

SVERIGES GEOLOGISKA UNDERSÖKNING

SER. C.

Avhandlingar och uppsatser.

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ÅRSBOK 42 (1948) N:o 10.

ON THE WINNING
OF SALT FROM THE BRINES IN
SOUTHERN SWEDEN

BY

GUNNAR ASSARSSON

Pris 1 krona

STOCKHOLM 1949

KUNGL. BOKTRYCKERIET. P. A. NORSTEDT & SÖNER

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Summary.

- 1) *A short survey of the systems containing KCl, NaCl, CaCl_2 , and H_2O is given.*
- 2) *Some analyses of the brines from the deep-borings at Höllviken and Trelleborg in Scania, Southern Sweden, are given.*
- 3) *With the support of the investigations of the four-component system of the compounds occurring in the brines, the theoretical possibilities for the production and for the refining of the solid phases, obtained at an evaporation, are discussed.*

Introduction.

In a technical exploitation of brines or salt layers the way, in which the ions present in the salt solutions crystallize, is important to know as on this the salt production depends. An intimate knowledge of the application of the phase rule to the possible combinations of the ions is also of fundamental importance. As the ion combinations existing in the brines are often limited to a special production, the crystallization of the solid phases are for quite natural reasons not always sufficiently investigated.

In connection with the work on the question of the winning of salt from the brines of the deep boring at Höllviken, Scania, Southern Sweden, it was apparent that some new investigations of the system $\text{Na}^+\text{-K}^+\text{-Ca}^{++}\text{-Mg}^{++}\text{-Sr}^{++}\text{-Cl}^-$ in water solutions should be taken up, and that some supplementary facts were necessary for a good knowledge of the salt refining processes, as the systems of some ion combinations are not completely known. Therefore, a critical review of earlier investigations of some of the systems was summed up, with especial regard to possible ion combinations available to the salt winning of the brines

of the deep boring. The investigations were started in 1943. Other laboratory work, however, detained their final accomplishment.

The results of the earlier investigations are put together in Gmelin's *Handbuch der anorganischen Chemie*, 8. Auflage, System-Nummer 22, Kalium, Anhangsband, Die Salze der ozeanischen Ablagerungen und ihre Lösungen (1942). In this book the literature up to the 1st of January 1940 is taken into consideration. When the present investigation was almost ready, four short papers were published (Prupton and collab.) dealing with the systems of interest for the problems treated here.

The report of the investigations of the systems $\text{CaCl}_2\text{-KCl-H}_2\text{O}$, $\text{CaCl}_2\text{-KCl-NaCl-H}_2\text{O}$ and $\text{CaCl}_2\text{-MgCl}_2\text{-H}_2\text{O}$ are published in *Journ. Am. Chem. Soc.* (Assarsson 1949).

The Conditions of the Winning of Salts from the Brines.

The problems of salt-winning from brines are generally connected with the evaporation methods in those cases where the degree of purity of the products is left out of account. Problems of a chemical nature arise when constituents of low percentages are to be extracted or when the products must have a certain degree of purity.

Some analyses of the brines from Höllviken and Trelleborg in Scania, Southern Sweden, mentioned below, show that the chief constituents of the brines are chlorides of calcium and sodium; there also occur small amounts of chlorides and bromides of potassium, strontium, and magnesium.

A short summary of the investigations on the systems in question known up to now will be given here. The properties of the solutions at the invariant points are summarized in Table 2.

Three-Component Systems.

The system $\text{KCl-NaCl-H}_2\text{O}$ has been worked out previously very thoroughly, as it is important for the production of alkali salts. In the system there occur only the components as solid phases. At low temperatures (between -2.3° and -23°) sodium chloride crystallizes with crystal water ($\text{NaCl} \cdot 2\text{H}_2\text{O}$) from solutions saturated with respect to potassium chloride.

The system $\text{CaCl}_2\text{-NaCl-H}_2\text{O}$. There are some isotherms published: at 0° , Igelsrud and Thompson, at 25° , van't Hoff and Lichtenstein 1889, Cameron, Bell and Robinson 1905, at 50° and at 94.5° , Pelling and Robertson 1923. At these temperatures there occur as solid phases the components and their earlier known hydrates. Equilibria between the chlorides of sodium and of calcium below 0° have not been determined. The results given in the investigations mentioned, however, do not satisfactorily accord in some points with those in the present work. Furthermore, the equilibria between the components of the system are fundamental for estimating the crystallization of the Swedish

Table 1. The ternary System $\text{CaCl}_2\text{-NaCl-H}_2\text{O}$.

 Concentration of the solutions at $18,0^\circ$, $50,0^\circ$ and $95,0^\circ$.

$18,0^\circ$		$50,0^\circ$		95°		Solid phase
CaCl_2	NaCl	CaCl_2	NaCl	CaCl_2	NaCl	
—	26.4	—	27.0	—	28.3	NaCl
3.0	22.6	3.0	23.6	3.0	25.2	»
6.3	19.6	6.3	20.6	6.4	21.3	»
12.3	14.3	12.3	15.0	12.8	16.7	»
15.1	11.8	18.2	10.5	17.6	12.8	»
18.2	9.6	28.1	4.3	28.1	6.1	»
28.1	3.5	41.5	0.8	41.5	1.9	»
40.80	0.62 ¹	56.45	0.65 ³	60.15	1.00 ²	
41.97	— ²	56.54	— ⁴	60.28	— ⁴	

¹ Solid phase: $\text{NaCl} + \text{CaCl}_2 \cdot 6 \text{H}_2\text{O}$
² » » : $\text{CaCl}_2 \cdot 6 \text{H}_2\text{O}$
³ » » : $\text{NaCl} + \text{CaCl}_2 \cdot 2 \text{H}_2\text{O}$
⁴ » » : $\text{CaCl}_2 \cdot 2 \text{H}_2\text{O}$

brines. For that reason the isotherms at 18° , at 50° and at 95° (Table 1) and the curves belonging to them (Fig. 1) are given here. The difference between the solubility of sodium chloride in solutions of calcium chloride at the temperatures mentioned is not great. The rise of temperature from 18° up to 95° causes an increase of dissolved sodium chloride of about 1—3 per cent of the solution at constant content of calcium chloride.

System $\text{CaCl}_2\text{-KCl-H}_2\text{O}$ has been investigated at 0° (Igelsrud and Thompson), at 25° (Lee and Egerton), at 30° (Barbaudy), at 35° , 75° and 95° (Lightfoot

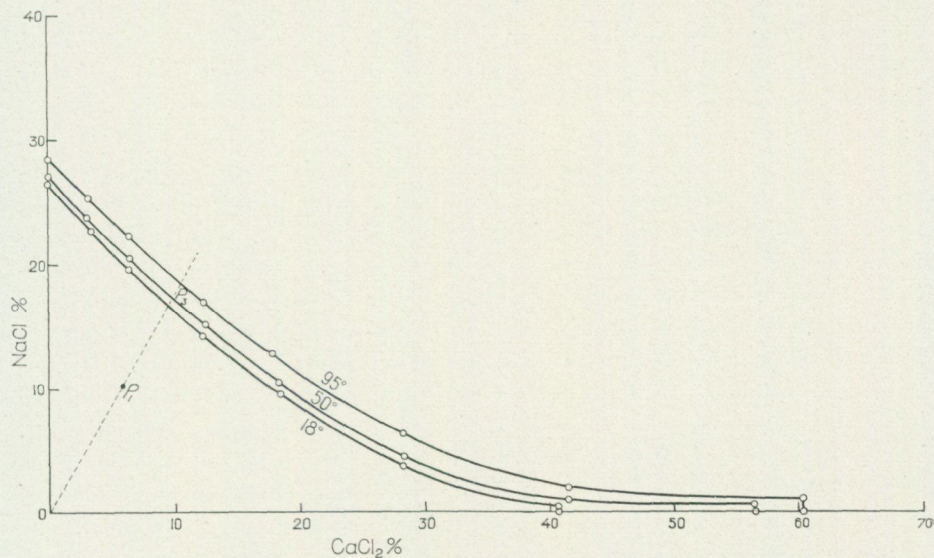


Fig. 1. The ternary system $\text{CaCl}_2\text{-NaCl-H}_2\text{O}$. The isotherms at 18° , 50° , and 95° (Cartesian coordinates). The point P_1 corresponds to the composition of the brine from Höllviken, Analyses I and II, Table 3.

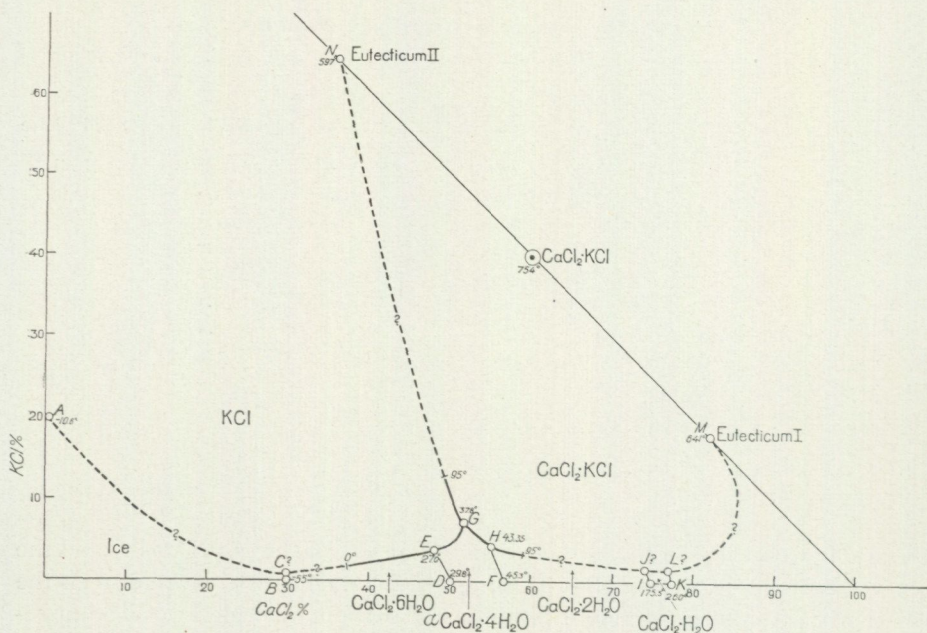


Fig. 2. The ternary system $\text{CaCl}_2\text{-KCl-H}_2\text{O}$. Diagram on the composition of the solutions at the invariant and univariant equilibria (Cartesian coordinates).

and Prutton). The present investigation was carried out at the same time as that by the last mentioned authors, but gave some different results. Because of the importance of the system, a diagram on the univariant and the invariant equilibria (Fig. 2) and a summary of the properties will be given here (cf. Assarsson 1949). The system contains as solid phases the single salts and their hydrates as well as a double salt ($\text{CaCl}_2 \cdot \text{KCl}$). The solubility of KCl in solutions of varying CaCl_2 contents shows a minimum at 35—40 per cent CaCl_2 ; of this property the conclusion may be drawn that a complex ion occurs in the solutions which is a condition for the crystallization of the double salt. The lowest temperature of the formation of the double salt is 37.8° . Solutions belonging to an isotherm within the area of the double salt show almost constant content of water. Thus, solutions belonging to this area, when evaporated isothermally, yield double salt and solutions of the same water content, and they become poorer in potassium chloride and richer in calcium chloride. The content of potassium chloride of the solutions diminishes the temperature of the invariant equilibria of the hydrates of the calcium chloride (See Table 2). The tetrahydrate of calcium chloride is known as trimorphous; the conditions of the rather complex equilibria between the three modifications in presence of potassium chloride are not known. These problems are being examined. The ions which cause the formation of the double salt are obviously connected with the appearance of the calcium chloride dihydrate. The very high viscosity of the concentrated solutions is another property allied to the aforesaid formation

of the ions. The double salt is probably identical with the minerals found in salt deposits and in volcanoes named bäumlerite, hydrophilite, and chlorocalcite.

The systems $\text{SrCl}_2\text{-NaCl-H}_2\text{O}$, $\text{SrCl}_2\text{-KCl-H}_2\text{O}$, $\text{SrCl}_2\text{-CaCl}_2\text{-H}_2\text{O}$, $\text{SrCl}_2\text{-MgCl}_2\text{-H}_2\text{O}$ are not yet investigated. The work on the three systems first mentioned is proceeding.

The system $\text{CaCl}_2\text{-MgCl}_2\text{-H}_2\text{O}$ is partly known. A summary is given in Assarsson 1949. As magnesium chloride can, however, be removed from solutions by well-known operations this system is not considered here.

Four-Component Systems.

The system $\text{CaCl}_2\text{-KCl-NaCl-H}_2\text{O}$.¹ In the temperature interval $18^\circ\text{--}95^\circ$ only those solid phases occur which are found in the three-component systems composing this four-component system. At increasing content of calcium chloride in the solutions, and at co-existing presence of the alkali chlorides as solid phases, their isothermal solubility decreases, sodium chloride in higher degree than potassium chloride. At the univariant point, where the alkali chlorides and the hydrates of calcium chloride, or the double salt $\text{CaCl}_2 \cdot \text{KCl}$, are present as solid phases, the solubility of sodium chloride is about one tenth of that of potassium chloride.

Fig 3 gives a survey of the composition of the solutions within practically the most important temperatures (0° and 100°). The line of the solubility of potassium chloride and that of the sum of potassium and sodium chloride (Fig. 3)

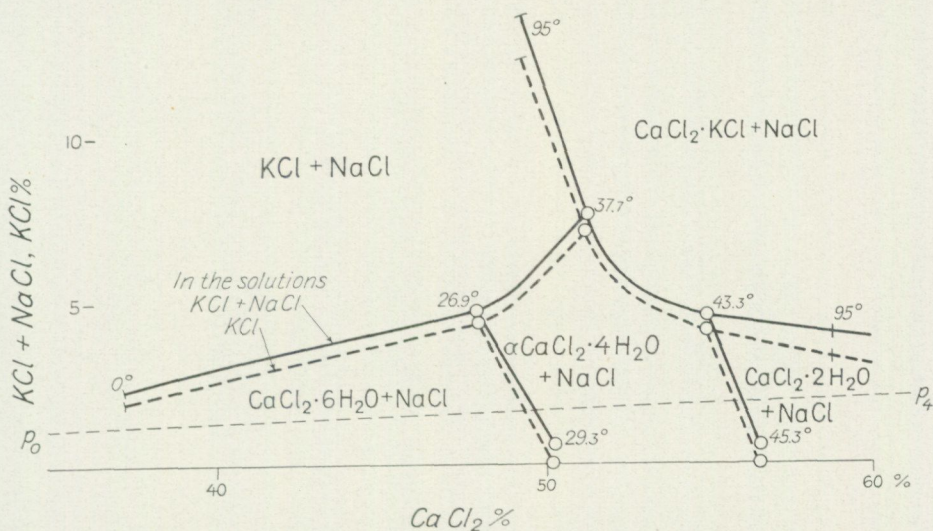
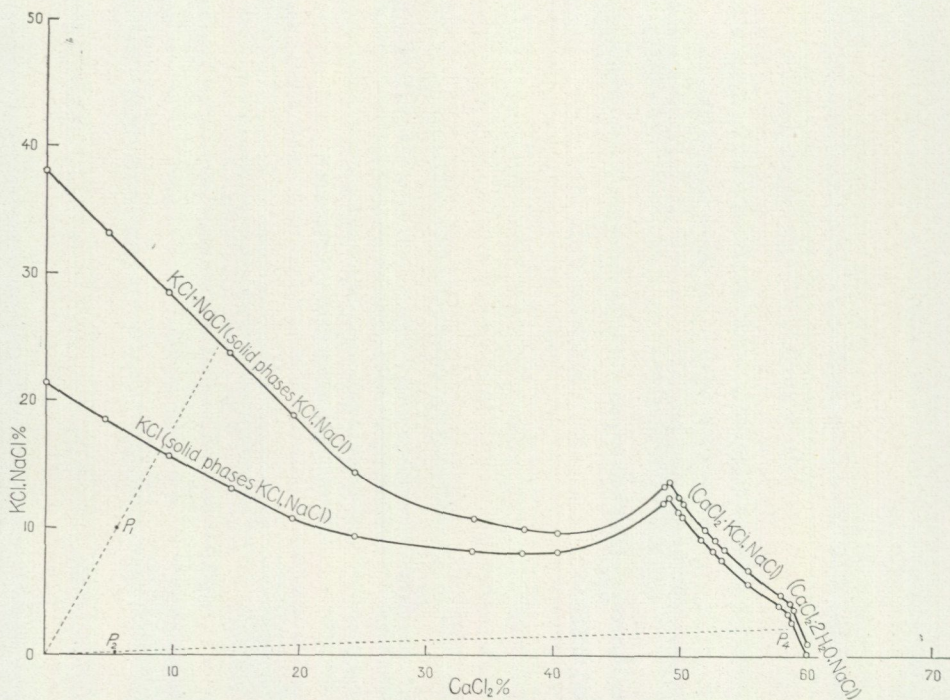
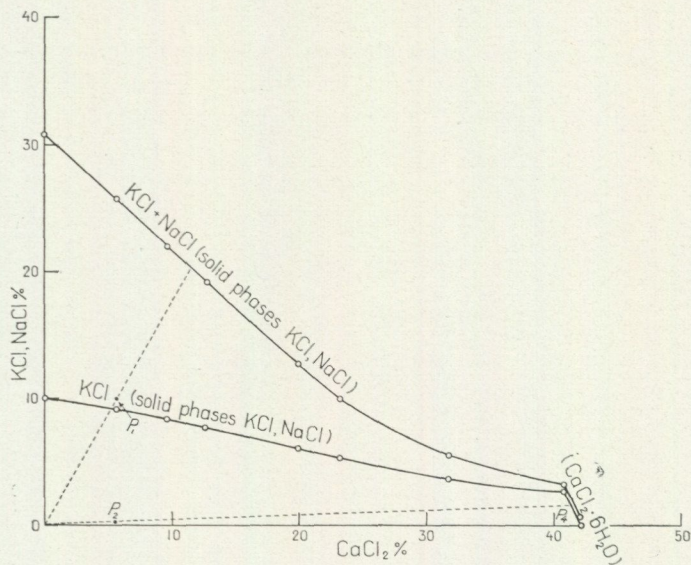


Fig. 3. The quaternary system $\text{CaCl}_2\text{-KCl-NaCl-H}_2\text{O}$. The composition of the solutions at the invariant and univariant equilibria between 0° and 100° . Solid lines: $\text{KCl} + \text{NaCl}$, dashed lines; KCl , found in the solutions (Cartesian coordinates). $P_2\text{--}P_4$ corresponds to the content of potassium chloride of the brine from Höllviken during a concentration.

¹ O. K. Yanatieva has published an investigation on the properties of the quaternary systems containing alkali, and alkaline earth chlorides in water between 0° and 50° . No chemical compounds were found to form in the aqueous systems in distinction from the fusibility diagrams.



Figs. 4 a and 4 b. The quaternary system $\text{CaCl}_2\text{-KCl-NaCl-H}_2\text{O}$. The isotherms at 18° (Fig. 4 a) and 95° (Fig. 4 b). The points P_1 and P_2 correspond respectively to the content of sodium chloride and of potassium chloride in the brine from Höllviken, Analyses I and II, Table 3 (Cartesian coordinates).

run parallel at low temperatures; at high temperatures they diverge. The presence of sodium chloride only slightly influences the transition points known from the system $\text{CaCl}_2\text{-KCl-H}_2\text{O}$, so that the solutions of the univariant equilibria can be treated as if they belong to the three-component system mentioned. As the isotherms at 18° and 95° are of special interest to the discussion below these are reproduced in Fig. 4 and 4 b.

The four-component systems $\text{MgCl}_2\text{-KCl-NaCl-H}_2\text{O}$ and $\text{CaCl}_2\text{-MgCl}_2\text{-NaCl-H}_2\text{O}$ are well known as they are essential for the production of alkali chlorides. Of the four-component system $\text{CaCl}_2\text{-MgCl}_2\text{-KCl-H}_2\text{O}$ two isotherms (35° and 75°) are determined (Prutton and collab. 1946—1949).

Other four-component systems containing SrCl_2 have not been investigated.

Table 2. The invariant Equilibria of the Systems containing KCl, NaCl, CaCl_2 and H_2O .

Temperature	Composition of the solution			Solid phase	
	KCl	NaCl	CaCl_2		
<i>Two-component systems</i>					
$\text{KCl-H}_2\text{O}$	-10.9°	19.7	—	Ice + KCl	
$\text{NaCl-H}_2\text{O}$	-21.2°	—	22.4	Ice + $\text{NaCl} \cdot 2\text{H}_2\text{O}$	
	+ 0.15°	—	26.3	$\text{NaCl} \cdot 2\text{H}_2\text{O}$ + NaCl	
$\text{CaCl}_2\text{-H}_2\text{O}$	-55°	—	—	Ice + $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$	
	+ 29.2°	—	—	$\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ + $\alpha\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$	
	45.3°	—	—	$\alpha\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$ + $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$	
	175.5°	—	—	$\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ + $\text{CaCl}_2 \cdot \text{H}_2\text{O}$	
	$\sim 260^\circ$	—	—	$\text{CaCl}_2 \cdot \text{H}_2\text{O}$ + CaCl_2	
<i>Three-component systems</i>					
$\text{KCl-NaCl-H}_2\text{O}$	-23°	6.1	19.5	KCl + $\text{NaCl} \cdot 2\text{H}_2\text{O}$ + Ice	
	-2.3°	7.0	22.5	KCl + $\text{NaCl} \cdot 2\text{H}_2\text{O}$ + NaCl	
$\text{KCl-CaCl}_2\text{-H}_2\text{O}$?	?	—	$\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ + KCl + Ice	
	+ 27.0°	4.0	—	$\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ + $\alpha\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$ + KCl	
	37.8°	7.0	—	$\alpha\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$ + $\text{CaCl}_2 \cdot \text{KCl}$ + KCl	
	43.4°	4.3	—	$\alpha\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$ + $\text{CaCl}_2 \cdot \text{KCl}$ + $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$	
	?	?	—	$\text{CaCl}_2 \cdot \text{KCl}$ + $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ + $\text{CaCl}_2 \cdot \text{H}_2\text{O}$	
	?	?	—	$\text{CaCl}_2 \cdot \text{KCl}$ + $\text{CaCl}_2 \cdot \text{H}_2\text{O}$ + CaCl_2	
$\text{NaCl-CaCl}_2\text{-H}_2\text{O}$	determinations not published				
<i>Four-component system</i>					
$\text{KCl-NaCl-CaCl}_2\text{-H}_2\text{O}$	26.9°	4.6	0.35	47.0	$\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ + $\alpha\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$ + KCl + NaCl
	37.7°	7.0	0.35	51.3	$\alpha\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$ + $\text{CaCl}_2 \cdot \text{KCl}$ + KCl + NaCl
	43.3	4.0	0.39	55.0	$\alpha\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$ + $\text{CaCl}_2 \cdot \text{KCl}$ + $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ + NaCl

¹ NaCl is dissolved into saturated solutions of CaCl_2 in small amounts and causes only slightly changes in the transition temperatures (van't Hoff 1905). At high temperatures the solubility of NaCl increases.

² The transition points at the high and low temperatures are not examined.

On the Methods used at the Analyses of Brines.

Samples of the brines from Scania were analyzed in the ordinary way. In some, all ions of interest present in the brine were determined, in other samples only the components which occur in rather large quantities.

The analytical methods applied in the present investigation are those generally employed. Some remarks will be made concerning the determinations of Br and Sr.

The best determination of bromine was carried out as follows. The sample of water (50—100 ml) was put in a little glass distillation apparatus. A small amount of Cl was generated in the sample by adding some KMnO_4 and HCl. Then the sample was heated and the bromine transported, by the aid of a current of carbon dioxide, to the absorption vessel containing some diluted ammonia. The halogenides of the ammonia solution were precipitated in the usual way by silver nitrate, the silverhalogenides were weighed, a weighed part of the halogenides was then heated in a current of chlorine and weighed again. From the decrease in weight of the silver halogenides the amount of bromine is known. The accuracy of the method was found to be 0.1—0.2 mg Br.

The content of strontium was determined by precipitation of strontium as nitrate in 80 per cent nitric acid (Willard and Goodspeed 1936). First, calcium and strontium were freed from alkali salts by precipitation with ammonium carbonate. The filtrate from this separation was controlled free from calcium and strontium. After transformation of the carbonates into nitrates the deposited strontium nitrate was weighed, and the degree of the purity of the strontium nitrate controlled by its transformation into sulphate. Only in this way could the determination of the strontium content of the brines be ascertained with complete accuracy.

The Composition of the Brines in Scania.

According to Brotzen (1949) the water samples from depths varying between 1200 m and 1600 m at Höllviken and at Trelleborg have nearly constant proportion between the ions through the layers bearing salt water. The amount of salt increases with increasing depth.

Analyses of the brines are mentioned by Brotzen, but only the percentage of the chief constituents is noted. Some analyses taking up most of the constituents found in the water are given in Table 3.

Analyses Nos. I—VI represent the brines of Höllviken mentioned by Brotzen. The sample of the brine of Analysis VII (Höllviken), on the other hand, was taken at the deepest layer reached during the boring, where it was possible to get pure brine at the corresponding level. This analysis shows a brine of another kind. It is nearly a saturated solution of sodium chloride owing to the special conditions prevailing at this depth. Finally, Analysis VIII, representing

Table 3. Analyses of Brines from Höllviken and Trelleborg.

Anal. nr

I	Brine from Höllviken	I, 1235—1260 m depth,	April 18, 1944
II	»	»	» , May 27, 1944
III	»	»	» , May 19, 1945
IV	»	»	» , June 4, 1945
V	»	»	» , January 21, 1946
VI	»	»	» , February 13, 1946
VII	»	»	» , October 13, 1946
VIII	»	Trelleborg,	1200 » , May 28, 1947

Grams in 1000 ml

Anal. nr	I	II	III	IV	V	VI	VII	VIII
Na ⁺	30.550	31.400	} 34.000	37.200	44.300	43.000	97.550	38.100
K ⁺	1.000	0.700						
Li ⁺	0.006							
Cs ⁺	<0.005							
NH ₄ ⁺	0.030	0.030						0.010
Ca ²⁺	13.860	14.200	17.650	18.500	21.600	22.400	0.900	20.300
Sr ²⁺	0.010	0.010						0.600
Ba ²⁺	0.001	0.001						
Mg ²⁺	1.200	0.900	1.000	1.000	0.900	1.100	0.650	0.780
Mn ²⁺	0.016	0.012						0.020
Fe ²⁺	0.047	0.030						0.070
F ⁻	0.004	0.004						
Cl ⁻	75.500	76.100	84.900	94.700	108.500	108.900	154.000	98.000
Br ⁻	0.390	0.430	0.510				0.040	0.520
J ⁻	0.003	0.004						
SO ₄ ²⁻	0.011	0.011	0.015		0.070	0.040	2.130	0.080
PO ₄ ³⁻	<0.001							
NO ₃ ⁻ , NO ₂ ⁻	0.018	0.015						0.001
SiO ₂	0.009	0.010						0.020
H ₂ S	0.000	0.000						0.000
BO ₃ ³⁻	<0.001							
Al ₂ O ₃		<0.005						
Total	122.660	123.860	139.080	151.400	175.370	175.440	255.970	159.500
Spec. gravity	1.088	1.088	1.102	1.101	1.125	1.127	1.172	1.113

another part of the basin (Trelleborg), is stratigraphically correspondent to the layers from which Analysis I—VI derive, but differs from them to a content of strontium of 0.6 g Sr per litre.

The Application of the Quaternary System CaCl₂-KCl-NaCl-H₂O at an Exploitation of the Brines.

Below we discuss the possibilities of separating some components which occur in the brine in small amounts. It may be of some interest to know whether it is possible, theoretically and founded on principle, to realize a process which

is suitable for separation of potassium chloride from the other chlorides. The content of potassium chloride hitherto found in the Swedish brines is too insignificant for an industrial production. The process is described below, but only for the purpose of showing all the possibilities which might arise. If larger quantities of potassium chloride were discovered the process could be modified.

First some ions may be removed by easily performed operations. Magnesium hydroxide and the small amounts of silica, hydroxides of iron, manganese and aluminium, are precipitated by calcium hydroxide, and bromine is removed by chlorination. Now the water contains chlorides of calcium, sodium, potassium (Analyses I—VII) and, in special cases, strontium (Analysis VIII).

When the brines are concentrated by evaporation the solutions first behave as if they contain only chlorides of calcium and sodium.

The composition of the brines (Analyses I—VI) has been dotted in Fig. 1 and corresponds to the position of the point P_1 (Analysis I) and of the extended tie-line $O—P_1$. During evaporation of the solution the composition of the solutions changes in this direction until this line cuts the curve of the solubility of sodium chloride in corresponding content of calcium chloride at P_3 . Sodium chloride is now deposited at further evaporation because the solution is richer in calcium chloride. The composition of the solutions is represented by the isotherm corresponding to the evaporation temperature. When most of the sodium chloride is deposited, the small amounts of potassium chloride gradually have an effect on the crystallization. The points $P_2—P_4$, Fig. 4, correspond to the potassium chloride content of the brine during the concentration.

The way in which the solid phases crystallize at further evaporation is now connected with the properties of the solution of the four-component system $\text{CaCl}_2\text{-KCl-NaCl-H}_2\text{O}$. The most characteristic part of this system is the very low solubility of sodium chloride in solutions very rich in calcium chloride. On the other hand, in such solutions the solubility of potassium chloride at 50° and at 100° is respectively about ten times and five times that of sodium chloride. As a consequence, when solutions corresponding to the Analyses I—VI are evaporated, after deposition of almost the whole amount of sodium chloride present, that point of the isotherm is reached where calcium chloride, too, crystallizes. In Fig. 3 this point is represented where the line $O—P_2$ cuts the isotherm of the four-component system (P_4 , Figs. 3—4). Thus, at this point the solid phases are sodium chloride and the hydrate of calcium chloride, which is stable at the temperature in question. At further evaporation only this calcium chloride hydrate crystallizes. As the transition of calcium chloride tetrahydrate into dihydrate takes place between 45.3° (saturated pure calcium chloride solution) and 43.3° (solutions also saturated with respect to sodium chloride and potassium chloride), it is evident that the crystallization of calcium chloride dihydrate may go on at temperatures higher than 45° .

Now we will suppose below that the evaporation is performed at 95° . On this assumption Fig. 5 gives the representation of the properties of the solutions at the evaporation and at the crystallization of the solid phases.

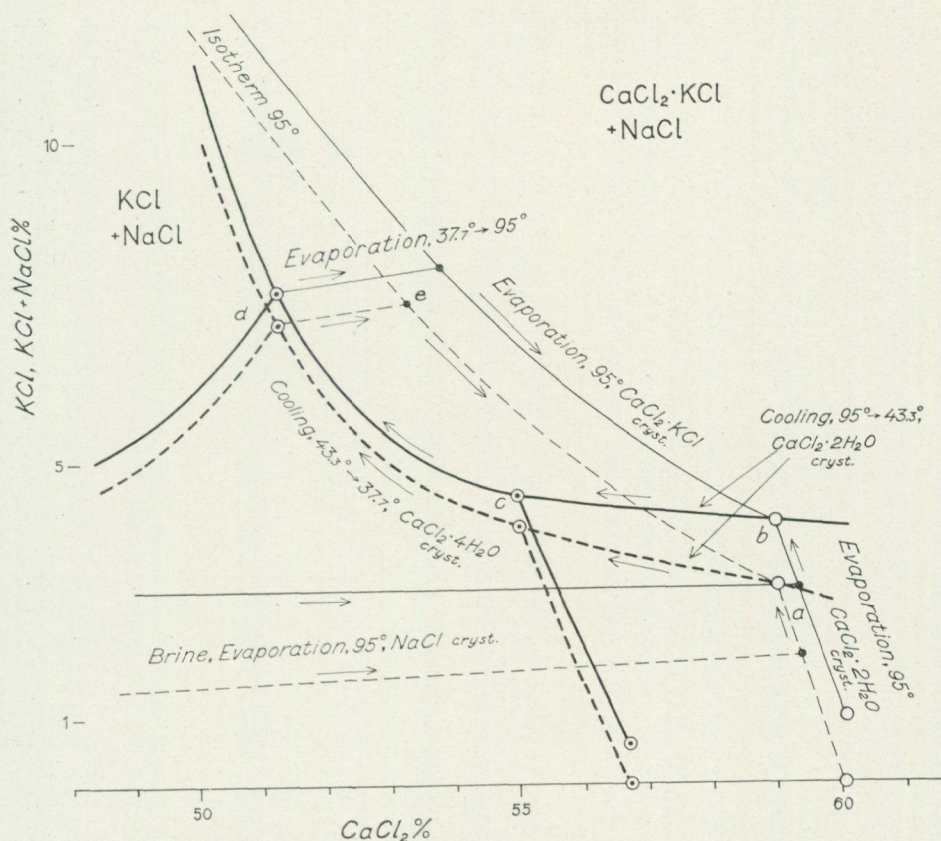


Fig. 5. Diagram on the cyclic process for crystallization of the solutions from the Höllviken brines. Solid lines KCl + NaCl, dashed lines KCl, found in the solutions (cf. Figs. 3 and 4).

When calcium chloride dihydrate crystallizes (Fig. 5, point a) the solution becomes richer in potassium chloride, and its composition changes along the isotherm until the univariant point (b) is reached, where calcium chloride dihydrate, double salt $\text{CaCl}_2 \cdot \text{KCl}$ and sodium chloride are in equilibrium with the solution. If the solution were evaporated further, the double salt would crystallize at the same time as the calcium chloride dihydrate. This should be avoided. Now the diagram Fig. 3 shows that a solution which is in univariant equilibrium at the boundary between the existence areas of calcium chloride dihydrate and the double salt, yields calcium chloride dihydrate when it is cooled down to 43.3° (Fig. 5, point c). Therefore, if the solid is removed at 43.3° after an evaporation carried out as described above, the solid consists of calcium chloride dihydrate, and small amounts of sodium chloride, the latter salt originating from its different solubility in saturated calcium chloride solutions at the temperatures applied during evaporation. The whole content of potassium chloride which was present in the sample at the start, is recovered in the final solution.

The solution at the invariant point at 43.3° has a property of importance for the further concentration. When this solution is cooled down to the invariant point d at 37.7° , where potassium chloride, calcium chloride, tetrahydrate, double salt and sodium chlorides are in equilibrium with the solution, the chief compound yielded is calcium chloride tetrahydrate. Temporarily, also, some double salt may crystallize, but on account of the alteration in the concentration of the solution this salt is decomposed by the dissolving of its potassium chloride. The composition of the final solution is very close to that represented by invariant point of the double salt of 37.7° . The solution contains, undiminished, the whole amount of the potassium chloride.

When potassium chloride is to be won from this solution, two methods may be employed. According to the first one, the solution is evaporated at higher temperature (Fig. d—e—b) by those means about half the content of potassium chloride is precipitated as double salt (at 95°). This is filtered off and decomposed by a diluted calcium chloride solution at a low temperature and the potassium chloride is precipitated as a crystal powder. In the second method the solution at 37.7° is diluted to about 35 per cent CaCl_2 and cooled down to a low temperature (0° — 15°), so that a part of the potassium chloride crystallizes. In the two methods mentioned the solutions remaining from the crystallisation may be added to a new part of the brine at a suitable stage during the evaporation.

If greater amounts of potassium chloride should occur in the brine, that point where the solid sodium chloride shall be removed (Fig. 5, point a), is at other parts of the isotherms. When the solutions contain potassium chloride and calcium chloride in the proportions 4 : 55 or 7 : 51.5 (the invariant points c and d, Fig. 5) the cyclic crystallization process may be started at 43.3° or at 37.7° . At still greater content of potassium chloride the cyclic process may start by deposition of the double salt.

The above process can be adopted for extraction of potassium chloride from a mixture of solid alkali chlorides (patents). In this case the solid alkali chlorides are extracted by a concentrated solution of calcium chloride or their solutions are concentrated together with calcium chloride and, after removing of the undissolved sodium chloride the double salt is deposited by evaporation.

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