

The Solution Behavior of CaSO_4 in Saline Water and Possible Precipitation

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In the FRIMA salt project in Harlingen (The Netherlands) rock salts of different degrees of purity are produced following the specifications of the clients. The salt plant is fed by solution mining of two caverns, which are located at depths down to 3,050 m. Consequently; they are currently the deepest caverns in the world. The depths of the cavities cause unusual temperature /pressure conditions. There were several factors that in the first phase of sump leaching induced a crystallisation of gypsum in the production annulus of one cavern. To avoid precipitations on the tubing walls it is necessary to distinguish between unchangeable parameters, such as the mineralogical/ chemical composition of the salt horizons, and variables, which can be influenced during the leaching process, such as the composition of the solution which is used for the leaching, and the injection pressure which influences the flow rate of the fluids.

This paper gives a brief introduction of the technical data of the FRIMA Zoutindustrie project. Afterwards, the processes that induce the gypsum crystallisation are discussed in context with the geochemical fundamentals of the ternary system $\text{NaCl-CaSO}_4\text{-H}_2\text{O}$.

1. INTRODUCTION

Caverns for the production of sodium chloride are in most cases, located between several hundred and 2,000 m below ground. For the production of magnesium-rich solutions cavities have been leached in depths down to 2,600 m. However, the following text summarises experiences which were made during the first phase of the operation of two caverns (BAS#1, #2), having sumps down to a depth of 3,050 m.

The well locations are located about 5 km from the salt plant on the production site. The distance between the well heads is about 20 m. One well is vertical; the other is deviated 500 m in a Northeast direction to obtain the required distance between the landing zones. For an optimal operation of the salt plant production rates per cavern of 300 m³/h are necessary. For this reason strings of casings of 7-inch and 10 3/4-inch diameter which are coated on the inner surfaces were used. The pumping station was built at the production site. Two pipelines, which were buried subterranean, have the functions to deliver the raw brine to the salt plant and to return the condensate of the plant to the pumping station. Losses of water during the brine processing in the salt plant due to technical reasons are compensated for by the addition of fresh surface water. Two

high-pressure rotary pumps were installed. They have a maximum performance of 350 m³/ h at a pressure of 190 bar.

For the commencement of the leaching process in 1995 the direct leaching process was chosen for both caverns. Due to the fact that initially no condensate was available, seawater was planned for leaching the first 10,000 m³ of cavern volume. Shortly after injecting the seawater the leaching had to be interrupted due to pumping problems caused by a blockage in the production annulus, between the 7-inch and 10 3/4-inch pipe. At a later stage this could be attributed to the precipitation of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$).

Normally the amount of anhydrite (CaSO_4) leached in caverns is not sufficient for the precipitation of gypsum during the cooling of the ascending brine. However, there are several important exceptions to this generalisation. One of these exceptions occurred at the first phase of the leaching process. For that reason the processes controlling the formation of the gypsum crust in the annulus of the production wells and the investigations that were carried out to explain this phenomenon will now be described in detail.

2. MATERIAL AND METHODS

Gypsum precipitates during the phase of cavern sump leaching. This part of the cavities is located at the basis of the Staßfurt rock salt ($\text{Na}_2\text{Zr}_2\text{HS}$). It consists of many fine to coarse, finest crystalline to crypto-crystalline anhydrite laminations, which are coloured light-grey to whitish grey, partly with a light bluish tinge. Because of the intensive closely spaced stripes the halite dominated sections achieve minor thicknesses up to 5 cm.

Mineralogical investigations were made of samples of the drilled cores and the precipitations on the tubing walls. The mineral phases were determined by X-ray diffraction (XRD) analysis and IR-spectrometry. Numerous anhydrite laminations of the rock salt were investigated by grain mounts. The textural features of gypsum were examined by thin-section microscopy. Before preparation the fragile samples were embedded in plastic resins.

Chemical analysis of solid samples, the waters used for salt leaching, and the raw brine produced was performed by standard analytical techniques [1].

3. MINERALOGICAL INVESTIGATION OF THE GYPSUM CRUST

Macroscopically the crust sampled consists of two 6 mm thick layers. Only two mineral phases were determined by XRD, IR and optical microscopy: gypsum and minor amounts of anhydrite. The gypsum on the tubing surface, which crystallized first, is bright yellow and has a microcrystalline, porous structure. It contains small particles of anhydrite, which caused a swelling of the material. The younger layer consists of parallel oriented, bright yellow brown gypsum crystals. Their size is on the average 2×6 mm. The long axes are inclined in the flow direction of the brine and enclose with the surface of the pipes an angle of approximately 80 degrees. In the thin sections it can be observed that a negligible amount of tiny anhydrite particles is located in individual gypsum crystals and on their surfaces. Additionally, the thin sections show that the crystals are either single or twinned; in the latter case mostly as swallow- (fish-) tails. This is of mineralogical interest, because the shape of gypsum crystals is a function of pH and of foreign cations

[2,3,4]. The pH of the brine varied between 6.3 and 6.7.

The distribution of anhydrite in the gypsum matrix justifies the assumption that the mineral is not crystallised at the place of occurrence due to short-term variations of the chemical conditions. The grains are obviously transported to the place where gypsum crystallisation took place in the ascending brine stream, due to the velocity, the density and the viscosity of the concentrated salt solution. Likewise, anhydrite was also detected in filters installed in the production pipes at the pumping station. A proof would be, for example, the comparison of the Ca/Sr-ratio, of anhydrite of the crust and of the laminae of the rock salt [5-8]. Unfortunately, the small particle sizes prevent a separation of the anhydrite from the gypsum matrix and therefore geochemical analysis.

At the beginning of a leaching operation it is possible that the chemical composition of the solution vary in a wide range. Hence, supposing short-term saturation of the brine with respect to NaCl, for example during breaks of the leaching process, halite may crystallise due to the low positive temperature coefficient of solubility. Presumably, this process explains the pores of the first gypsum layer, which were initially filled with halite. In that case halite was washed out during the preparation of the samples. In contrast, the second layer indicates a stabilisation of the physico-chemical conditions, which enabled the formation of larger gypsum crystals.

In addition, saturated sodium chloride solutions may explain the higher anhydrite content of the first layer. The gypsum-anhydrite transition temperature sinks with increasing NaCl content of the fluid. As anhydrite is more stable at higher temperatures it may be, at least partly, of primary origin.

4. THE INTERPRETATION OF THE GEOCHEMICAL RESULTS

For the explanation of the gypsum crystallizations it is necessary to consider the solubility of calcium sulfate modifications in relation to the pressure/temperature conditions and the NaCl concentration of the fluids. The amounts of other components of the solutions are negligible. The general process is

the leaching of anhydrite in the cavities and the precipitation of the dissolved CaSO_4 as gypsum.

The precipitation of gypsum necessitates high amounts of Ca^{2+} and SO_4^{2-} ions in the concentrated salt solution. However, the dissolution rate of anhydrite is very low in comparison to the great majority of evaporite minerals [9]. Another parameter, which in most cases prevents a precipitation of gypsum, is the negative temperature coefficient of solubility of anhydrite (Figure 1). For this reason the amount of dissolved anhydrite is normally not sufficient for gypsum crystallisation during a cooling of the solution.

In the case under review these theoretical principles are compensated for factors, which reduce the time for the adjustment of stable equilibrium conditions (1-3), and by parameters that influence the grade of saturation itself (4,5):

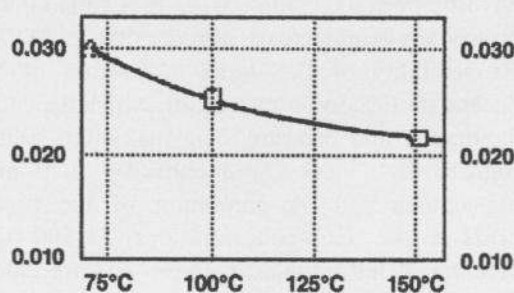


Figure 1. Solubility of anhydrite in moles $\text{CaSO}_4/\text{kg H}_2\text{O}$, in a $\text{NaCl-H}_2\text{O}$ solution of 6 moles $\text{NaCl}/\text{kg H}_2\text{O}$ [10].

- 1) the use of seawater as leaching fluid,
- 2) the relatively large surface area of anhydrite in the Staßfurt rock salt,
- 3) the increase of reaction rate as a result of the high temperature in the caverns,
- 4) the difference of pressure between the caverns and the place of crystallization, and
- 5) the dependency of anhydrite solubility on NaCl concentration of the brine.

The dissolved components of the produced raw brine consist of the elements that are brought into the cavities and the substances that are leached in the caverns. The higher the input of compounds in solution, the lower the amount of minerals that must

be leached to get a saturation of the fluid. Thus, the first essential for the process observed was the use of seawater as leaching liquid, instead of the condensate of the salt plant used nowadays. The chemical contents of calcium and sulfate of seawater and freshwater are summarised in Table 1. The data clearly indicate the difference of the Ca and SO_4 concentrations that is partly responsible for the saturation of the brine.

Anhydrite occurs in the rock salt as laminae and is dispersed in the halite matrix. During the leaching process it is washed out of the rock salt and thicker particles are sedimented on the floor of the cavities. For this reason, the surface of anhydrite increases in relation to other more soluble salts. Although anhydrite dissolves very slowly in water or brine, the amount dissolved can be large, owing to the extremely small particle size and the natural distribution in the rock salt. Therefore the mineralogical conditions are ideal for a maximum dissolution of anhydrite.

Table 1: Concentrations of calcium and sulfate in seawater and condensate of the salt plant in mg/l . The concentration of the fictive component CaSO_4 in seawater about $1,247 \text{ mg}/1000 \text{ g}$ solution or $171 \text{ mmol}/1000 \text{ l H}_2\text{O}$. Average values are marked in bold.

	seawater	condensate
Ca	400-412	0.5- 25 -122
SO ₄	2,715 - 2,800	2.5- 30 -132

In technical processes the duration of interactions between solutions and mineral phases is very short in comparison to natural environments. Thus, the composition of a fluid is influenced by the contact time between the mineral phases and the solution. If the duration of the dissolution process is not long enough the stable phase equilibrium conditions are not reached. The fluid is therefore undersaturated. This principle can easily be observed during breaks of leaching processes, when the brine outflows are only due to the convergence of the salt formation. In these phases the concentrations of elements, which originated from minerals that dissolve very slowly in water or brine, such as anhydrite, polyhalite ($\text{Ca}_2\text{K}_2\text{Mg}(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$) or kieserite ($\text{MgSO}_4 \cdot \text{H}_2\text{O}$), increase significantly.

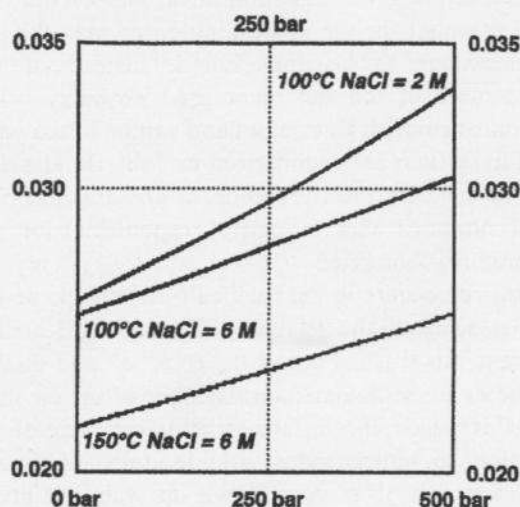


Figure 2. Anhydrite solubilities as a function of pressure, at several constant temperatures and NaCl concentrations [10].

Unfortunately, at the beginning of the leaching process of the wells the injection rate was too low. This improved the condition for maximum dissolution of anhydrite. Another factor contributing to the growth of gypsum crystals is the low velocity of the fluid in the annulus, which additionally decreases due to friction near the surface of the tubing walls.

In this special case the temperature-dependency of the reaction kinetics plays a major role. Below 70 °C the reaction rate of anhydrite with fluids is very low because of the existence of a kinetically hindered region. Above this temperature the dissolution rate increases dramatically. Hence, the temperature causes effects, which at first sight seem to be contrary: increasing temperature decreases the amount of anhydrite that can be dissolved, but it shortens the time, which is necessary to reach a saturation of the brine. Thus, the temperature in the caverns (~100 °C) permits a short-term adjustment of the equilibrium conditions.

Other parameters, which have to be taken into account, are related to the physico-chemical fundamentals of the system NaCl-CaSO₄-H₂O. Experimental studies of this ternary system have been carried out, for instance, by Bock [11], Blount and Dickson [10,12,13], Cameron [14], D'Ans et al.

[15], Clew [16], Madgin and Swales [17], Shternina [18], and Zen [19,20] (cf. [21,22]). The investigations show that an increase of pressure causes the solubility of anhydrite to become greater at all temperatures and NaCl concentrations (Figure 2).

The main factors that control the pressure in a cavern are the injection pressure and the hydrostatic pressure of the brine column which, due to the maximum depths of the cavities and the density of the solution (> 3,000 m), is significantly more than 300 bar (> 30 MPa). The injection pressure is a variable, which is influenced by the friction of the solutions on the walls of the casings and the production rate. In the FRIMA production wells the friction in the production annulus at high injection rates alone is up to 100 bar (10 MPa). Thus, a total pressure in the caverns of about 450 bar can be estimated. According to Blount and Dickson [10] this difference raises at 100°C the solubility of anhydrite from 0.0254 to 0.0293 mol/kg H₂O, which corresponds to an increase of more than 15 %.

The solubility of CaSO₄ as a function of NaCl concentration shows a maximum, which depends on temperature and pressure. The maximum becomes progressively less pronounced at higher temperatures and the minimum of the function occurs at low NaCl concentrations. At 100 °C the curvature of the function between sodium chloride contents of 3 and 6 mol / kg H₂O is very weak. Thus, the conditions for a maximal dissolution of anhydrite are relatively good.

The most important parameter for the formation of the crust is the positive temperature coefficient of the gypsum solubility in the temperature range of the ascending solution. The drop of the temperature is caused by the injection of the fresh water, which has a temperature of about 30-40 °C. As a result of the length and the high surface area of the string of casings, the dual string completion used in the wells acts as an almost ideal heat exchanger. Thus, the temperature of the raw brine, arriving at the ground surface is only approximately 3 to 5 °C higher than the temperature of the fresh water.

Eventually, the growth of gypsum crystals was induced by small amounts of calcium sulfates that act as seeds. Additionally, it is possible that halite crystallised on the tubing walls acts as a trap for particles transported in the brine. Of prime

importance is the observation that the crystallisation rate of gypsum is high enough to cause a narrowing of the annulus in a very short time [23,24].

Under natural conditions or during evaporation of seawater in artificial salt works, gypsum crystallisation starts at a two-fold supersaturation of the salt solution with respect to the conditions of stable equilibrium [25]. Factors that may prevent the nucleation of gypsum are the presence of magnesium, phosphates, and/or dissolved and particulate organic matter in the water. These can form chelates and can thus influence the solubilities to a yet unknown extent [26-28]. Additionally, traces of certain organic impurities can control the modification of calcium sulfate precipitating [29] (cf. [30,31]). However, these processes have no influence on the gypsum precipitation in the tubing, because the brine *contains negligible amounts* of Mg, phosphate and/or organic substances. Thus, *the* Mg contents of the brine were at the phase of sump leaching about 0.2 wt.-% (BAS#1) or 0.6 wt.-% (BAS#1) of *the dissolved* amount of sodium chloride. Actual values are lower than 0.38 mg Mg/l. This corresponds to about 0.1 wt.-% magnesium of the dissolved amount of sodium chloride or the total content of dissolved salts, because the concentration of CaSO_4 is actually of minor importance. For this reason it can be assumed that gypsum crystallises at nearly stable equilibrium conditions, which are determined by laboratory experiments.

5. SUMMARY AND CONCLUSIONS

In the caverns of the FRIMA Wt production *project solutions* with high amounts of calcium and sulfate had developed at commencement of the leaching operations in 1995. It was the result of several effects which was responsible for the saturation of the fluids, for example, the unusual temperature and pressure conditions and the use of seawater as leaching agent. The dissolved calcium sulfate caused a crystallisation of gypsum on the tubing walls which was a result of the progressively falling temperature and pressure during the ascent of the brine. At the time of blockage hot fresh water was pumped down the annulus and had the effect of a mechanical and chemical cleaning of the tubing walls. Factors which actually prevent a

crystallisation of gypsum are the increase of the injection rate, which is currently about $300 \text{ m}^3/\text{h}$ per cavern, that causes a decrease of the contact time of the brine with anhydrite in the cavities and a faster movement of the fluid in the annulus. The velocity of the fluids is approximately between 3 and 4 m/s at a production rate of $300 \text{ m}^3/\text{h}$. An additional improvement was the use of condensates of the salt production plant. However, the decreasing depths of the leaching horizons combined with a drop of the temperature and the pressure in the caverns has only a slight effect.

At present the chemical composition of the raw brine produced is analysed daily. A sampling of the solution above ground has the disadvantage that in the case of gypsum precipitation the analytical results have a deficiency of calcium sulfate. However, the practical knowledge showed that only a part of the CaSO_4 which is available for the formation of gypsum (supersaturation) is removed from the solution. Thus, the analytical results are an eminent basis to recognise a saturation of calcium sulfate and to undertake appropriate steps to prevent a crystallisation of gypsum promptly.

At present, the NaCl concentration of the raw brine is about 300 g/l and the CaSO_4 content approximately $0.48 \text{ mol}/1000 \text{ mol H}_2\text{O}$ ($0.027 \text{ mol}/\text{kg H}_2\text{O}$). The calcium and sulfate values of the well BAS#1 are insignificantly higher as the contents of the brine of the well BAS#2. The calculated mineral affinities of gypsum are significantly negative. These results indicate that in the case of the actual processing parameters and physico-chemical conditions the raw brine is highly undersaturated. However, there are alternative strategies for solving the problem of gypsum precipitation: for example the use of growth inhibitors [32-35], such as sodium polyphosphate, which has the additional advantage of preventing metal corrosion of the cavern installation, when a high saturation of oxygen is present in the circulating salt solution. However, the economical effect also has to be considered. Because of the extremely high volume of the water used, relatively high amounts of growth inhibitors are needed. Additionally, this method has the disadvantage that impurities are added to the solution. In some cases this demands an extensive cleaning of the brine.

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