kieserite | 9 = anhydrous $MgSO_4$ | 10 = sylvite |

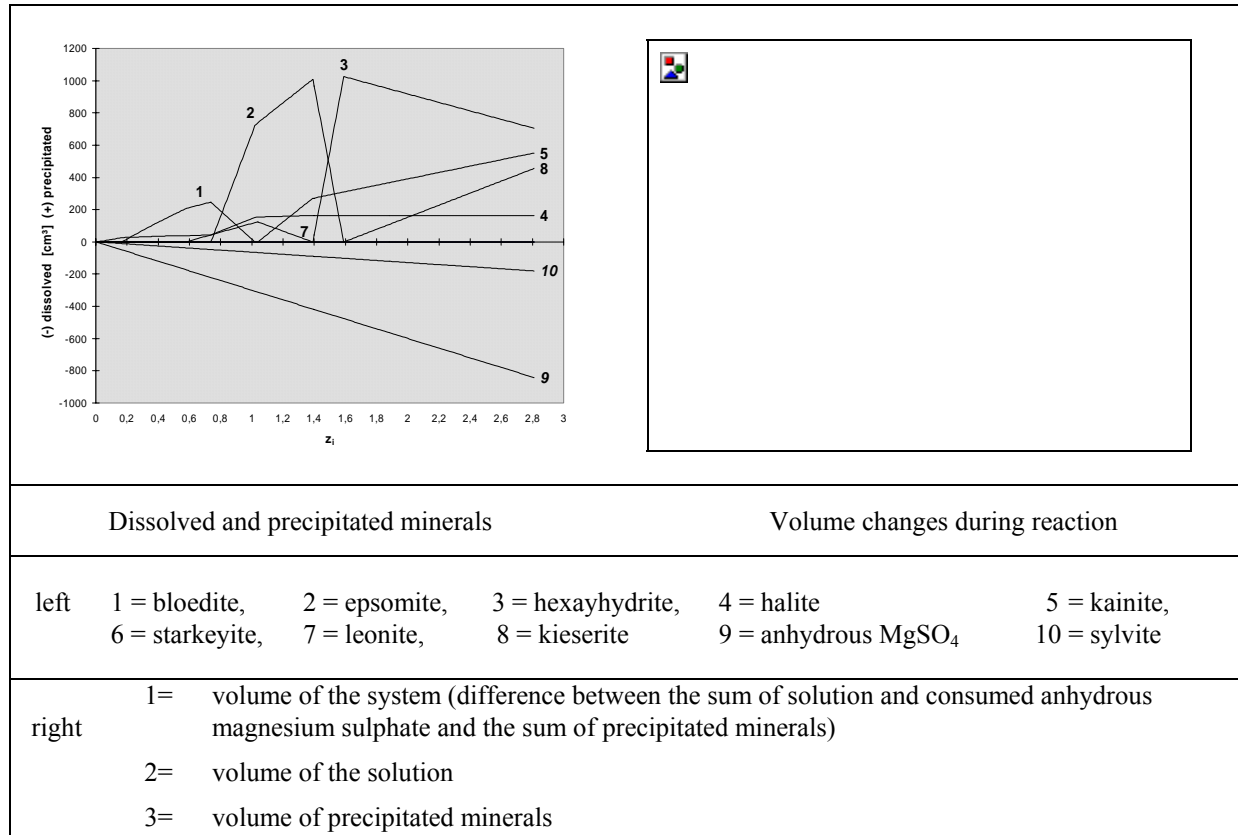| | | |
|---|---|---|
| right | 1= | volume of the system (difference between the sum of solution and consumed anhydrous magnesium sulphate and the sum of precipitated minerals) |
| | 2= | volume of the solution |
| | 3= | volume of precipitated minerals |

**Fig. 2. Calculated reaction of self sealing backfill (80 wt-% anhydrous magnesium sulphate plus 10 wt-% halite plus 10 wt-% sylvite) with a halite-anhydrite saturated solution.**

**In-situ Experiments**

In-situ tests were performed in three horizontal boreholes (GB-1, GB-2 and GB-3) in the ASSE salt mine at the 850-m level situated in the salt series Na2s of the STASSFURT formation. The length of the boreholes was 15 m with a diameter of 50 cm. Two mixtures of self sealing material were used as backfill. Borehole GB-1 was backfilled with anhydrous magnesium sulphate and sylvite and borehole GB-2 and GB-3 were filled up with pure anhydrous magnesium sulphate. GB-3 was instrumented with pressure and temperature sensors. The initial porosity of the loose backfilling was in the order of 50 % (n ≈ 0.5). The backfilled boreholes were flooded with natural brines from the ASSE salt mine (see Table I).

Two types of brine were used:
- type 1 for GB-1; a sodium chloride rich brine saturated with respect to halite and anhydrite and
- type 2 for GB-2 and GB-3; a magnesium chloride rich brine saturated with respect to halite, carnallite, sylvite and kainite

**Table I.  Composition of Natural Brines used as Test Solutions**

| Species | Na-brine (type 1) | Mg-brine (type 2) |
|---|---|---|
| | Concentration mg per litre water | |
| Cations | | |
| Calcium | 688 | 49 |
| Potassium | 2916 | 9136 |
| Magnesium | 9997 | 98017 |
| sodium | 98453 | 6577 |
| Ions | | |
| Chloride | 196475 | 275132 |
| sulphate | 9658 | 30261 |
| Density [g cm$^{-1}$] | 1.2084 | 1.3010 |

The objectives of the tests were focussed on the time needed for the accomplishment of hydraulic seal (GB-1; GB-2) and, on the magnitude of crystallisation pressure and the temperature development during the reaction (GB-3). The test design was adjusted to a supposed equivalent brine intrusion into a gallery of 5 to 25 m$^3$ per m$^2$ per year.

The backfilled boreholes consisted of a flooding chamber at the back end, a section with the backfill material, and an abutment at the front face of the gallery. The injection tubes were placed inside of the backfill. The backfill in the boreholes GB-1 and GB-2 was not equipped with sensors. In GB-3 an instrumentation of pressure cells and temperature probes was installed in intervals of 2 m. High pressure pumps (HPLC-pump) were used to control the stationary flow and pressure (max. 50 bar) during brine injection. Each test was run at constant flow rates (4 to 40 ml min$^{-1}$). At the beginning, the brine was injected more or less un-pressurised at atmospheric pressure ($P_{liquid} \cong 1$ bar).

**Accomplishment of a Hydraulic Seals in GB-1 and GB-2**

Within the tests the injection pressure was monitored continuously as the most significant parameter.  The beginning of self-sealing is assumed to be indicated by the increase of the injection pressure, which is synonymous with the decrease of the hydraulic permeability and the consolidation of the seal.  In GB-1 it took more than 4,000 hours until the increase of the injection pressure indicate the accomplishment of a hydraulic seal. In GB-2 this self-sealing effect occurred within 2,000 hours.  In any case, a sharp peak in the liquid pressure appeared if available pathways are closed suddenly.  On the other hand, sharp pressure drops indicated a mechanical break of the seal.

From that it is assumed that the measured liquid pressure is equivalent to the permeability of an integral sealing section. Test cycles with injection and pressure recovery periods are used for the estimation of the integral permeability of the achieved seal.  At a liquid pressure of approximately 10 bars from test cycles each with an injection period and a pressure recovery period an integral permeability of about k < 10-18 m2 is derived. During the injection period of approximately 1 ½ hours with a constant flow rate of 4 ml min-1, the pressure is increased by

about 0.5 bars. The following pressure recovery, down to 10 bars, takes at least 9 hours which corresponds with an effective flow rate in the range of 0.1 ml min-1 and an effective thickness of the seal of 10 cm. Latter is assumed, because the consolidation process within a seal is not homogeneous. From core analysis it is known that the seal is highly affected by the formation of preferential pathways. The integral permeability of the seal depends on the size and the configuration of such preferential pathways. From that, it has to be emphasised that the consolidated seal is not really a hydraulic system in terms of DARCY. We suppose that initially formed preferential pathways are be destroyed by the ongoing reaction of metamorphism.

**Self Sealing Effects Measured in GB-3**

The development of a hydraulic seal requires the supply with water. In GB-3 the first increase of pressure was observed within 10 days of flooding. Following pressure peaks and drops correlate with periods of brine injection. When the injection was stopped after 53 days the liquid pressure had reached a level of 10 bars. The development of a seal is accompanied by a built-up of crystallisation pressure within the solid matrix and a temporary increase of the ambient temperature. The test results support the thesis that the tightness of the seal and the crystallisation pressure depend on the solid/liquid ratio. When brine supply is interrupted, the crystallisation pressure is limited. In borehole GB-3 the crystallisation pressure increases up to 12 bars. The shape of the pressure curves indicates the ongoing consolidation process. At a distance of 2m and 4m to the flooding chamber the crystallisation pressure increases in the beginning although the supply with brine was interrupted in the interim. The continuing decrease of the crystallisation pressure after 53 days indicates that their maximum was reached. In contrast the ongoing increase of the crystallisation pressure at 6m, 8m, and 10m indicate that the swelling capability was not yet utilized. The spontaneous increase of temperature from an ambient temperature of 35°C indicates the contact with water. Due to the exothermic conversion of the anhydrous magnesium sulphate to meta-stable species the ambient temperature arise temporary from 35°C up to 65°C. The process is singular and has no impact on the ongoing development of the crystallisation pressure.

**Consolidation and Preferential Pathways**

During consolidation, a compact matrix system of low permeability and high mechanical strength is build up. While on laboratory scale the crystalline matrix of the seal was found to be homogeneous, the seal on in-situ scale show inhomogeneity and preferential pathways. These are probably due to the inhomogeneous distribution of brine. We expect that the consolidation process starts with the reaction of water vapour which is very mobile with the anhydrous magnesium sulphate followed by the liquid/solid reaction. The changes and structure variations of the inhomogeneous distribution are depending on the distance to the injection point (flooding chamber).

The experiments lead to the conclusion that anhydrous magnesium sulphate based materials in contact with brine will build up in any case a consolidated seal with graded properties. Extraordinary hydraulic properties and likewise a high crystallisation pressure are achieved, when the brine/solid ratio is increased to a maximum. The type of brine and the compaction of the material are of minor importance, but are contributing to the complex dynamic of the consolidation

**Conceptual Model of the Consolidation Process and Parameters**

In case of an intrusion of brine the self sealing set in immediately by water consumption and precipitation. Both effects lead to a reduction of the initial porosity and a confining contact to the surrounding rock. The associated deformation is concentrated on the intrinsic pore space and minor on the deformation of the rock formation as a result of the crystallisation pressure. Concurrently with the development of the crystallisation pressure the radius of the borehole and the mechanical parameters of the SVV backfill material are altered. A uniform solid matrix of high mechanic strength is formed. A set of available parameters of the consolidated backfill is given in Table II.

The maximum obtainable consolidation of the self sealing backfill depends on the following variables:
- Total volume of the system
- Type of reactive material and type of brine
- Initial pore space which can be filled with brine, i.e. the maximum volume of initial brine
- Maximum reaction progress

**Table II.  Set of Parameters of the Consolidated SVV-Backfill Obtained in Laboratory and In-Situ Experiments**

| Parameter | Symbol | Dimension | SVV + Na-brine | | SVV + Mg-brine | |
|---|---|---|---|---|---|---|
| | | | lab | In-situ | lab | In-situ |
| Sealing effect | $P_{liquid}$ | MPa | <20 | <5 | <20 | <5 |
| Integral permeability (brine) | $k_{eff.}$ | $m^2$ | | $\sim 10^{-18}$ | | $\sim 10^{-18}$ |
| matrix permeability (gas) | k | $m^2$ | $10^{-21}$ - $10^{-17}$ | | $10^{-21}$ - $10^{-17}$ | |
| effective porosity | n | - | 0.01- 0.07 | | 0.01 – 0.05 | |
| crystallisation pressure [1)] | $P_{cryst.}$ | MPa | 1 to 15 | $\sim 1$ | 1 to 15 | $\sim 1$ |
| uniaxial strength | $\sigma$ | MPa | 6 – 24 | | 64 - 66 | |
| bulk density | $\rho_{bulk}$ | g cm$^{-1}$ | 1.88-2.08 | | 2.02 – 2.04 | |
| matrix density | $\rho_{matrix}$ | g cm$^{-1}$ | 2.03 – 2.16 | | 2.10-2.14 | |
| Temperature of reaction | T | °C | 55 - 65 | | | |
| thermal conductivity | W | W m$^{-1}$K$^{-1}$ | $\sim 0,2$ | | | |
| thermal coefficient of expansion | $\alpha$ | K$^{-1}$ | $\sim 4*10^{-5}$ | | | |

1)  depending on reaction of volumes (ratio of solid to liquid)

**Expected Hydraulic and Geotechnical Behavior of SVV Backfill Compared with Crushed Salt and Natural Rock Salt**

During the consolidation process the initial porosity is reduced and also the depending permeability (see Fig. 3). Results measured on core samples of borehole GB-1 and GB-2 indicate a reduction of the porosity from $n = 0.5$ to $n < 0.04$ and a reduction of the effective permeability (D) from $k = 10^{-15}m^2$ to $k = 10^{-20}m^2$ in case of brine intrusion. The data correlate with the functional relationship determined on crushed salt [8], [9]. Latter results derived from in-situ (A) and laboratory experiments (B) and (C) indicate that the mechanical compaction of normal crushed salt will also be minimised but not in case of an un-expected intrusion of brine.

The expected geotechnical behaviour of the SVV backfill can be estimated from the loading path of rock salt (compare Fig.4). The achieved results of the strength of the SVV matrix during consolidation are comparable with those of the natural rock salt. Under 'normal' stress condition SVV backfill will have the same integrity as the host rock as long as the dilatancy criterion is met.
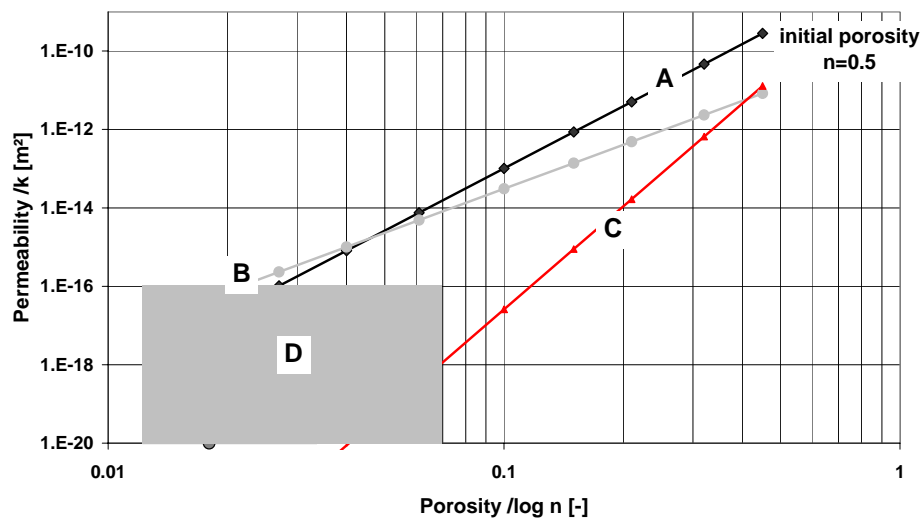


**Fig. 3.  Relationship of the porosity and the permeability of crushed salt (A, B and C) and data – measured on core samples from GB-1 and GB-2 (field D).**
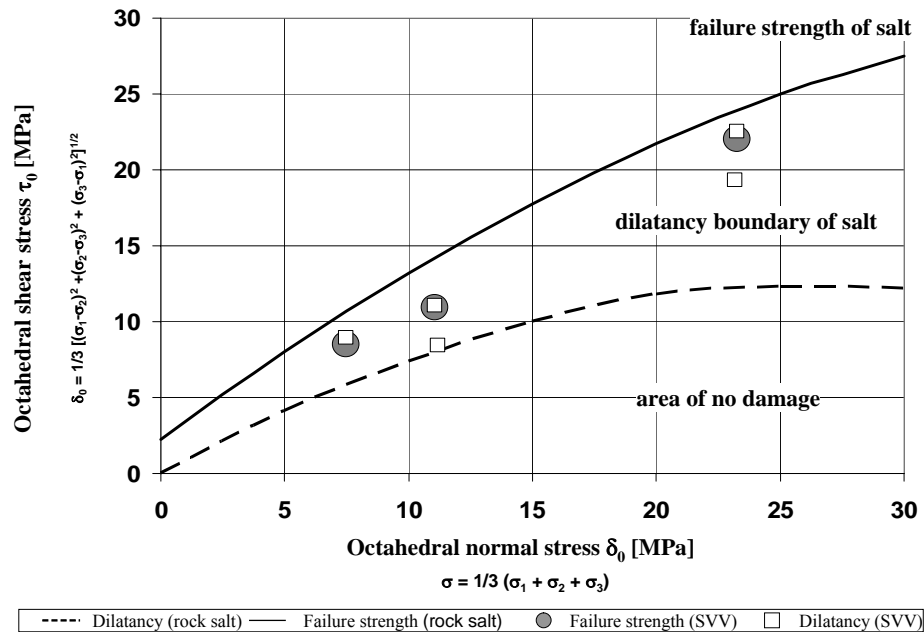
**Fig. 4. The diagram shows the octahedral shear stress, $\tau_0$, versus octahedral stress, $\delta_0$, including the dilatancy boundary and the short-term failure strength of rock salt. The data of the SVV backfill (markers) fit to the 'normal' behaviour of natural rock salt.**

## SUMMARY AND CONCLUSIONS

Self sealing salt mixtures are based on anhydrous magnesium sulphate and salt other additives as halite and sylvite. Such mineral mixtures lead upon contact with high saline brines to efficient hydraulic seals independent of the initial brine composition. The seal is self-healing; In case of new brine intrusion triggered by fracturing the seal or by rising brine pressure the reaction can start again and seal new pathways, as long as un-reacted anhydrous $MgSO_4$ persists. The mineralogical assemblage of the resulting seal is in thermo dynamical equilibrium with the mineralogy of the host rock as well as with all possible brine compositions and thus long-term stable from a geochemical point of view. The reaction of SVV-backfill with brines leads to a volume increase of the total system and thus to crystallisation pressures. The initial pore space is filled completely due to the formation of hydrated magnesium sulphates and due to the precipitation of salt minerals from the oversaturated brine. During the reaction the initially intruded brine is used up nearly completely. The resulting solid matrix contains no mobile water. The initial loose material with a high porosity is transformed into a dense salt matrix of high mechanical stability. These general processes have been observed in all experiments independent of their scale. Scale effects however occurred in the upscaling experiments with respect to:

a) Time needed for the accomplishment of the hydraulic seal
b) the distribution of the residual effective pore space
c) the quality (permeability) of the seal
d) the maximum obtained crystallisation pressure

In the large scale in situ experiments we observed in homogeneities and preferential pathways

which are not yet fully understood. However, the resulting in-situ crystallisation pressure leads to an ideal contact with the surrounding rock salt and reduces the permeability not only of the seal itself but also of the excavation disturbed zone.

From the results obtained so far we conclude that the investigated self sealing mixtures on the bases of anhydrous magnesium sulphate are very effective materials for the building of brine tight and long-term stable engineered barrier systems. For the materials and procedures were patented [10].

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