Long-Term Behavior of Salt Concrete - a Material for Engineered Barriers in Final Repositories in Salt Formations - Development of Reactive Transport Models for Matrix Corrosion and Corrosion on Cracks – 14177

Horst-Jürgen Herbert, Gesellschaft für Anlagen-und Reaktorsicherheit,
Theodor-Heuss-Str. 4, 38122 Braunschweig, Germany

ABSTRACT

The paper summarizes the experimental and modeling results of a R&D program conducted by GRS in the field of salt concrete and describes the ongoing activities. Salt concrete consists of crushed salt, coal fly ashes and CEM III B cement. This material is used in Germany for drift and shaft seals in repositories for radioactive wastes in salt formations. Salt concrete proofed to be stable in the presence of pure saturated NaCl solutions. Higher Mg contents in the solutions however trigger a fast corrosion of the concrete. Originally present calcium-silicate-hydrate (CSH) phases in the concrete are transformed brucite ($Mg(OH)_2$) and will finally result in magnesium-silicate-hydrates (MSH). 1 m^3 of a Mg-rich IP21 brine occasionally encountered in German salt formations can corrode up to 2.5 m^3 of a salt concrete M2. The corrosion degrades the mechanical properties of the concrete and increases its permeability. The sealing properties deteriorate. Based on experimental results a model was developed which describes the corrosion in the undisturbed matrix of salt concretes. In-situ tests however showed that the existence of cracks in the sealing constructions cannot be excluded. Accordingly the matrix corrosion model must be extended. New experiments and procedures had to be developed to investigate the kinetics of the corrosion on cracks. The paper describes the different experimental procedures employed for the investigation of the chemical corrosion as well as for measurements of permeability changes due to the corrosion in the concrete matrix as well as on cracks. Ongoing activities for extending the matrix corrosion model towards the description of the corrosion an cracks are outlined.

INTRODUCTION

Long-term safety assessments for radioactive waste repositories must prove that no hazardous impact on the biosphere will be be caused by the emplaced waste. Repositories in deep geological formations must safely be sealed for at least several 100.000 years. Water or brines in the repository can react with the waste and mobilize and transport radionuclides. Sealing constructions shall therefore avoid or retard the contact of the waste with water. Repository closure concepts must be based on a detailed planning of adequate sealing constructions. This planning includes detailed knowledge of the long term behavior of materials and constructions. Extensive laboratory experiments and large scale in-situ tests are needed along with predictive models. Experimental results are the indispensable bases of the predictive models. These are needed for reliable predictions of the long term behavior of the complex system seal-excavation disturbed zone-host rock.

Salt concretes are used as sealing materials for the construction of drift and shaft seals in German repositories for low and intermediate level radioactive wastes in salt formations. They consist of crushed salt, additives like fly ashes and CEM III B cement. From a chemical point of view salt concretes are stable in pure saturated NaCl solutions. But they are not stable in the presence of high Mg concentrations in salt solutions. In contact with Mg-rich brines the calcium silicate hydrates (CSH phases) which are responsible for the mechanical strength of concrete are transformed in magnesium silicate hydrates (MSH phases). IP21 solution is such a Mg-rich brine (4 mol Mg/kg H_2O, Table 3) occasionally encountered in salt formations in the vicinity of potash beds with carnallite ($MgCl_2KCl*6H_2O$) and kieserite ($MgSO_4*H_2O$). One m^3 of IP21 can degrade the CSH phases of 2.5 m^3 salt concrete. The mechanical stability of such a corroded salt concrete is lost and its permeability increases. The concrete can lose its sealing capacity. For long term safety assessments it is important to understand the chemical corrosion processes and the resulting changes of permeability and mechanical strength

GRS has investigated the short and long term behavior of cemented materials in contact with brines in general and of the specific salt concretes M2 and M2-4 in particular. The chemical corrosion processes were elucidated in specially designed batch experiments, the so called “GRS Cascade Experiments” as well as in large scale in-situ experiments in the Asse salt mine, in 160 liter drums with cemented simulated radioactive waste forms. The experimental results were reproduced by geochemical modeling showing that the corrosion process is well understood and that extrapolations are feasible and reliable.

Inflow and flow through experiments were used to determine the velocity of the corrosion and the permeability change of the salt concrete as a function of brine composition and brine pressure. These experiments could be reproduced as well. For the modeling a reactive transport model was developed. The geochemical code CHEMAPP was coupled with the transport code OpenGeosys.

By assuming that the corrosion front advances uniformly in a sealing structure the permeability increase over time of the seal with a given length and brine pressure was calculated. These modeling results served for planning and building of a 1:1 scale test construction in the repository for low and intermediate level radioactive waste in Morsleben (Fig. 1). This construction however showed unexpected results. The salt concrete in the structure developed cracks which had not been anticipated.

Fig. 1 Drift seal in the low and intermediate level radioactive waste repository Morsleben – 484 m^3 salt concrete M2 in a construction of 4 – 5 m height, 4.5 m with and 25 m length

The reactive transport model for matrix corrosion had to be extended in order to take into account also the corrosion on cracks because it must be assumed that the corrosion on cracks proceeds differently and probably much faster than the corrosion in the undisturbed matrix. New experimental procedures were developed. These experiments are under way. The paper describes the experimental procedures as well as the parameters needed for the models and shows examples of the experimental and modeling results.

CHEMICAL CORROSION PROCESSES IN SALT CONCRETE BY Mg-, SO_4- AND Cl-RICH SOLUTIONS

Solutions with high Mg-, SO_4- and Cl-contents are considered to be the most aggressive agents for Ca-based cements [1], [2]. The chemical corrosion is due to several chemical processes (Fig. 2):

- Formation of brucite $(MgOH)_2$ on the surface of the concrete

- Gypsum corrosion - Dissolution of $Ca(OH)_2$ and CSH phases in the concrete matrix and precipitation of gypsum ($CaSO_4 \cdot 2H_2O$). Gypsum has a 17.7 % times higher molar volume than $Ca(OH)_2$ and destroys therefor the concrete.

- Mg corrosion – Dissolution of the network of CSH phases (Fig. 3) and formation of a MSH gels. This reaction takes place in two steps. The CSH phases react with Mg and sulfate from the solution and precipitate gypsum, brucite and silica gel. In the second step brucite and silica gel form MSH phases and water.

- Cl corrosion – The mineral Friedels salt ($3\,CaO \cdot Al_2O_3 \cdot CaCl_2 \cdot 10\,H_2O$) is built if Cl-rich solutions react with calciumaluminte phases. Friedel’s salt is one of the most stable chlorine containing phases in concretes.

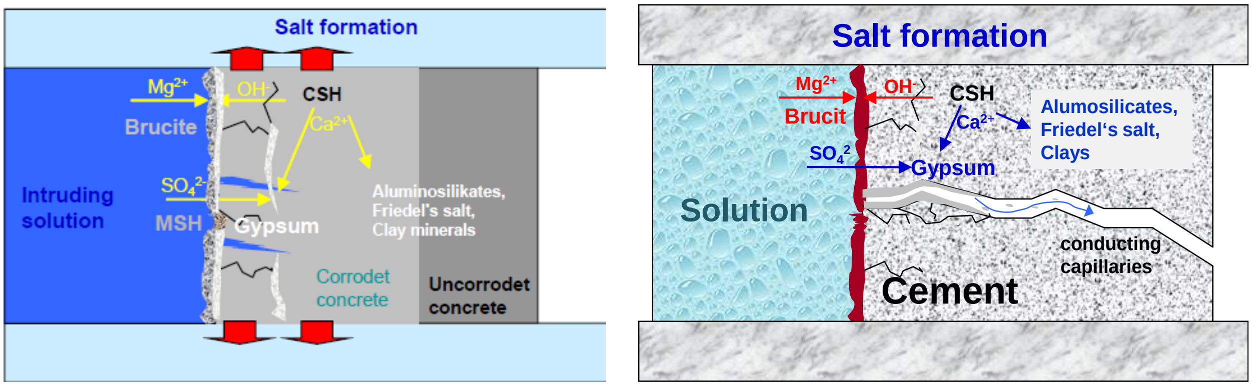


Fig. 2 Schematic representation of the chemical corrosion processes in salt concrete due to the interaction with Mg-, SO_4 and Cl-rich salt solutions (left) diffusive matrix corrosion, (right) advective corrosion on cracks (in [1] modified after [2])

If a Mg- and SO_4-rich salt solution attacks Salt concrete first brucite ($Mg(OH)_2$) will be formed at the surface of the sealing construction. This leads to a mass flux of OH^- from the matrix towards the exterior of the structure and to a SO_4 flux from the intruding solution into the matrix. Due to the depletion OH^- in the concrete CSH phases will be dissolved. The released Ca reacts with the SO_4 and forms gypsum (Fig. 2). The crystallization pressure of the newly built phases can lead to the formation of cracks in the sealing structure.

After the portlandite ($Ca(OH)_2$) from the concrete matrix is used up the pore fluids are not buffered anymore and the pH decreases from about 13 to 9. The CSH phases in the concrete matrix become instable and will gradually disappear (Fig. 2 corroded part). If the diffusion velocity of the OH^- from the concrete body towards the surface of the structure is higher than the formation of brucite, Mg enters into the matrix and can lead there to the formation of high amounts of MSH phases. If the fluid pressure at the exterior of the sealing structure is high enough and if the pores in the concrete are interlinked and conductible the corrosive brine can enter far into the structure and lead to an accelerated corrosion.

Fig. 3 (above) Salt concrete in contact with salt – core form the contact of a salt concrete seal in the Asse mine; (below left) CSH-phases in salt concrete covered by halite; Friedels salt (hexagonal plates); (below right) CSH phases

These processes have been observed in many experiments with cemented materials [3] and could be reproduced by geochemical modeling [4]. The described reactions take place in the matrix of the concrete as well as on cracks and at the boundary of the concrete with the salt formation The experiments showed that the formation of $Mg(OH)_2$ first leads to a decrease of permeability and the subsequent formation of MSH phases increases the permeability.

These chemical corrosion processes of Salt concrete in contact with the corrosive Mg-, SO_4- and Cl-rich brine are shown schematically in Fig. 2. The left part of the figure shows the diffusion controlled corrosion process in the undisturbed concrete matrix. On the right the corrosion on cracks is illustrated. The corrosion processes are reflected also in the brine composition (Fig. 8). Dissolution of CSH phases rises the Ca content in solution. The thermodynamical activities of the Ca containing minerals gypsum and Friedel's salt are rising until their solubility limits are reached. With the precipitation of these minerals Ca contents in solution begin to decrease again. Parallel Mg from the solution is integrated in the newly formed MSH phases, therefore Mg contents in solution decrease continuously until Mg is consumed.

The chemical processes which are responsible for the corrosion are the same indifferent if the corroding solution enters the sealing structure very slow (only driven by diffusion) or faster (driven by advection of the brine). But for the velocity of the corrosion and kinetics of permeability increase it is very important to know if the inflow of brine into the sealing structure is driven by a slow diffusion process or by much faster advection. From Permeabilities lower than 10^{-18} m^2 the inflow of brine into the concrete structure becomes very slow. The actual initial permeabilities of fresh salt concretes general are considerably lower than 10^{-18} m^2 leading to flow velocities in the order of 10^{-8} m/a. This flow rate can be assumed in the undisturbed matrix without cracks. The corroding solutions advances so slowly that the corrosion is controlled by diffusion only.

The corrosion velocity is dependent on the pore structure of the concrete. The corrosion advances faster the more pores are interlinked thus enabling mass exchange. The degree of interconnectedness of the pores depends largely on the initial water/cement-ratio. Higher initial water/cement-ratios in a concrete result in a higher initial porosity and permeability of the concrete.

MATERIALS

Cemented materials

Beside crushed salt and Portland cement Salt concretes contain fly ashes (brown or hard coal fly ash). Crushed salt does not react with salt solutions. Halite is in chemical equilibrium with the solutions. Therefore the chemical corrosion of salt concrete can be studied by using cemented fly ashes only. The presence or absence of salt has no influence on the reaction. GRS has performed experiments with different fly ashes as well as with the salt concretes M2 and M2-4 (Tab. 1, Tab. 2). Fig. 3 shows a photograph of salt concrete in contact with rock salt and TEM pictures of the initial mineralogy of salt concrete M2-4.

Tab. 1 Chemical compositions of investigated cemented materials

Element	Cemented brown coal fly ash [mg/kg]	Cemented hard coal fly ash [mg/kg]	Cemented waste forms [mg/kg]	M2 salt concrete [mg/kg]
Al	16.710	81.012	16.998	30.759
Ca	36.610	151.214	294.172	54.746
Cl	506.800	40.340	n.d.	313.378
K	11.160	22.553	n.d.	10.202
Mg	5.760	9.473	5.833	7.583
Na	299.130	77.690	n.d.	201.825
S	2.330	9.700	6.413	5.322
Si	35.060	126.750	60.203	57.294

Tab. 2 Composition of the salt concretes M2 and M2-4

Salt concretre	Water/cement ratio	Crushed salt	Cement	Fly ash	Water
M2	0.8	1072	328	328	267
M2-4	1.8	1380	148	148	267

Salt solutions

In Tab. 3 the chemical compositions of two salt solutions are given which have been used in the experiments. NaCl solution is saturated in halite. This solutions contains only NaCl. It will be formed when water enters in a salt formations with pure halite. The IP21 solution is an invariant solution which is formed if water dissolves the soluble potash minerals carnallite ($MgCl_2KCl_2 \cdot 6H_2O$), sylvite (KCl) and kieserite ($MgSO_4 \cdot H_2O$). Both solutions are typical for German salt formations.

Tab. 3 Salt solutions used in corrosion experiments

	NaCl solution [mol/kg H_2O]	**IP21 solution [mol/kg H_2O]**
Density [g/cm^3]	1.200	1.292
Viscosity [Ns/m^2]	$2.04*10^{-3}$	$5.63*10^{-3}$
Temperature [°C]	25	25
Na	6.1	0.463
K	--	0.556
Ca	--	0.001
Mg	--	4.250
Cl	6.100	8.892
SO_4	--	0.314

EXPERIMENTAL METHODS

GRS Cascade Experiments

An experimental procedure, the so-called “cascade experiment”, was developed for the investigation of the chemical corrosion reaction path of different concretes with two different brines [3]. Fig. 4 shows the scheme of this procedure which is based on a succession of batch experiments (cascades). Basically the cascade experiment is a titration experiment. Each step or cascade is an own batch experiment. In the first step a certain volume of fine grained solid is mixed with a certain volume of brine. The reaction takes place in an air tight vessel which is shaken continuously in an over head rotator. After several days all soluble components of the solid are leached. The new brine composition is in chemical equilibrium with the amount of added solid. Now the brine is separated from the solid and transferred to another vessel where new solid is added. This procedure is repeated for several times. During the succession of these batch experiments in each step more solid is added to the initial brine volume. In each step the solid/liquid ratio is kept constant and the attainment of the chemical equilibrium is achieved. After each step only a part of the initial brine volume can be recovered and used in the next cascade. Therfore the cascade experiment ends when not enough brine can be recovered for the next batch.

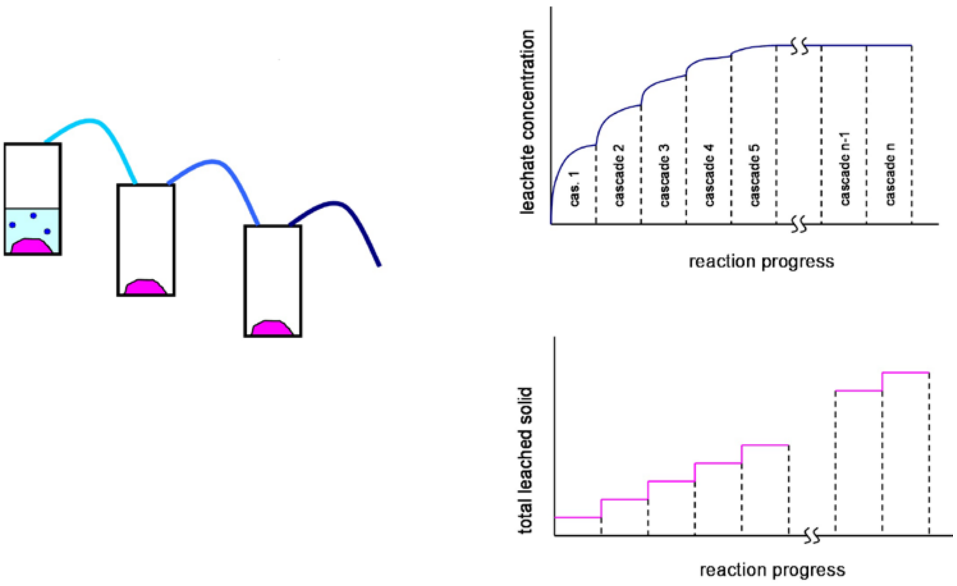


Fig. 4 Principle of cascade leaching experiments [7]

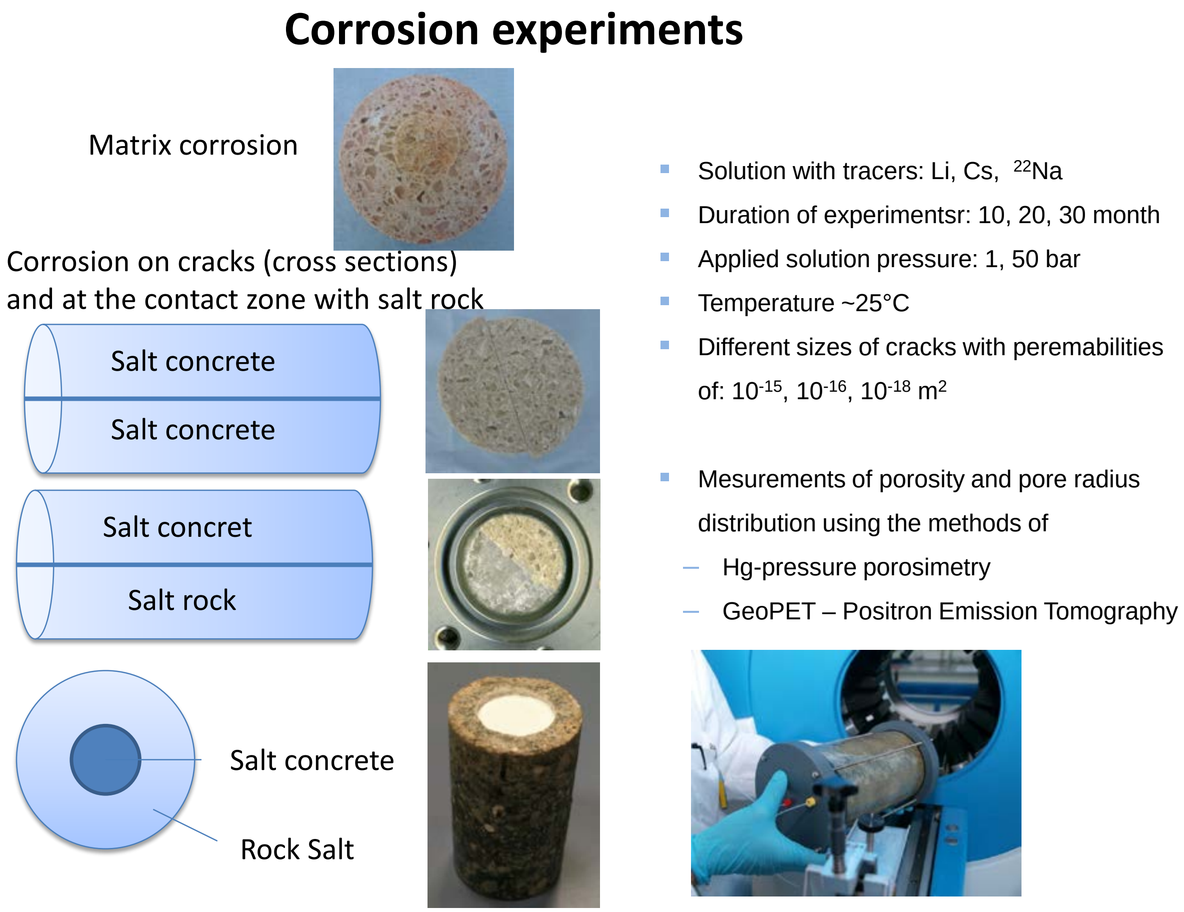
Hydro-chemical experiments

In long term safety analyses the permeability and changes of permeabiliy of sealing structures over time are key elements. Permeability controls the amount of brine which can access the waste and mobilise and tranport radionuclides. The permeability of the initial uncorroded material is well known. The material design results in a low permeability <10^{-18} m². This important boundary condition idealy should not change over time. Only materials which are in chemical equilibrium with their environment can fullfill this requirement. The geochemical investigations show to what degree this requirement can be fullfilled. If corrosion processes can not be avoided it is important to know how fast the corrosion deteriorates the materials and how much the initial permeability is changed over time.

An experimental procedure was developed which allows to determine the time dependant progress of the corrosion front in the concrete as well as the changes of permeability due to the corrosion progress. Fig. 5, Fig. 6 and Fig. 7 illustrate the procedures employed for the study of the corrosion in the undisurbed matrix as well as on cracks and at the boundary with the host rock. The solutions are spiked with tracers which don't react with the concrete and which can easily be measured. The concrete samples are cylinders of 10 cm length and 5 cm in diameter. They are introduced in steel or titanium tubes. The anular space is filled with resin. At both ends of the tubes brazen screw caps are attached. 12 of these pressure vessels can be installed in the set up for the reaction with brine (Fig. 6 and Fig. 7). As indicated in Fig. 5 the experiments are conducted with different brine pressures. For the investigation of the corrosion on cracks artificial cross sections are used with a well known aperture, geomtry and initial permeability. This procedure facilitates the modeling because the hydrological boundary conditions are well defined. The corrosion on the contact zone between the concrete and the salt host rock is studied in samples where cylindrical holes in salt rock are filled with concrete.

After the end of the allocated reaction time the samples are analysed. Starting from the side where the solutions enter the sample the surface is analysed with a combination of laser ablation – ICP. With sand paper the analyzed surface is removed and the next surface can be analysed. In this way analyses are obtained in steps of 10 micrometers. Profiles are obtained which show how far the corrsion front has advanced. By comparing the chemical analyses with the results of the geochemical modeling the input data are obtaine which are needed for reactive transport calculations.

A new procedure for the investigation and illustration of the reaction progress is PET (Positron Emission Tomography, Fig. 5). PET can visualize and quantify the pore volume, the distribution of pore radiuses, cracks and the structure of interlaced cracks. For the experiments where the samples analysed by PET the solutions are spiked with ^{22}Na. The measurements of the corrosion progress with PET are much easier and can be done more often than with the conventional method described above without destroying the sample. After the PET analyses the pressure vessels can be attached again in the est up and the experiment can continue. For the samples where this method is applied pressure vessels of titanium are needed. The ordinary vessels (Fig. 7) are made of steel. Steel absorbes the positrons during the PET measurements and can therefore not be used.



Corrosion experiments

- Solution with tracers: Li, Cs, ^{22}Na
- Duration of experimentsr: 10, 20, 30 month
- Applied solution pressure: 1, 50 bar
- Temperature ~25°C
- Different sizes of cracks with peremabilities of: 10^{-15}, 10^{-16}, 10^{-18} m^2

- Mesurements of porosity and pore radius distribution using the methods of
  - Hg-pressure porosimetry
  - GeoPET – Positron Emission Tomography

Fig. 5 Experimental procedures for the investigation of the corrosion in the matrix, on cracks and at the boundary salt concrete - rock salt

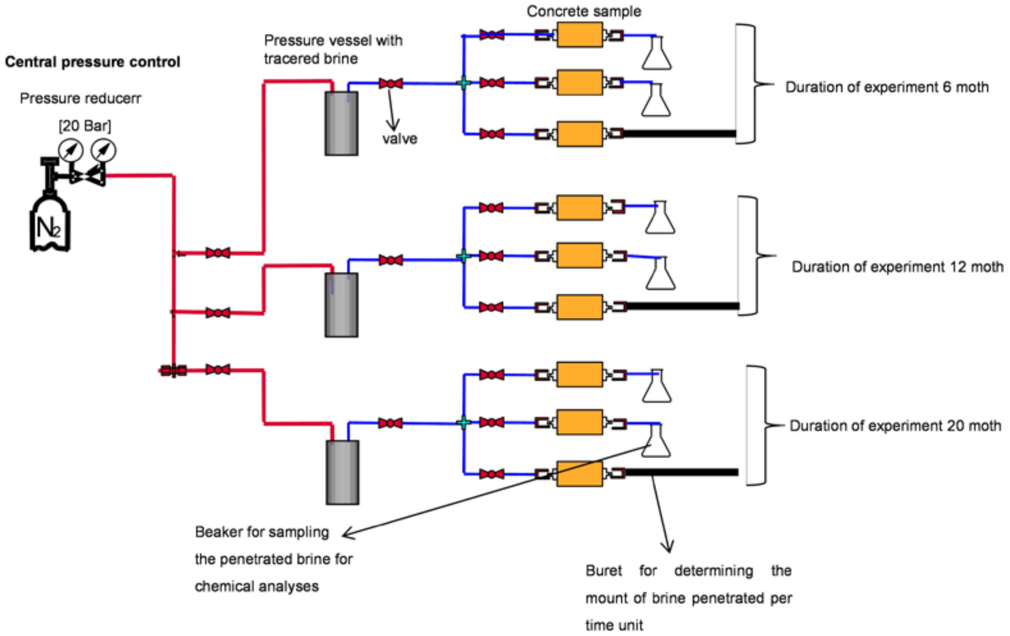


Fig. 6 Experimental set-up (inflow and percolation experiments) for measurements of the matrix corrosion and the corrosion on cracks as well as permeability changes due to the interaction of brine with concrete [2]

Fig. 7 Photograph of the experimental set-up for measurements of corrosion progrsss and permeability changes during the interaction of brines with concretes [2]

GRS has conducted experiments with the salt concretes M2 and M2-4 in contact with NaCl and IP21 salt solutions. The recipe M2-4 is very similar to that of M2 with regard to its chemical and mineralogical composition. The main difference is the higher Water/cement ratio (1.8 in M2-4 instead of 0.8 in M2, Tab. 2). The higher W/C ratio in M2-4 was chosen in order to increase the initial permeability of the concrete. This was necessary in order to obtain a faster intrusion of the corroding solution into the concrete and thus a faster and more visible corrosion progress.

NUMERICAL MODELING

Geochemical modeling

The cascade experiments correspond to the titration mode in the geochemical modeling. The experiments reproduce the corrosion reaction step by step with increasing solid/liquid rations until a final chemical equilibrium is reached at the end of the corrosion process. This is excactly how the geochemical modeling works. To the initial amount of solution containing one kg of water the solid is added in small amounts (steps = zi) and the thermodynamical equilibrium is calculated. Geochemical modeling is a powerful tool for understanding and extrapolating the chemical corrosion path beyond the experimental limits. Experiments can reproduce only a relatively small part of the entire reaction path with relatively small solid liquid ratio. In reality the amounts of fluid which reacts with the concrete is small. It is limited by the volume of pore space in the concrete. Such realistic solid/liquid ratios are not accessible by experiments. They however can be predicted reliably by the modeling if the experimental results can be reproduced. A good agreement between experiments and modeling shows that the process is understood; that the modeling takes into account all the implied mineralogical phases and that the thermodynamic database employed for the calculations is complete and consistent.

The geochemical modeling has been performed with EQ3/6 and the Pitzer data from [4] and [5].

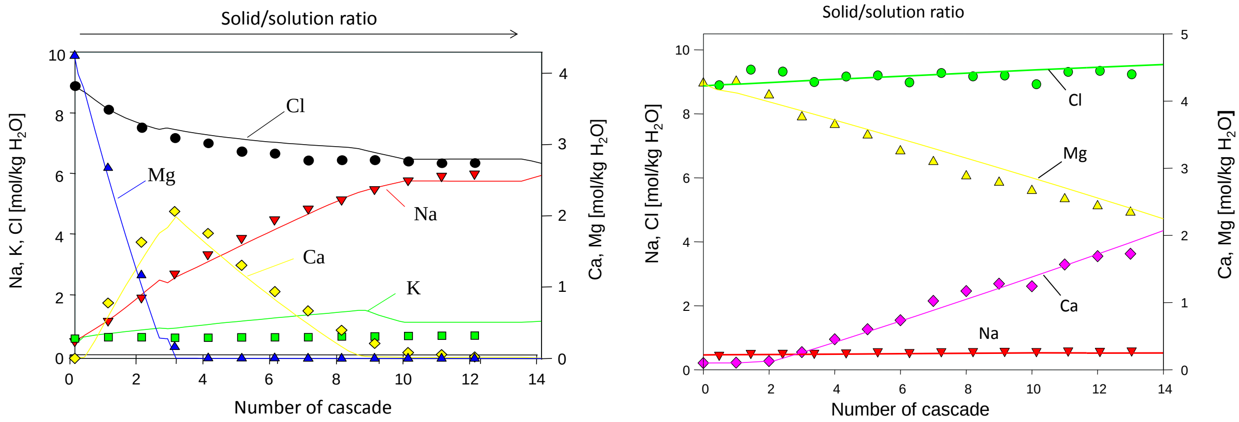
Reactive transport modeling

From geochemical modeling only one part of the information needed can be obtained. By geochemical modeling the chemical evolution of the corroding brine and the mineralogical and volume changes in the corroded material can be calculated. If all the minerals involved in the corrosion reaction have been taken into account and if their molar volume is known the volume changes during the reaction can be calculated. The modeling results can be trusted if the calculated volume changes can be verified by measurements. In order to obtain further very important information for long term safety assessments, the permeability changes must also be calculated. A reliable correlation between porosity and permeability is needed. In the reactive transport model the chemical reaction path and the most important hydraulic boundary conditions like total porosity (pore volume), pore size distribution, the porosity-permeability relation were implemented. With this model it was possible to reproduce the experimental results obtained for the matrix corrosion experiments. At the time being only the matrix corrosion is well understood and can be modeled [5]. The experiments needed for the development of the model which takes matrix corrosion and corrosion on cracks have been started. The theoretical model has been developed and it will be tested in the near future.

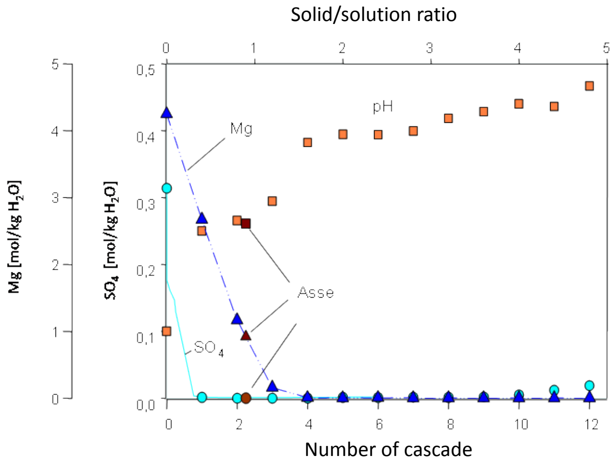
RESULTS

Chemical corrosion path of cemented materials and comparison with geochemical modeling

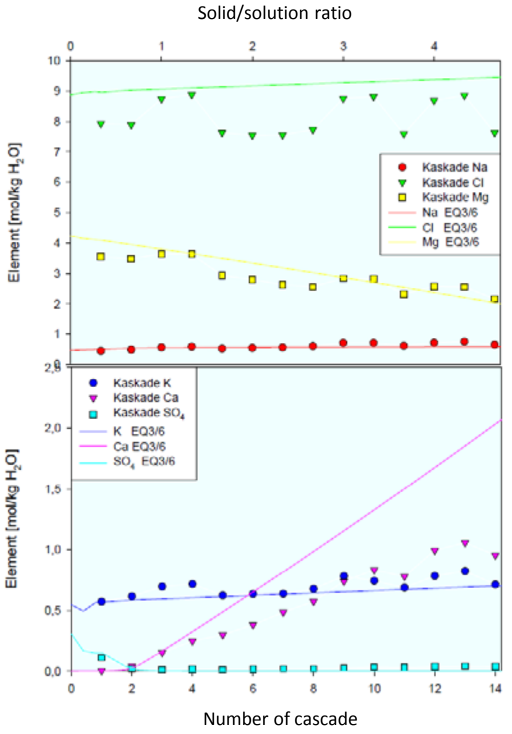
Experimental results of the cascade experiments with different cemented materials and the geochemical modeling of these experiments are shown in Fig. 8. The chemical corrosion path is well understood and can be extrapolated beyond the limits of the experiments.



(a) Corrosion path of cemented Hard Coal Fly Ash (b) Corrosion path of cemented Hard Coal Fly Ash



(c) Corrosion path of cemented Ordinary Portland Cement (OPC) and measured corrosion fluids in cemented waste forms from the Asse mine [KIE 00]



(d) Corrosion path of M2 salt concrete

Fig. 8 Chemical evolution of the pore fluid chemistry during the corrosion of different cemented materials by a Mg-, SO_4- and Cl-rich IP21 salt solution – comparison between experimental data (symbols) and results of geochemical modeling (continuous lines)

Kinetics of the corrosion – permeability changes

The chemical and mineralogical compositions of the M2 and M2-4 are similar. Therefore the chemical corrosion processes of the two materials are also identical. Experimental results obtained with the more permeable M2-4 can be used also for predictions of the long term chemical behavior of M2.

The water cement ratios of the two materials is different, 1.8 in M2-4 and 0.8 in M2. The higher water cement ratio in M2-4 leads to a higher porosity and hence to a higher permeability of M2-4 (10^{-16} m^2). The initial permeability of M2 is $<10^{-20}$ m^2. The different ratio affects the mechanical properties too. M2 has a higher mechanical strength (Tab. 4). The better hydraulic conductivity of M2-4 was chosen by purpose. It was important for the investigation of the kinetics of the corrosion process and its impact on the hydraulic properties. The maximum time span allowed for the investigations was five years. As it was not probable that M2 with its extreme low initial permeability would change very much within the allocated time, the chemically identical but more permeable M2-4 was chosen for the investigations of the kinetics of the chemical corrosion processes. But the mechanical and hydraulical changes registered in flow through experiments with M2-4 during 5 years cannot be used for forecasts of the behavior of M2.

In one set of experiments with M2 and M2-4 the pore volume was exchanged once. The pore water chemistry of the pore solution and the permeability of the concrete were measured after 1 year, after 3 years and after 5 years. In 5 years the initially very permeable M2-4 was totally penetrated by the corroding IP21 solution. The permeability decrease and the mechanical strength deteriorated considerably. In the M2 concrete the corroding solution did not enter far into the sample because of the very low initial permeability. Accordingly the corrosion did not affect the permeability and the mechanical properties to a measurable extend in fife years. In fife years the permeability of M2-4 decreased from by 1 – 1.5 orders of magnitude compared with the permeability of the material 28 days after curing. This result is interpreted as follows: 28 days after curing the hydration process on the concrete was not yet finished. It went on over a much longer time. The ongoing hydration process reduced the initially high permeability. The hydration process was overlain by the corrosion with an opposed effect, increase of permeability. After 5 years hydration effect still outbalanced the corrosion effect in terms of permeability changes.

In a second set of experiments the pore volume was exchanged 34 times by applying a brine pressure of 20 bar. In these experiments the hydration effect was not relevant. It was negligible compared to the fast corrosion by the continuous supply of fresh corrosive solution with high Mg content. Fig. 9 shows that during the first 5 pore volume exchanges the permeability decreased from $4 \cdot 10^{-16}$ m^2 to $4 \cdot 10^{-18}$ m^2 than it rose again up to the starting value. After the 20th pore volume exchange a sharp increase of the permeability took place which ended at the end of the experiment at a permeability of about $2 \cdot 10^{-14}$ m^2. Whereas the first decrease of permeability can be explained by the clogging of pores due to the formation of brucite gel the following increase is due to the flushing away of brucite and an increase of permeability due to the disintegration of the CSH phases. The sharp rise of permeability after the 20th pore volume exchange is not due any more to a chemical corrosion but probably to a physical corrosion. This explanation seems plausible because the chemistry of the penetrating solution shows that the last CSH phase are totally destroyed already before the 20th pore volume exchange. The experimental results could be reproduced by reactive transport modeling up to the 20th pore volume exchange. This model cannot describe physical corrosion which probably took place at the end of our experiments (beyond the 20th pore volume exchange).

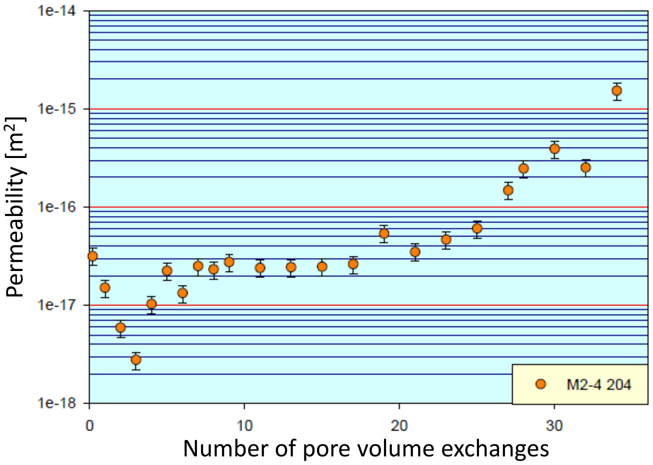


Fig. 9 Permeability changes of M2-4 salt concrete in contact with IP21 solution at rising numbers of pore volume exchange

Mechanical strength of corroded salt concretes

Tab. 4 Mechanical strength of the salt concrete M2-4 and M4

Salt concrete	Salt solution	Failure stresses after different reaction times [MPa]			
		Initial value (28 days after curing)	after 1 year in solution	after 3 years in solution	after 5 years in solution
M2-4	NaCl	3.1	9.7	9.7	8.6
	IP21		4.2	4.4	5.1
M2	NaCl	23	24.2	22.6	23.6
	IP21		25.1	24.8	30.2

DISCUSSION

Due to the corrosion of CSH phases salt concrete loses its mechanical stability and increases its permeability. Nevertheless this material can be used for sealing constructions as long as the increasing permeability does not exceed certain values in a certain time frame. In safety assessment calculations it is assumed that the initial permeability of 10^{-18} m^2 will increase up to 10^{-14} m^2 in the corroded construction. The safety concept relies on the fact that salt concrete will corrode slowly enough in order to fulfill these requirements. Matrix corrosion and permeability changes of a specific salt concrete M2 by Mg-rich IP21 salt solution are well understood. Laboratory experiments and modeling results (geochemical and reactive transport modeling) agree satisfactorily well. A direct correlation exists between corrosion progress and the decrease of Mg-content in the corroding brine. The linear decrease of Mg in solution is due to the incorporation of Mg in the MSH phases. Mg depletion in solution can be used for the calculation of a corrosion potential of the brine. The corrosion potential of IP21 solution for M2 salt concrete is 2.5, i. e. 2.5 m^3 of salt concrete can be totally corroded by 1 m^3 of IP21 solution. The corrosion indicates the amount of corroded material in a sealing construction of a known geometry assuming uniform matrix corrosion.

These geochemical results combined with transport parameters like diffusion coefficients/permeation coefficients and changes of porosity and permeability allow the calculation of the time frame in which a salt concrete dam of a known geometry is totally corroded. These modeling results can be used for an optimization of the length of the sealing construction. This length is a function of the time in which a certain permeability value of the construction shall not be exceeded.

By assuming that the corrosion front advances uniformly in the sealing structure and that it is driven only by diffusion the permeability increase in the sealing structure of a known length and a known brine composition and brine pressure can be calculated. These calculations can serve for the planning of the length of sealing structures. According to the results of such calculations a 1:1 scale drift seal was built in the Morsleben repository. This construction however showed unexpected results. The salt concrete in the structure developed cracks which had not been anticipated. It can be assumed that the corrosion on cracks proceeds differently and much faster than the calculated corrosion. The matrix corrosion model must be extended in order to take into account also the corrosion on cracks. To do this new experiments are needed. These experiments are under way.

CONCLUSIONS

Salt concrete is stable in Mg-free NaCl-rich brines but it is not stable in the presence of high amounts of Mg, SO_4 and Cl in solution. The chemical corrosion processes are well understood. Experimental results from small scale laboratory tests as well as from large scale in-situ tests can be reproduced accurately by geochemical and reactive transport modeling. Corroded salt concrete loses its mechanical stability and increases its permeability. A direct correlation exists between the corrosion progress and the decrease of Mg-content in the corroding solution. The Mg content in solution can be used for the calculation of a corrosion potential of the brines for salt concrete. Geochemical modeling and sensitivity analyses are powerful tools for the optimization of the concrete recipes regarding it's long term stability in salt solutions. The velocity of the corrosion and permeability changes of sealing structures can be measured and modeled. A reactive transport model was developed which is able to describe the corrosion of salt concrete driven by diffusion or advection of the penetrating brine. The chemical corrosion is the same, independent from the velocity of fluid flow through the sealing structure. The velocity however depends largely on the velocity of the fluid flow which depends on total porosity and the pore structure. Fluid flow driven only by diffusion is very slow. Even though salt concrete is not stable in the presence of Mg, SO_4 and Cl in the solutions permeability changes of the intact undisturbed matrix are very slow and so minor that salt concrete can be used as a sealing material even in regions where such brines may be expected. This however may not be the case if cracks in the sealing construction cannot be excluded.

REFERENCES

[1] Bonen, D. (1992): Composition and appearance of magnesium silicate hydrate and its relation to deterioration of cement-based materials – J. Am. Ceram. Soc. (75), p 2904-2906

[2] Hagemann, S. und Meyer Th, (2003): Unsicherheits- und Sensitivitätsanalyse zur Korrosion von Salzbeton durch salinare Lösungen - GRS-A-3458, Projekt Morsleben, PSP Element

9M 232 200 11, 114 p.

[3] Herbert, H.-J. (2000): Zur Geochemie und geochemischen Modellierung hochsalinarer Lösungen – Geol. Jhb. Reihe D, Heft SD 1, 191p.

[4] Harvie, C. E. Moller, N. and Weare, J. H. (1984): The prediction of mineral solubilities in natural waters: the Na-K-Mg-Ca-H-Ck-SO4-OH-HCO3-CO3-CO2-H2O system in high ionic strength at 25°C – Geoch. Cosmoch. Acta, v 48, 723-751.

[5] Altmaier, M., Brendler, V., Bube, Ch., Marquardt, Ch., Moog, H., Richter, A., Scharge, T., Voigt, W. and Wilhelm, St. (2011): THEREDA Thermodynamic Referenc Database – GRS Report GRS-265 ISBN 978-3-939355-41-0, 63p.

[6] Meyer, Th. & Herbert, H.-J. (2007) Langzeitversuche zur Korrosion von Salzbeton durch salinare Lösungen – GRS-Z-2007 report for BfS, PSP Element 9M 232 200 11, 15 p.

[7] Meyer, Th. & Herbert, H.-J. (2008): Modelltheoretische Untersuchung der Umlösekapazität von IP21-Lösung bei der Korrosion von Salzbeton – GRS-A-3384, Projekt Morsleben, PSP Element 9M 232 100 51, 36p.

ACKNOWLEDGEMENTS

The GRS research work was funded by the German Federal Ministry of Education and Research (BMBF) under contract numbers 02 C 0830, 02 C 1275, 02 C 1335 and by the German Federal Ministry of Economics and Technology (BMWi) 02 E 9047 via the Projektträger Karlsruhe (PTKA-WTE) as well as by the Federal Office for Radiation Protection (BfS) for the Morsleben specific project work.