The behaviour of sodium silicate solutions (water glass) in the saline environment and their use in salt mining

Hans-Joachim Engelhardt & Lieselotte Ernestine von Borstel*

Abstract: Alkaline sodium silicate solutions, also known as water glass, are a combination of sodium oxide, silica and water. The solutions react with soluble salts and brines which induce the formation of solids. The solutions have a long history of use as a particle-free grout to seal pathways for fluids in rocks and building materials. The applications demonstrate the ability of sodium silicates to seal active brine intrusions. For the grouting of rock salts it was necessary to prove the long-term stability of the reaction products. The investigations showed a formation of silicate phases and halite. In contact with $MgCl_2$-dominated brines or $MgCl_2$ containing minerals, e.g. bischofite or carnallite, the main additional reaction products are magnesium oxichlorides. The silicates and oxichlorides are characterised by a very low solubility, and halite is insoluble in the brines. Accordingly, sodium silicate solutions are capable to seal rock salts permanently.

Kurzfassung: Alkalische Natriumsilikat-Lösungen, die auch als Wasserglas bezeichnet werden, enthalten Natriumoxid, Silikatkomplexe und Wasser. Die Lösungen reagieren mit löslichen Salzen und Salzlösungen, wobei Festkörper entstehen. In Folge dieser Reaktionen werden Wasserglaslösungen bereits seit längerer Zeit zum Abdichten von Wegsamkeiten in Gesteinen und Baustoffen eingesetzt. Die Anwendungen belegen die Fähigkeit der Natriumsilikate aktive Lösungszutritte abzudichten. Als Grundlage der Injektion von Steinsalz war die Langzeitstabilität der Reaktionsprodukte nachzuweisen. Die Untersuchungen belegen die Bildung von Silikatphasen und Halit. Im Kontakt mit $MgCl_2$-haltigen Lösungen und $MgCl_2$-haltigen Mineralen entstehen zusätzlich Magnesiumoxichloride. Die Silikate und Oxichloride sind gekennzeichnet durch eine geringe Löslichkeit und Halit ist in den Salzlösungen unlöslich. Demzufolge sind Natriumsilikat-Lösungen geeignet dauerhaft Wegsamkeiten im Steinsalz zu verschließen.

Keywords: grout, halite, long-term stability, magnesium oxichlorides, rock salt, sodium silicate, solubility

Schlüsselwörter: Halit, Injektionsmaterial, Langzeitstabilität, Löslichkeit, Magnesiumoxichlorid, Natriumsilikat, Steinsalz

1. Introduction

Sodium silicate solutions are derived from soluble sodium silicate glasses. They are water solutions of sodium oxide (Na_2O) and silicon dioxide (SiO_2). The solutions are generated in different grades that are characterised by their $SiO_2:Na_2O$ ratios, varying between 2:1 and 3.75:1, and differing in water contents. Because of their low viscosity, the silicate solutions are called water glass or liquid glass. A common property of the solutions is a high alkaline milieu. A decrease of the pH-value and/or an increase of electrolytes (salt) induce a visual initial gelation and a subsequent hardening.

Their range of viscosity, the small size of colloidal silica, and the comprehensive quality control of the products suggest their application as grout (cf. Miwa & Yonekura 1994). As the penetrating capability of particle-based grouts is lim-

ited, the solutions are often applied subsequent to a pre-grouting with slurries. Since 1925 sodium silicate has been used as chemical grout for the stabilisation and sealing of rocks and soils. Traditionally, the works comprise a post-grouting with salt solution, a so-called hardener, which causes the deposition of solids which in turn seal fine pores or fissures (Joosten 1953). Guidelines for the injection of building grounds are given by the standard EN 12715 (2000). Information about the properties of injected materials is summarised by Kutzner (1968).
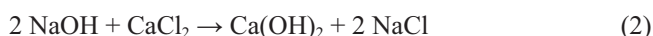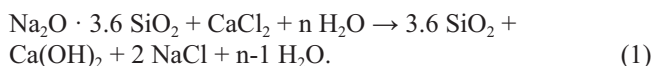
Lohmann (1930) describes a successful application in the course of a dam construction in a potash mine. However, for the construction of long-term seals, a profound knowledge of the chemical and mineralogical interactions with the rocks and brines is of vital importance. A first insight is given by Engelhardt et al. (2012). This study considers new experi-

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mental results, gives an overview of the relevant chemical systems, and describes application fields arising from the material behaviour of sodium silicate solutions.

2. Basics of water glass reactions

In a non-saline environment, a post-grouting with $CaCl_2$ solution mainly initialises the formation of solid particles. The reactions can be described by the simplified equations 1 and 2, which assume a SiO_2/Na_2O mol ratio of 3.6. SiO_2 acts as a substitute for silicate phases, which contain H_2O.

$$Na_2O \cdot 3.6\ SiO_2 + CaCl_2 + n\ H_2O \rightarrow 3.6\ SiO_2 + Ca(OH)_2 + 2\ NaCl + n\text{-}1\ H_2O. \tag{1}$$

$$2\ NaOH + CaCl_2 \rightarrow Ca(OH)_2 + 2\ NaCl \tag{2}$$

The chemical system containing $CaCl_2$ is of subordinate importance in marine evaporate rocks. Most of brines saturated with halite contain high amounts of $MgCl_2$. The system $MgCl_2$–$NaOH$–H_2O was described by Bilinski et al. (1984) and Mazuranic et al. (1982). Other relevant investigations were carried out by D'Ans & Katz (1941) and D'Ans et al. (1955; cf. Bodine 1976, Xiong 2010). It is accepted that $Mg(OH)_2$ (brucite) crystallises in brines containing up to 50 g $MgCl_2$/kg H_2O. This reaction can be described in a simplified way by equation 3.

$$2\ NaOH + MgCl_2 \rightarrow Mg(OH)_2 + 2\ NaCl \tag{3}$$
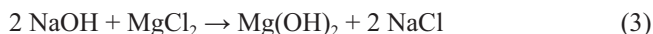
At higher $MgCl_2$ concentrations reaction products are magnesium oxichlorides (MOC). They are characterised by their mol ratio of $Mg(OH)_2$, $MgCl_2$ and H_2O. In the range of common rock temperatures, the 5-1-8 MOC phase (phase 5) is metastable and converts to the 3-1-8-phase (phase 3). The crystal structure of these phases was determined by De Wolff & Walter-Lévy (1953) and Sugimoto et al. (2007; cf. Ma-

linko 1983). The data prove that the solubility of the phase 3 is negligible in solutions having $MgCl_2$ concentrations comparable to natural brines.

The initial formation of amorphous silica depends on the pH-value, the salt content of the solution as well as on its pressure and temperature.

The lowest pH-value of brines in evaporate rocks is 5.4 (Usdowski & Herrmann 2002), and most of the brines are characterised by near neutral pH-values. The capability of dissolved Mg^{2+} ions to form hydroxides impedes the development of alkaline pH conditions. According to experiments with low saline solutions (cf. Palmer & Palmer 1995), the dissolution of amorphous silicates results in a SiO_2 concentration of approx. 115 μg/g (54 μg Si/g) at neutral pH conditions. Solutions, saturated with respect to quartz have a SiO_2 concentration of approx. 5.4 μg/g. Rykart (1995) describes an upper limit of 11 μg SiO_2/g (5 μg Si/g).

Investigations on the solubility of amorphous silica in salt solutions were performed by Marshall & Warakomski (1980) and Hamrouni & Dhahbi (2001; cf. Felmy et al. 1994). According to Fig. 1, SiO_2 solubility decreases with increasing NaCl and $MgCl_2$ concentration of the solutions (cf. Millero 1996). The salting-out effect of NaCl results in a maximum SiO_2 content of approx. 35 μg/g (16 μg Si/g) in the saturated solution (26.5 wt%, 25 °C). Most solutions stored in evaporite rocks contain $MgCl_2$ contents higher than 20 wt%. These solutions are characterised by a maximum SiO_2 content of 21 μg/g (10 μg Si/g).

At a temperature of 40 °C the solubility of amorphous silica is about 150 μg/g (Haiyan 2008). However, no data exist on the solubility of silica species in concentrated salt solutions in the temperature range of interest. Loucaides (2009) stated that the amounts of silicate dissolved in seawater at 200 bar (20 MPa) were practically identical to those measured at atmospheric pressure. The overburden pressure is 200 bar at a depth of approx. 950 m below the earth's surface. Accordingly, it is possible to neglect the pressure dependence of silicate solubility.
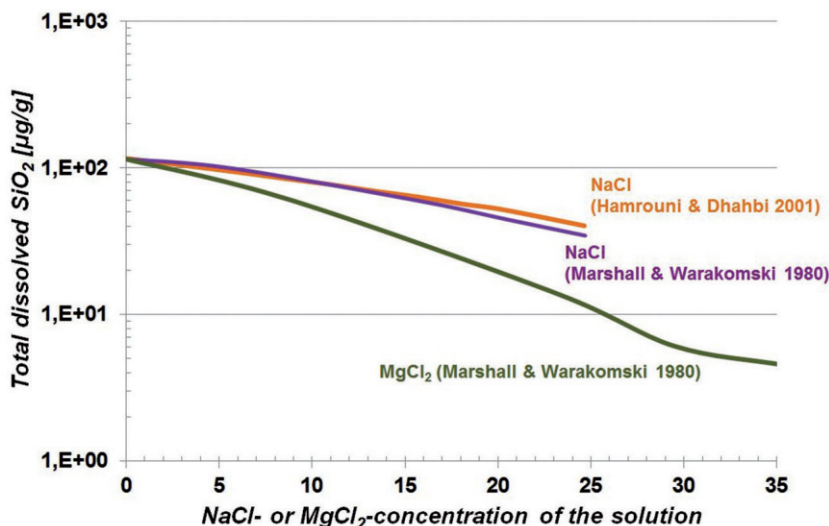

Fig. 1: Solubility of amorphous silica in solutions containing NaCl or $MgCl_2$.

In the temperature and pressure ranges under consideration amorphous silica is metastable and low quartz is the stable form of SiO_2. Consequently, it can be assumed that the structural order of the amorphous silica will increase over time (cf. Henisch 1996, Shroff & Shah 1993). Although all solids tend to exist in the crystalline state, little is known about the reaction rate. In the case of silica, the energy difference between the amorphous and crystalline state is small. Furthermore, a high energy of activation is required to induce the rearrangement of the bonds. As a result the amorphous silica can preserve its stability for years.

3. Laboratory investigations

The main objectives of the investigations were to verify the assumed reactions and to detect the potential reaction products halite, magnesium oxichloride, and silicate phases.

Sodium water glass with a density ranging between 37 and 40 °Baumé is a common grout. Thus, it was decided to use this water glass (1.36 g/cm³), which consists of approx. 8.2 wt% Na_2O, 28.5 wt% SiO_2 and 63.3 wt% H_2O. These values correspond to a SiO_2:Na_2O ratio of 3.5 (by weight) and 3.6 (molar ratio). The pH-value of the solution is approx. 11.4.

Hitherto, investigations of the gelation time focuses on the reaction of the water glass with salt solutions. For instance, Funehag & Axelsson (2003) describe that the gelation time decreases significantly from approx. 85 minutes to less than 10 minutes when the NaCl concentration of the solution is increased from 1.3 to 2.0 mol/litre (cf. Shroff & Shah 1993).

The reaction of water glass with minerals depends for example on the mineral dissolution rate. New small-scale experiments were performed to gain insight into the behaviour of the predominant salts in sodium silicate solutions. After the preparation of strewn slides, the dry crystals were covered by drops of the solutions to observe the reaction at the
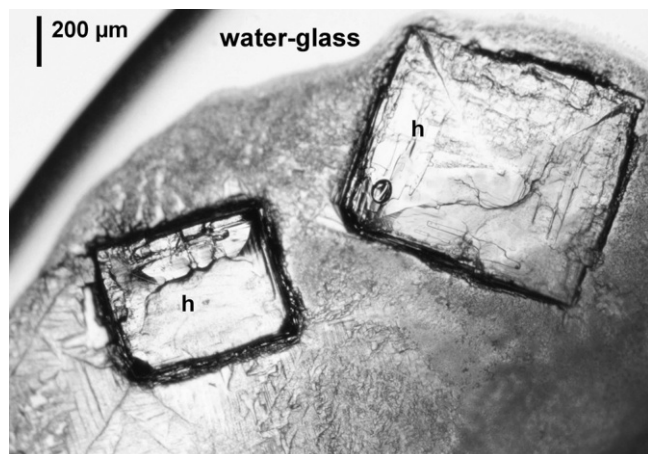
Fig. 2: Optical photomicrograph showing the secondary halite crystals (h) with bands rich in fluid-inclusions.
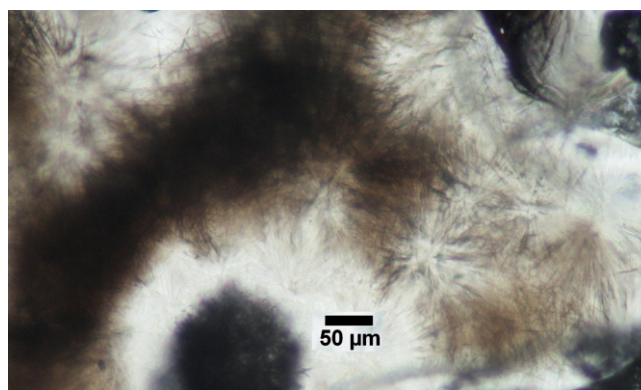
Fig. 3: Optical photomicrograph illustrating the formation of magnesium oxichlorides due to the reaction of a sodium silicate-halite mixture with concentrated $MgCl_2$-solution.

crystal surfaces by means of optical microscopy. The observations document a rapid reaction of the water glass and the salts. In the case of halite as raw material, a spontaneous growth of halite crystals in the layer covering the single particles is noticeable (Fig. 2). The results were independent of the grain size of the salt crystals.

The next steps focused on the reaction of silicate gels with salt solutions. In NaCl solutions modifications of the material were limited to a growing of dendritic formations and visual changes of the silicates. In brines containing $MgCl_2$, long needles of magnesium oxichlorides crystallise. Over time, crystal lawns and networks form (Fig. 3).

The laboratory experiments considered an injection of rock salt with water glass. The influence of the contact with NaCl and $MgCl_2$ solutions on the mineral content and the composition of the solutions were investigated over time up to an experimental duration of one year.

3.1 Sample preparation

Barrels of 60 millilitre syringes were filled one halfway with halite grit and halfway with water glass. The porosity of the salt was about 35 vol%. Immediately after inserting the plungers, the syringes were clamped in a bench vice and the water glass was pressed upwards through the salt. After replacing the air in the pore space of the salt, the syringes were sealed air-tight to prevent a reaction with carbon dioxide in the air which would induce the formation of sodium carbonate crystals (Fig. 4).

The samples were stored at room temperature for half a year. After this storage period, attempts to press water glass and salt solutions into the samples failed. The plastic syringes were cut in order to remove the hardened cylinders, which had a diameter of 28 mm and a length of approx. 45 mm.

For the subsequent experiments, the surface areas of the samples were enhanced by crushing and milling. To avoid problems during the grain size fractionation, which may arise due to residual moisture, it was decided to dry the mate-
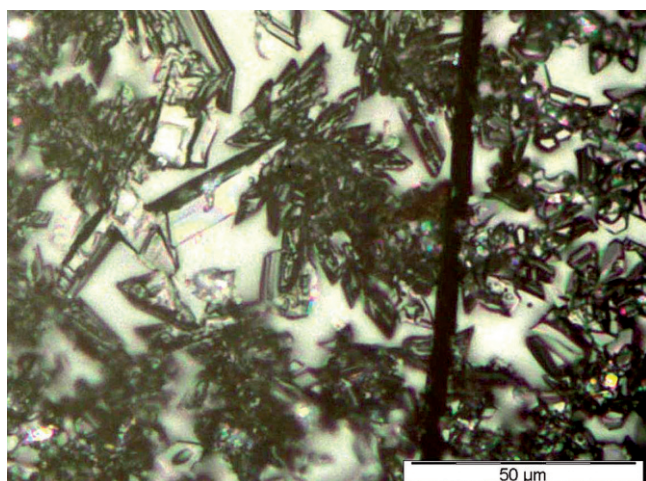
Fig. 4: Optical photomicrograph showing sodium carbonate crystals on the surface of a sodium silicate-salt mixture.
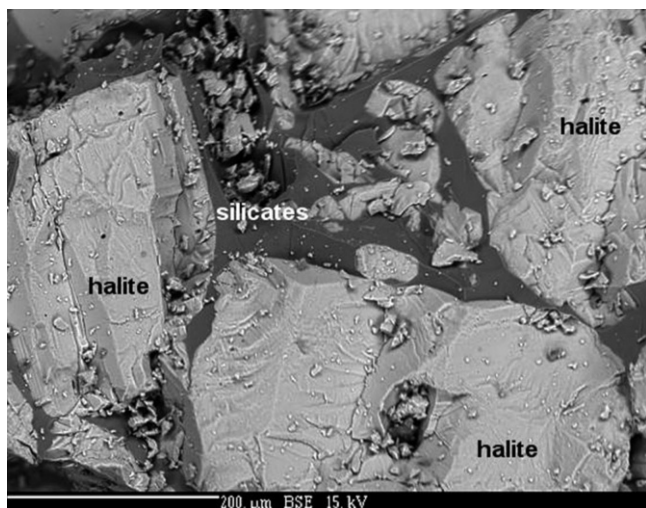
Fig. 5: Backscattered electron image of the dried raw material showing halite and silicates, which were formed by the reaction of water glass with halite.

rial at 32 °C. A particle size fraction of 450 to 2000 μm was used for the experiments with salt solutions. All experiments, with the exception of one at 35 °C, were performed at room temperature.

Fig. 5 shows a backscattered electron image of the particles. The sample was washed with ethyl alcohol to avoid mineral crystallisations during the drying process (35 °C) that was necessary for the sample preparation.

3.2 Composition of the test solutions

A pure NaCl-saturated solution was used to investigate the reactions in the system $NaCl–NaOH–SiO_2$. The NaCl concentration of the solution was about 26.2 wt% (73.8 wt% H_2O). Brines stored in marine evaporate formations are dominated by $MgCl_2$. Their composition is mostly comparable to

the invariant solutions R or Q of the quinary salt system (cf. Braitsch 1971). The R-solution is saturated with the minerals kieserite, carnallite, kainite and halite, and the Q-solution with carnallite, kainite, sylvite and halite. A Q-solution was chosen for the experiments. However, the KCl and $MgSO_4$ content of the Q-solution broadens the potential of chemical reactions. Therefore, NaCl-saturated brines containing 4.4 wt% $MgCl_2$ (74.2 wt% H_2O), 10.4 wt% $MgCl_2$ (74.6 wt% H_2O) and 20.2 wt% $MgCl_2$ (73.9 wt% H_2O) were produced for the experiments, allowing a well-directed crystallisation of magnesium oxichlorides.

3.3 Execution of the solid-solution tests

The dried material and the brines were mixed in a mass ratio of 1 to 3 and 1 to 5 (NaCl-$MgCl_2$ solution). The air-tight polyethylene bottles were moved daily on a shaking platform. After 90 days the mixtures were stored without any movement. Samples of the brines were centrifuged over a time span of 30 minutes at a speed of 20 000 rounds per minute. Solid samples were cleaned, washed with ethyl alcohol, filtered (45 μm), and dried at 35 °C in order to prepare the specimens for mineralogical and chemical analysis and to impede mineralogical changes of the solids after sampling.

The solids were studied by means of X-ray diffraction analyses (XRD) and backscattered electron imaging including semi-quantitative energy dispersive X-ray microanalysis (EDX, EDRFA). The oxygen contents were calculated on a stoichiometric basis prior to a scaling to 100 wt%. The contents of dissolved Na^+, K^+, Mg^{2+}, Cl^-, and SO_4^{2-} were analysed by ion chromatography. The concentrations of dissolved Si were determined by inductively coupled plasma mass-spectrometry. The pH-values were measured with a calomel electrode.

3.4 Experimental results

The analyses show that the SiO_2:Na_2O ratio (by weight) increased to a value of 4.0 due to the reaction of the sodium silicates with halite. This ratio corresponds to an amount of 0.52 wt% secondary halite in the halite–water glass samples. The results of the experiments with salt solutions make it possible to describe the behaviour of water glass injections in rock salt during the contact with salt solutions.

3.4.1 Pure NaCl solution

The XRD patterns show the dominant peaks of halite and the elevated background between 50 and 52 °2theta, which were assigned to amorphous silicate phases. A peak at 28.56 °2theta, according to a d-spacing of 3.124 Å, indicates the build-up of a mineral structure. The EDX analyses indicate a general increase of the SiO_2:Na_2O ratio of the silicates. In one extreme case it was possible to calculate the formula $Na_2Si_{22}O_{45}$, which corresponds to a SiO_2:Na_2O mass ratio of

21.3. This documents a release of NaOH leading to a crystallisation of halite, which can be identified as idiomorphic crystals in the backscattered electron images.

In addition, this release of NaOH causes an increase of the pH-value from 7.2 to almost 11. The Si contents varied between approx. 20 and 40 µg/g (ppm), with an average value of 28 µg/g. Compared with Fig. 1 (16 µg/g), these values are slightly increased, which is a result of the alkaline pH-value. During the experiments no significant change in the NaCl content, pH value and Si content of the brines were observed.

3.4.2 NaCl-MgCl$_2$ solutions

For the silicate phases the XRD patterns of the solids in the pure NaCl and the NaCl-MgCl$_2$ solution are comparable. A background signal in the range 20–25 °2theta can be assigned to the amorphous or poorly crystallised magnesium oxichlorides. Peaks document the formation of 5-1-8 MOC, which transfers into 3-1-8 MOC. Figs. 6 and 7 show the crystal morphology.
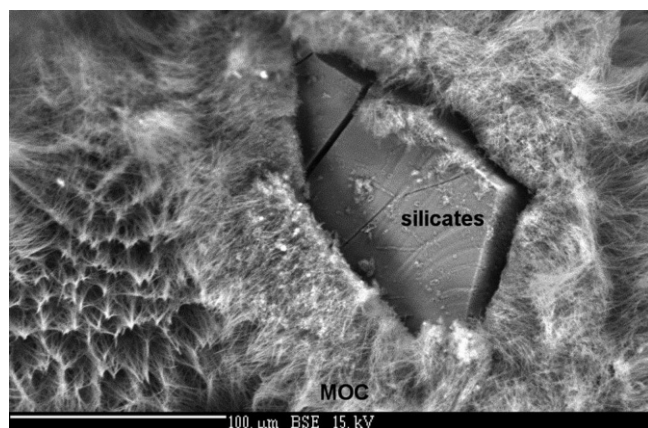

Fig. 6: Backscattered electron image of magnesium oxichloride needles (MOC) and Na-silicates after ten days in NaCl-MgCl$_2$ solution (4.4 wt% MgCl$_2$, 20 °C).
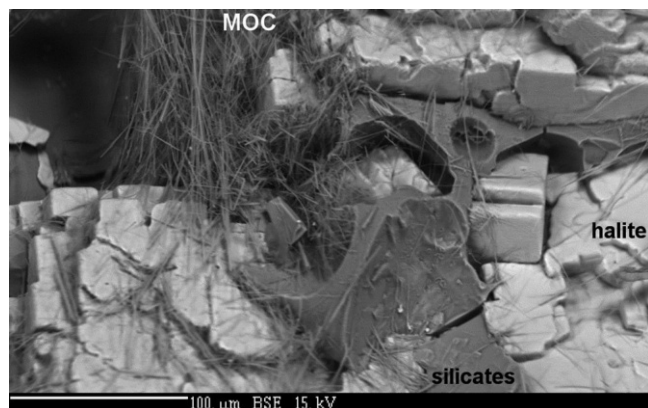
Fig. 7: Backscattered electron image of magnesium oxichloride needles and halites after ten days in NaCl-MgCl$_2$ solution (20.2 wt% MgCl$_2$, 35 °C).

The MOC already crystallises in the 4.4 wt% MgCl$_2$ solution (0.62 mole MgCl$_2$/kg H$_2$O). An increase in the MgCl$_2$ concentration or rather the MgCl$_2$/H$_2$O ratio of the solution facilitates the formation of 3-1-8 MOC. Equation 4 illustrates the reaction of the dissolved ions into MOC and the fixation of free water into its crystal structure.

$$6\ Na^+ + 6\ OH^- + 4\ Mg^{2+} + 8\ Cl^- + 8\ H_2O \rightarrow$$
$$3\ Mg(OH)_2 \cdot MgCl_2 \cdot 8\ H_2O + 6\ NaCl \qquad (4)$$
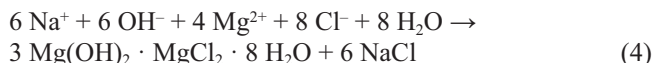
EDX analyses of the silicates prove that the release of Na$^+$ is coupled with a fixation of Mg^{2+}. In some cases it was not possible to detect sodium in the silicate structure. The calculated formula of these particles is Mg$_4$Si$_7$O$_{18}$.

Fig. 8 illustrates the changes in the Mg^{2+} (MgCl$_2$) content of the solutions as well as the coupling with the pH-values. The release of NaOH out of the structure of the silicates causes the corresponding increase in Na$^+$, and accordingly NaCl.

In the solutions with 4.4 wt-%, 10.4 wt% and 20.2 wt% MgCl$_2$, Si reaches a maximum value of 4 µg/g. Considering the arithmetic mean of 28 µg Si/g in the pure NaCl solution, the Si solubility decreases by a factor of approx. 10. A temperature rise (35 °C) is not coupled with an increase of the Si-amount.

3.4.3 Q-solution

The mineralogical investigation shows no significant differences to the experiments with NaCl-MgCl$_2$ solutions. According to the high MgCl$_2$:MgSO$_4$ ratio of 9.9 (by weight) or 12.6 (molar ratio), a low amount of magnesium oxisulfates crystallises (Cole & Demediuk 1957). The formula 2 MgSO$_4$·Mg(OH)$_2$ · 2 H$_2$O could be estimated based on the energy dispersive X-ray microanalysis. Similar to the NaCl-MgCl$_2$ solutions the amount of dissolved Na$^+$ increases, the concentration of Mg^{2+} decreases and the pH-value rises from approx. 5 to 6.9. The crystallisation of magnesium oxisulfates causes no significant change in the SO$_4$$^{2-}$ content. The concentration of K$^+$ decreases from 1.22 wt% to 1.12 wt%, although no minerals containing potassium could be detected. The amount of dissolved Si was less than 1 µg/g due to the high ionic strength and Mg content of the Q-solution.

3.4.4 Geochemical calculations

According to XRD analysis poorly crystallised magnesium oxichlorides as well as the 5-1-8 phase transform to the thermodynamically stable 3-1-8 phase. Mineralogical changes are coupled with the corresponding changes in the solution composition. This fact was used to verify the XRD results as well as the conclusion that the 3-1-8 phase is the final reaction product.

The chemical results of the experiments with NaCl-MgCl$_2$ solutions (chapter 3.4.2) were used for calculations on the basis of the data base developed by Harvie et al. (1984), enhanced by thermodynamic data of the 5-1-8 MOC phase. This data base can be used to model solutions up to high concentra-
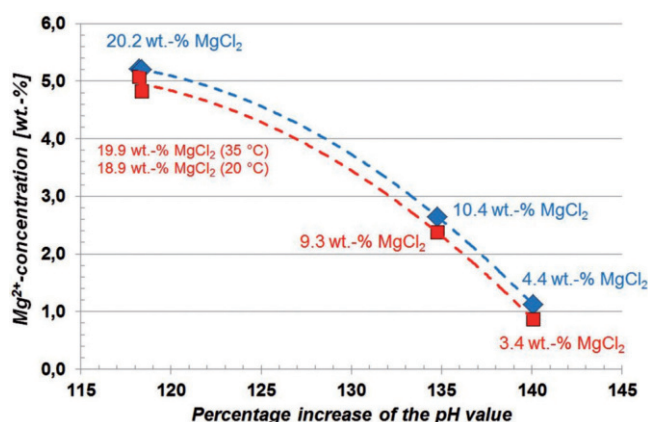
Fig. 8: Mg^{2+} concentration of the solutions vs. percentage increase in the pH-value in the course of the experiments. Mg^{2+} concentration of initial solutions (blue line) and at the end of the experiments (red line).
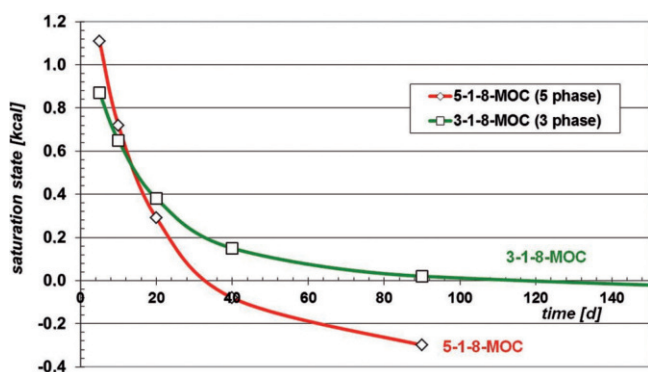

Fig. 9: Calculated saturation state of the MOC phases during the first 150 days of the experiment at room temperature. Squares and diamonds indicate the calculated saturation states. The red and green lines represent equations adjusted to the calculated saturation states.

Fig. 10: Calculated saturation state of the MOC phases (ordinate) during the experiment at 35 °C. The axis of abscissa shows the duration of the experiment in days. Squares and diamonds indicate the calculated saturation states. The red and green lines represent equations adjusted to the calculated saturation states.
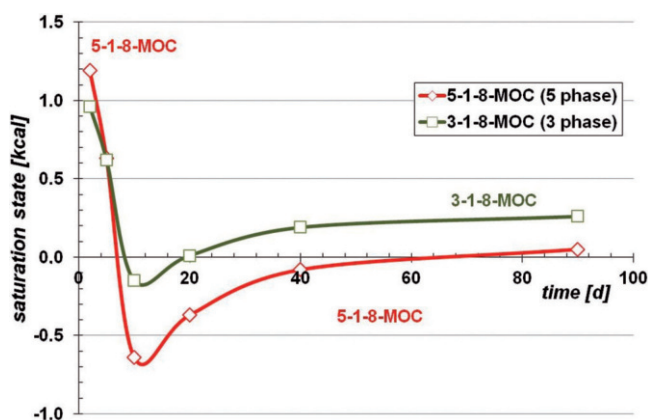
tions. However, it only covers the set of major cations and anions in seawater. The calculated results refer to the ratio between the activity product and the equilibrium constant for a dissolution reaction. Values within the range of -0.5 kcal to +0.5 kcal indicate mineral saturation (saturation tolerance). Values below -0.5 kcal and above +0.5 kcal account for an undersaturation and oversaturation, respectively.

Figs. 9 and 10 show the saturation states. The values confirm the results of the mineralogical investigation. Consequently, subsequent reactions of the 3-1-8 phase to soluble compounds can be excluded, even over long periods of time.

3.5 Discussion of the experimental results

The long-term closure of the flow paths in permeable rocks requires grout components with a sufficiently low solubility. The investigations prove that a rapid reaction of the water glass with rock salt takes place. Optical microscopy and backscattered electron imaging showed that the solids formed consist of secondary halite and amorphous silicates. In brines, which are to be expected in salt mines, the minerals halite and magnesium oxichlorides (3-1-8 phase) are thermodynamically stable reaction products according to the XRD analysis and geochemical calculations.

The stability of the silicates can be evaluated on the basis of the Si-amounts in the solution. The experimental MgCl$_2$ solutions contained very low Si contents, i.e. between <1 μg/g (Q-solution) and 4 μg/g (20.2 wt% MgCl$_2$). These values confirm the results published by Marshall & Warakomski (1980). Long-term reactions will comprise an increase of structural order of amorphous phases and the formation of Mg-silicates, which will further reduce the dissolution of silicate phases. In natural waters the solubility of macrocrystalline quartz results in Si values up to 5 μg/g (Rykart 1995). This comparison proves that the solubility of the SiO$_2$ phases, too, is negligible. All solutions occurring in evaporate rocks are hardeners in the classical sense.

The experimental results comply with investigations of natural analogues. Authigenic Mg-silicates (talc) and quartz occurs in many evaporate rocks (cf. Engelhardt et al. 2012). Quartz grown under the influence of saline conditions represents the most important portion of authigenic quartz in sediments (Kühn 1968). In addition, these findings allow the conclusion that the natural salt solutions are saturated with respect to quartz.

Regarding the use of sodium silicate solutions in a salt mine, it can be concluded that mineralogical transformations or solution reactions, which may induce a significant reduction of the mineral volumes, can be excluded. Consequently, sodium silicate solutions have the capability to seal rock salt in the long term.

4. Use of water glass in salt mining

The application of water glass began as salt mining was often performed in the vicinity of adjoining rocks, such as

Fig. 11: Rock salt particles consolidated by a sodium silicate solution. The inner diameter of the tube is 100 mm.

close to the salt table of diapirs. As a consequence of this practice protective layers were damaged and brine intrusions occurred. Two strategies were used to protect mines; the closure of the flow paths in the rocks by grouting or the construction of dams.

Generally, rocks were grouted in several steps. Sodium silicate was used after a pre-grouting with suspensions, which was followed by the use of highly concentrated salt solutions (cf. Joosten 1953). Investigations and practical experience show that this post-grouting is not necessary. Regarding the permeability of dams, the dam construction itself, the contact zone to the rock formation, and the excavation damaged zone near the drift contour need to be considered separately. Experience shows that silicate solutions are able to seal all these hydraulically active components. Water glass is particularly suited for dams of building materials containing salt, e.g. salt concrete or magnesia binder. Calculations show that the viscosity and the surface tension have a positive effect on the penetrating capacity of the water glass. Measurement results illustrate the high hydraulic resistance of the fissure seals.

Wellbore flow due to excessive outbreak of production water or brine influx in salt formations is a common problem in deep drilling. An effective measure to reduce wellbore flow is to use sodium silicate and take advantage of its gelation capacity. The method is described by Garba (2012).

A new application of sodium silicate solution is the filling of open pore space in salt backfill material. Thus, it is possible to reduce the convergence of underground openings which may result in a damage of the surrounding rocks. The penetrating behaviour of water glass was investigated in tubes filled with crushed salt with a maximum grain size of 4 mm and a porosity of approx. 30 vol%. Fig. 11 illustrates the filling of the pore space as well as the consolidation of the salt particles.

5. Acknowledgements

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