

## The Production of Halite of High Purity

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The leaching of rock salts is an economical production method of brines to be used for the production of halite. However, in the case of production of halite of high purity for industrial applications, such as the chemical and pharmaceutical industry, it is of prime importance to know, besides the contents of the major and minor elements, the distribution of the trace constituents in the leached salt sequences. The most important trace element of sodium chloride is bromine. For that reason, the theoretical fundamentals of the behaviour of bromine, during the precipitation of NaCl in concentrating salt solutions, are summarised. Additionally, data from the FRIMA salt project are presented. Located in the NE Netherlands, it leaches salt of the Staßfurt rock salt ( $\text{Na}_2\text{Zr}_2\text{HS}$ ) for production of sodium chloride of different degrees of purity following the specifications of the clients.

### 1. INTRODUCTION

Solution mining operations in salt formations are generally undertaken to develop space for underground storage or waste disposal and/or production of brine to be used as feedstock for salt production or chemical plants. In the latter case, especially for the production of halite of high purity it is of great advantage to leach evaporite horizons, which has besides NaCl negligible amounts of mechanical or chemical admixtures such as trace elements. Additionally, as a basis for halite production, knowledge of the factors influencing the behaviour of trace elements is required.

This paper describes the theoretical fundamentals of the behaviour of bromine during the phase of halite precipitation. Br is the most important trace element of chlorides. Afterwards, the situation of the two solution mining brine production wells of the FRIMA Zoutindustrie at Harlingen near the North Sea coast of The Netherlands is discussed, which are at present the deepest caverns of the world and produces each 300 m<sup>3</sup> raw brine per hour.

### 2. FUNDAMENTALS

The contents of trace elements in halite are normally very low. Thus, fluorine occurs principally in sulfate deposits and salt days. Rubidium and ammonium substitute potassium in the crystal lattice of chlorides (e.g. sylvite, carnallite). Cesium does not occur in halite and lithium, in water-soluble form, is only

found in concentrations up to 0.2 ppm. Iodates are much more soluble than chlorides, and thus remain in the residual solution during halite crystallisation. Its relatively large ionic radius impedes its replacement of chlorine. The colouring of halite often feigns higher amounts of heavy metals. However, only 2 ppb of trivalent iron suffice to give halite a yellowish colour, and a few more parts per billion turn the salt red [1]. Concentrations of other elements are listed in publications of Dean [2], Stewart [3] and Herrmann [4] (e.g. [5-8]).

An overview of the behaviour of bromine in the marine environment is presented by Braitsch [9]. Bromine, which is after  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ , and  $\text{HCO}_3^-$  fourth in order of abundance among the anions in sea water (0.0671 g/1000 g seawater, 0.0157 mol/1000 mol  $\text{H}_2\text{O}$ ) occurs as minor and trace constituent in various salts. Bromine (ionic radius 1.96 Å) substitutes chlorine (1.81 Å) in the crystal lattice of evaporite minerals. In the case of halite the Br-concentration increases with the bromide content of the saline solution, the temperature, and the speed of crystallisation. Additionally, the fixation of bromide in the structure of NaCl is dependent on the amount of other species present in the fluid. It decreases with increasing  $\text{MgCl}_2$ -amount of the solution and the grade of secondary recrystallizations. The distribution of bromine between a crystal and the coexisting solution is described by the partition coefficients

$$b = \text{wt.}\% \text{Br}_{(\text{mineral})} / \text{wt.}\% \text{Br}_{(\text{solution})} \quad (1)$$

or

$$D = [\text{Br}/\text{Cl}_{(\text{mineral})}] [\text{Br}/\text{Cl}_{(\text{solution})}]. \quad (2)$$

The coefficients  $b$  and  $D$  of individual chlorides are different. Thus, the ratio of the Br-content of paragenetic, coexisting halite and carnallite is between 1:7 and 1:10 [10]. It is possible to determine Br partition coefficients in simple systems under laboratory conditions (e.g. [11,12]). An alternative is the thermodynamic modelling applying Pitzer equations [13,14]. Additionally, it is possible to study the behaviour of trace elements during the evaporation of seawater under natural conditions at artificial salt pans (salt works) [15,16]. Bromine partition coefficients of halite, sylvite, and carnallite are listed in Table 1. The data clearly show the dependence of the Mg-content of the solution on the partition coefficients of halite. Thus during the evaporation of seawater  $b$  decreases significantly from 0.14 at a  $\text{MgCl}_2$ -content of about 4 g/ 100 g  $\text{H}_2\text{O}$  to 0.073, at the beginning of Na-Mg-sulphate (bloedite) crystallisation (~22 g  $\text{MgCl}_2$ /100 g  $\text{H}_2\text{O}$ ). This dependence is also recognisable on the halite line of Figure 1, which show the calculated bromine distribution during static evaporation of seawater

from the beginning of the NaCl crystallisation to the bischofite precipitation.

An interesting phenomenon is the behaviour of bromine in contact with days in the marine environment. Thus, a filtration of high electrolytic fluids through day horizons causes a decrease of the Br-content in the fluid. The effect is a result of adsorption on the surface of the minerals. It is possible that the enrichment of bromine in  $\text{MgCl}_2$ -containing fluids, which are stored in salt clays, have the same reason [18].

In rivers and streams the Br-content of the waters is normally very low. Most literature data (e.g. [19,20]) are varying about 20  $\mu\text{g/l}$  (ppb). Additionally, river waters have lower Br/Cl ratios than the chlorides in salt formations. For that reason, in the case of leaching salt sequences, the bromine values of the fresh waters do, in most cases, not have to be taken not to take into account.

When leaching caverns in salt bodies with intercalations of minerals containing considerable amounts of Br, it is important to examine the sum of the Br-concentrations of all soluble minerals. This fact must be taken into account, because during the processing Br remains in solution, whereas  $\text{SO}_4$  and the cations, with the exception of sodium, are removed from the brine. The bromine, previously fixed by potash salts, is therefore

Table 1 Bromine partition coefficients of halite (NaCl), sylvite (KCl), and carnallite ( $\text{KMgCl}_3 \cdot 6\text{H}_2\text{O}$ ) [10: 7]. pr. precipitation. (cf. [17]).

Mineral	partition coefficient $b$		
	25°C	55°C	83°C
halite	0.16 ± 0.01		
with KG in solution	0.14 ± 0.01		
± 3 wt.-% $\text{MgCl}_2$ : beginning of halite pr.	0.14 ± 0.01 (D~0.038)		
± 11 wt.-% $\text{MgCl}_2$ : before bloedite pr.	0.088 ± 0.005		
beginning of Na-Mg-sulphate (bloedite) pr.	0.073 ± 0.004		
± 16 wt.-% $\text{MgO}_2$ : end of halite phase	0.073 ± 0.004	0.078 ± 0.004	0.079 ± 0.004
± 28 wt.-% $\text{MgCl}_2$ : beginning of carnallite pr.	0.073 ± 0.004 (D~0.026)		
sylvite 0.81 ± 0.05			
with NaCl in solution	0.80 ± 0.05		
$\text{MgCl}_2$ (nearly saturated of carnallite)	0.73 ± 0.04 (D-0.31)	0.77 ± 0.04	0.83 ± 0.04
± 12 wt.-% $\text{MgCl}_2$ and ± 10 wt.-% $\text{CaCl}_2$	0.75 ± 0.04		
camallite	0.52 ± 0.03 (D~0.30)	0.56 ± 0.03	0.59 ± 0.03

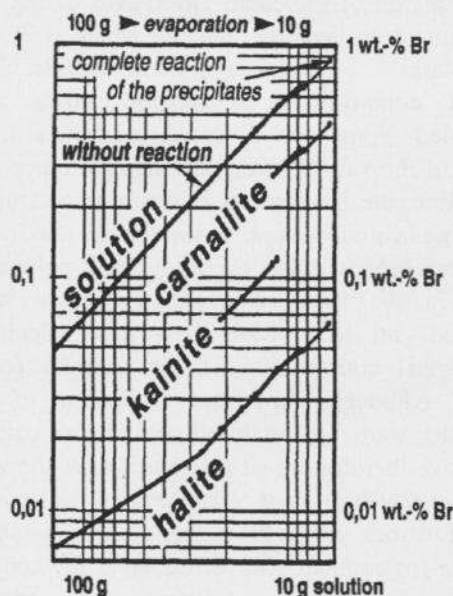


Figure 1.

Calculated bromine distribution during the static evaporation of seawater at 35 °C after the beginning of halite crystallisation, without and with reaction of the primary precipitates along reaction lines and at transition points. Abscissa = amount of solution. The original amount was 1000 g seawater (after [10: 109]).

incorporated in the structure of the end-product NaCl.

In salt formations, such as the Zechstein sequences, bromide distribution profiles show an overall increase in the bromide content and a maximum value in the potash seams. However, curves indicate dilutions (decrease of Br) or concentrations (increase of Br) of the saline solution for short periods of time (e.g. [21,22]). The Bromine content behaves irregularly, if secondary halites are present, because they have lower values as the surrounding primary rocks.

The most important horizon for the installation of cavities in salt is the Staßfurt rock salt ( $\text{Na}_2\text{ZHS}$ ). Numerous publications [17,23-26] show how the bromine content increases consistently through the Staßfurt sequence in Northern Germany (cf. [27,28,29]). in the case that the evaporite minerals are of primary origin, differences of Br-content can be correlated with specific mineral occurrences. Generally, with increasing Br-content of a salt

sequence, an anhydrite polyhalite ( $\text{Ca}_2\text{K}_2\text{Mg SO}_4$ ) \* $2\text{H}_2\text{O}$ , kieserite, and carnallite zone can be distinguished (see Table 2), although the sulfates fix no bromine in their structures.

Table 2

Bromine content of halite in the mineral zones of a evaporite sequence [17,30-32].

Source of halite	wt.-% Br per 100 NaCl
Carnallite zone	0.028 - 0.048
Kieserite zone	0.023 - 0.028
Polyhalite zone	0.017 - 0.023
Anhydrite zone	0.003 - 0.017

### 3. THE FRIMA SALT PROJECT

In the FRIMA salt project rock salts of different degrees of purity following the specifications of the clients are produced, such as road salt, salt for food flavouring and preserving, products for water softening, and halite for the chemical processing industry. For the successful operation of the salt plant it is necessary to consider the geological situation of the brine exploitation area and the geochemical properties of the occurring minerals.

#### 3.1. Stratigraphic overview

The exploited salt deposit belongs to the Zechstein Salt Succession, out of the region of halokinesis. The strata conditions are therefore uncomplicated. The dip of the bedding is about 5 degrees, without any greater folds. Two solution mining brine production wells (BAS#1 #2) are drilled down to the basis of the Staßfurt Salt Na<sub>2</sub> (z2HS), which is the dominating part of the Upper Permian. In the well BAS#1 the top of the Staßfurt rock salt is at 2534 m and the basis at 3048 m. Hence the thickness is about 515 m. In the well BAS#2 are the corresponding depths lower, because of the dip of the horizons. Table 3 gives some informations about the depths of the units of the Zechstein column.

#### 3.2. Mineralogical results

The wells are investigated by means of a series of logs and cores to analyse the quantitative mineral composition of the salt. The cored interval in BAS#1



reaches from 2600 m to 2960 m. The well-known mineral composition enables the planning of a detailed leaching program for the caverns.

The Staßfurt Salt is characterised by many, mm-thick finest crystalline to cryptocrystalline anhydrite laminations, which are coloured light grey to whitish grey, partly with a tinge of light bluish. The pure halite layers form stripes of 1 to 10 cm among the anhydrite laminations. The halite is in reflected light colourless, milky-whitish to light-greyish marbled, very rarely light brown to yellow. In transmitted light it is slightly and dimly translucent colourless to white, sometimes yellowish or brownish. The halite is predominantly medium crystalline (5-20 mm).

In contrast to Germany, where an polyhalite content is only detectable in the upper part of the Staßfurt: Salt in the NE Netherlands Zechstein Basin, north of the Texel-IJsselmeer-inlet, the z2HS can be subdivided by primary polyhalite beds (cf. [33]). However, in the production wells an increased amount of polyhalite of the rock salt was only determined between approximately 2680 and 2700 m (BAS #1).

### 3.3. Geochemical investigations

According the above mentioned fundamentals the anhydrite layers point to low Br-contents of the rock salt. However, the increased polyhalite content

marks a region of increased Br-content of the salt and an anhydrite layer at 2857 m, which is 30 cm thick, marks a minimum content of Br. The chemical composition of several cores was investigated. Some results are listed in Table 4. Because of the varying mineral amounts, especially of carnallite, the Br-contents of the whole samples are varying in a wide range. However, the maximum value corresponds with the increased polyhalite content in the rock salt. The Br-values were corrugated on the basis of the calculated mineralogical composition of the samples (right column). Although, the exact Br-content of the K-Mg-salts were not analysed and the calculated values have therefore great tolerance, they show an increase of the Br-content of halite from the basis of the Staßfurt rock salt to the horizons with increased polyhalite (p) content. Above this layer the content decreases significantly. Without the samples between 155 and 172 m, relative to the top of the Staßfurt rock salt, the values are falling into the range of values of the anhydrite zone (see Table 2). Although the values of the polyhalite bed are falling into the kieserite zone the data show generally a good correlation with the mineralogical results. Otherwise, they demonstrate that the polyhalite layer is of primary origin (cf. [331]).

Table 3 Stratigraphic divisions of the Zechstein cycles Z1-Z6 (Barradeel Salt Well I BAS#1). The corresponding depths are in the boring BAS#2 about 30 m lower. The maximal primary thickness of the Ohre (Z5), Aller (Z4), Leine (Z3), and Staßfurt (Z2) Series is 20 m, 150 m, 300 m, and 650 m, respectively [331].

Cycle	Name	Symbol: Stratigraphic description	depth
Z6-Z4	Friesland-/Ohre-/Aller Series		2229 -2250
Z3	Leine Series	Na3 [z3BS-z3TM): Leine rock salt ("Younger" rock salt)	-2442
		A3 [z3HA]: Main Anhydrite (Hauptanhydrit)	-2467
		W [z3LK]: Leine carbonate, T3 [z3GT]: Grey Salt Pelite	-2470
Z2	Staßfurt Series	A2r [z2DA]: Cover Anhydrite, Na2r [z21)S]: Cover Rock Salt,	- 2534
			- 3048
		K2 [z2SF): Staßfurt potash seam	
		Na2 [z2HS]: Staßfurt Rock Salt	
		A2 [z2BA): Basalanhydrite	

Table 4

Bromide content of samples from the production well borings BAS#1 [1] and BAS#2 [2]. The depths of the samples of BAS#2 are corrugated according to the dip of the salt layers. Listed are the relative depths to the top of the Staßfurt rock salt (Na<sub>2</sub>z<sub>2</sub>HS) and the absolute depths in parenthesis. p = rock salt with polyhalite.

Depth [m]	Br <sub>sample</sub> [wt.-%]	Br <sub>halite</sub> [wt.-%]
111 (2645) <sup>1</sup>	0.026	0.011
147 (2682) <sup>2</sup>	0.019	0.017
155 (2690) <sup>2</sup>	0.029 p	0.026
159 (2694) <sup>2</sup>	0.032 p	0.027
172 (2707) <sup>2</sup>	0.028 p	0.025
216 (2750) <sup>1</sup>	0.022	0.016
336 (2870) <sup>1</sup>	0.021	0.017
367 (2902) <sup>2</sup>	0.015	0.011
387 (2922) <sup>2</sup>	0.020	0.017
406 (2940) <sup>1</sup>	0.019	0.016
549 (3084) <sup>2</sup>	0.018	0.008
567 (3102) <sup>2</sup>	0.020	0.005

The results gained by the interpretation of the logs and by the mineralogical/ geochemical investigations of the cores have been confirmed by observations made during the leaching process.

The brine fields were fed by the effluents discharged by the vacuum plant. Because of losses during the production process small amounts of fresh water were added. The raw brine to be purified is nearly saturated of NaCl, because of the cooling of the ascending solution combined with the low positive temperature coefficient of NaCl. Thus, during cooling from 100 °C to 20 °C of a saturated sodium chloride solution 11 mol NaCl (~643 g; 5.5 mol NaCl) are precipitating out of initial 121 mol (~7072 g).

During the last 20 months the Br contents of the fluids vary in relation to the sum of salts in solution between 0.019 and 0.023 wt.-%. These values agree very well with the results of the solids (Table 4). Until now, it is not possible to observe a time dependable tendency of the data.

In consideration of the chemical composition of the used fresh water the correlations between the leached components were calculated. It is not surprising that in accordance with the mineralogical results of the core samples chlorine shows a strongly

negative correlation with sulfate. Calcium correlates best with sulfate (particularly because of anhydrite). Potassium is highly correlated with magnesium (e.g. carnallite). In the case of sodium all calculated correlation coefficients, with the exception of bromine, were negative (Ca, Mg & K, SO<sub>4</sub>). However, only a poor correlation was found to exist between chlorine and bromine. This observation allows the speculation that several mineralogical phases with different bromine partition coefficients are responsible for the bromine content of the produced brine, such as halite, carnallite, and/ or sylvite.

#### 4. CONCLUSIONS

The caverns of the FRIMA project are positioned in the "anhydrite region" of the Staßfurt salt sequence. The deepest parts (> 3000 m) of the caverns, the cavern sumps, are near the basis of the Na<sub>2</sub>z<sub>2</sub>HS. Consequently, the Br amounts of the leachable minerals are low and the concentration of primary minerals with high Br (e.g. carnallite) partition coefficients negligible. During the progress of the leaching process an increase of the bromine concentration of the salt and therefore of the raw brine can be predicted. This fact bases on the increasing Br-content in the upper parts of a salt sequence and the higher Br-amount of the rock salt, which contains polyhalite. However, the investigations show that the Staßfurt Salt column and the quality of the leached brines afford good preconditions for the successful operation of the salt plant. The thickness of the z<sub>2</sub>Na is approximately 515 m and the maximum value 650 m [33] in the central Zechstein basin of The Netherlands. Thus, the location is suitable for leaching of high volume caverns. Additionally, the steadiness of the element concentrations in the raw brine is a good precondition finding the optimal processing parameters in the salt plant.

#### REFERENCES

1. P. Sonnenfeld, Brines and Evaporates, Academic Press, Orlando, 1984.
2. W.E. Dean, Trace and minor elements in evaporites. In: W.E. Dean and B.Ch. Schreiber (eds.), Marine Evaporites, Lecture Notes for

- SEPIA Short Course No. 4, Oklahoma City, 1978.
3. F.H. Stewart, Marine Evaporites. In: M. Fleischer (ed.), Data of Geochemistry, Geol. Surv. Prof. Pap., 440-Y, Washington, 1963.
  4. A.G. Herrmann, N. jb. Miner. Mh., 1 (1961) 60-67.
  5. H. Glee, BE. Eur. J. Miner., 8, 1 (1996) 72.
  6. A.G. Herrmann, Fresh. Forsch.-Hefte, A88 (1958) 80-84.
  7. A.G. Herrmann Kali u. Steinsalz, 3 (1961) 209-220.
  8. W.T. Holser, Ref. Mineral., 6 (1979) 295-346.
  9. O. Braitsch, Salt Deposits. Their Origin and Composition, Springer, Berlin, 1971.
  10. M. Mattenklott Die Bromid- und Rubidiumverteilung in Carnallitgesteinen. Kriterien für die Genese mariner Evaporite, Thesis, TU Clausthal, Germany, 1994.
  11. H.E. Boeke, Z. Kryst., 45 (1908) 346-391.
  12. O. Braitsch and A.G. Herrmann Geochim. Cosmochim. Acta, 27 (1963) 361-391.
  13. M.G. Siemann and M. Schramm, Beih. z. Mgr. J. Miner., 11, 1 (1999) 213.
  14. M. Schramm and MUG. Siemann, EUG10, J. Conf. Abs, 4 (1999) 586.
  15. A.G. Herrmann D. Knake, J. Schneider and H. Peters, Contr. Mineral. and Petrol, 40 (1973) 1-24.
  16. J. Schneider, Kali u. Steinsalz, 11, 10 (1995) 325-330.
  17. R. Kuehn Geol. Soc. Amer, Spec. Pap, 88 (1968) 427-504.
  18. L. v. Borstel, Loesungen in marinen Zechsteinevaporiten Deutschlands, Thesis, TU Clausthal, Germany, 1992.
  19. G.S. Kononov, Dokl. Akad. Nauk USSR, 129,4 (1959) 912-915 (Translated into English by M. Fleischer, U.S.G.S.).
  20. D.A. Livingstone, Chemical Composition of Rivers and Lakes. In: M. Fleischer (ed.), Data of Geochemistry, Geol. Surv. Prof. Pap., 440-1963.
  21. S.M. Billo, AAPG Bulletin, 75, 6 (1991) 1123.
  22. O.B. Raup and R.J. Hite, Bromine Distribution in marine halite rocks. In: W.E. Dean and B.Ch. Schreiber Marine Evaporites, Lecture Notes for SEPM Short Course No. 4, Oklahoma City, 1978.
  23. G. Schulze, Fresh. Forsch.-H., A123 (1958) 175-196
  24. G. Schulze, Fresh. Forsch.-H., C83 (1960) p. 116.
  25. G. Schulze and H. Seyfert, Z. f. angew. Geol., 5,2 (1959) 62-69.
  26. P. Simon, Geol. Jb, 90 (1972) 67-126.
  27. O. Braitsch, Naturwissenschaften, 48. 10 (1961) 402.
  28. Fischbeck, R. and H. Gundlach, Laboratory report BGR Hannover, Arch.-No. 92305 (1982), p. 22.
  29. S. Mueller-Schmitz, Mineralogisch- petrographische und geochemische Untersuchungen an Salzgesteinen der Staßfurt-, Leine- und Aller-Serie im Salzstock Gorleben (Niedersachsen, B.R. Deutschland), Thesis, Univ. Heidelberg Germany, 1986.
  30. J. D'Ans and R. Kuehn Kali, 34 (1940) 43-46, 59-64, 77-83.
  31. J. D'Ans and R. Kuehn Kali, 38 (1944) 167-169.
  32. R. Kuehn Kali u. Steinsalz, 9 (1955) 3-16.
  33. M. Geluk, Z. dt. geol. Ges., 146 (1995) 458-465.