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STUDY OF THE EVAPORATION OF A BRINE INVOLVING THE SYSTEM Na^+, Mg^{2+}, K^+, Cl^-, SO_4^{2-}–H_2O
Crystallisation of oceanic salts

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Abstract

The evaporation of a Tunisian brine sample involving the system Na^+, Mg^{2+}, K^+, Cl^-, SO_4^{2-}–H_2O was studied under atmospheric pressure and at ambient temperature. The selective densities of precipitation of halite (NaCl) and of co-precipitation of halite and astrakanite ($Na_2Mg(SO_4)_2\cdot 4H_2O$), halite and kaïnite ($MgSO_4\cdot KCl\cdot H_2O$) and epsomite $MgSO_4\cdot 7H_2O$ were determined.

During the evaporation of the studied brine, calculations related to the hypothetical composition of the solution in terms of the simple salts NaCl, $MgSO_4$, KCl and $MgCl_2$.

Keywords: brine, crystallisation, salt, solubility system

Introduction

Industrial needs for mineral salts such as sodium sulphate (Na_2SO_4), magnesium sulphate ($MgSO_4$) and potassium sulphate (K_2SO_4) are constantly increasing worldwide. The brines that exist in salty lakes, lagoons, sebkhats and chotts are sources for some such salts. It is evident then that a great number of researchers have been interested in the study of brines since the beginning of this century [1].

The exploitation of these deposits demands considerable investment, and preliminary multidisciplinary studies (chemical, geological, hydrogeological and others) are necessary. These studies allow an evaluation of the reserves and the optimisation of the conditions extraction and exploitation of useful compounds.

Sebkhat El Adhibat, which has been studied in many works, is in the south-east of Tunisia. It has an area of 125 km^2 and represents a total reserve of 245 million m^3, of which 40% has been estimated to be recoverable [2].

The present study was carried out in order to determine the crystallisation conditions relating to the natural evaporation of sodium, potassium and magnesium sulphates under the climatic conditions in the south of Tunisia, characterised essentially by:

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- an average temperature of 33°C in summer;
- an evaporation rate of 9 mm per day;
- an average relative humidity of about 66%;
- an average wind velocity of about 3.5 m s^{-1};
- an average annual rainfall of 202 mm;
- an average annual evaporation of 1123 mm.

We report here results obtained in the laboratory during the polythermic evaporation of a brine sample by ventilation under atmospheric pressure and at ambient temperature.

Experimental

Evaporation of brine

The brine sample was extracted from a pit in the central part of the aquiferous area, situated about 3 km from the north and west borders of the sebkhat.

The operative conditions in the laboratory were as close as possible to those existing in the sebkhat. During the evaporation, the brine was in polyethylene containers and submitted to a continuous current of air at ambient temperature.

Density measurement

As a density gradient is established in the liquid during crystallisation, previous agitation was indispensable to obtain a homogeneous solution before each measurement. Density was determined after decantation of the solids in suspension.

Sampling of solid and liquid samples

During the evaporation of the brine, solid and liquid samples were taken for analysis (chemical analysis and X-ray diffraction) after times allowing appropriate changes in density. The supernatant brine was separated from the solid by decantation.

The solid in the saturated liquid was slightly crushed, filtered on a sintered-glass crucible No. 2, and stocked in small plastic bags for protection from the atmospheric humidity.

As the supernatant brine was saturated, after separation from the solid it was diluted two-fold with distilled water in order to avoid any further precipitation due to evaporation or a decrease in temperature.

Analysis

The changes in composition of the brine were followed by analysis of the major elements (Na^+, K^+, Ca^{2+}, Mg^{2+}, SO_4^{2-} and Cl^-). Mg^{2+} and Ca^{2+} were analysed by complexometric titration with EDTA [3, 4]. Na^+ and K^+ were analysed by flame emission spectrometry [5]. The SO_4^{2-} concentration was determined by gravimetry [6, 7]. Cl^- was analysed by potentiometry in a nitrate medium [8]. X-ray diffraction was used to identify the solid phases which precipitated out.

Results and discussion

The physico-chemical characteristics (chemical analysis and density) of the natural brine collected from the site were as follows:

Density	Ca^{2+} g l^{-1}	Na^+ g l^{-1}	K^+ g l^{-1}	Mg^{2+} g l^{-1}	Cl^- g l^{-1}	SO_4^{2-} g l^{-1}
1.187	1.00	88.55	3.63	13.7	154.21	37.52

The changes in the composition of the brine were followed by studying

– the variation in the concentrations of the different ions as a function of the density;

– the variation in the numbers of moles of the ions in relation to 1000 moles of water as a function of the density;

– the progress of representative points of the brine in the system Na^+, K^+, Mg^{2+}/Cl^-, SO_4^{2-}–H_2O;

– the variation in the numbers of moles of the different salts as a function of the number of dissolved $MgCl_2$ of moles.

Variation in the concentrations of ions in the solution as a function of the density

The concentrations of Na^+, Mg^{2+}, K^+, SO_4^{2-} and Cl^- in the liquid at various densities, expressed in g l^{-1}, are reported in Table 1.

Variation in the numbers of moles of ions in relation to 1000 moles of water as a function of the density

These data are given in Table 2, calculated from the concentrations in g l^{-1} by using the following equation:

$$(C_i)_j = \frac{(c_i)_j 1000}{M_i (n_{H_2O})_j} \qquad (1)$$

where $(C_i)_j$ is the concentration of the i-th ion in the j-th sample, expressed in moles per 1000 moles of water, $(c_i)_j$ the concentration in g l^{-1} of the i-th ion in the j-th sample, M_i is the molar mass of the i-th ion and $(n_{H_2O})_j$ is the number of moles of water in one litre of the j-th sample.

Figure 1 reveals that the concentration of Ca^{2+} decreases to zero rapidly. This is due to the low solubility of $CaSO_4$. Indeed, the presence of a great quantity of SO_4^{2-} in the brine leads to the precipitation of Ca^{2+} in the form of $CaSO_4$.

For densities between 1.187 and 1.236, all the ionic species except Ca^{2+} exhibit an increase in mole number. The evaporation involves a concentration of the brine without any precipitation of salts.

At densities between 1.236 and 1.298, there are simultaneous and rapid decreases in the Na^+ and Cl^- concentrations, which seems to correspond to NaCl precipitation. This was confirmed by the X-ray diffraction spectra of the solid obtained. This decrease is less accentuated for densities higher than 1.298.

The concentration of SO_4^{2-} increases up to a density of 1.298 and then decreases.

Table 1 Chemical analysis of liquid (concentrations expressed in g l^{-1})

Density	Na^+	K^+	Ca^{2+}	Mg^{2+}	Cl^-	SO_4^{2-}
1.1870	88.55	3.63	1.00	13.70	154.21	37.52
1.2000	93.86	4.32	0.79	14.78	164.00	40.10
1.2360	104.08	5.16	1.97	18.00	185.52	47.22
1.2400	100.00	6.42	0.52	20.76	180.10	55.45
1.2510	96.00	6.83	0	22.74	176.45	60.00
1.2610	89.20	7.36	0	29.12	174.88	73.78
1.2650	80.30	8.56	0	35.50	170.50	87.23
1.2740	77.50	11.36	0	41.93	167.48	114.90
1.2830	70.11	12.40	0	45.33	161.01	122.94
1.2910	60.36	12.48	0	49.17	155.54	125.27
1.2980	59.00	14.35	0	52.48	162.97	127.67
1.3030	52.43	20.31	0	62.67	193.57	120.47
1.3120	45.33	20.90	0	69.35	204.43	118.05
1.3105	40.60	21.20	0	72.05	206.14	116.79
1.3150	25.88	28.20	0	77.91	214.58	106.27
1.3230	11.60	20.40	0	84.67	213.69	94.87
1.3250	7.60	11.80	0	88.44	219.43	83.10

The chemical analysis and X-ray diffraction of the solids obtained at densities between 1.298 and 1.315 show the presence of sulphated salts. They correspond to a mixture of NaCl and astrakanite ($Na_2(Mg(SO_4)_2\cdot 4H_2O)$).

The curve illustrating the variation in the concentration of K^+ in the brine as a function of the density displays a maximum at a density of 1.315, where the crystallisation of K^+ salts starts. This result is confirmed by analysis of the X-ray diffraction spectra of the solids deposited.

The curve illustrating the variation in the concentration of Mg^{2+} as a function of the density shows an ascending tendency in spite of the precipitation of Mg^{2+} salts such as astrakanite ($Na_2Mg(SO_4)_24H_2O$), epsomite ($MgSO_4\cdot 7H_2O$) and double K^+ and Mg^{2+} salts. This is probably due to the strong solubility of $MgCl_2$.

Karsen representation of the system Na^+, K^+, Mg^{2+}/Cl^-, SO_4^{2-}–H_2O at 25°C

In the Karsen representation mode (Fig. 2), the molar percentages of K_2^{2+}, Mg^{2+} and SO_4^{2-} are expressed in relation to their sum:

$$\sum(\%K_2^{2+} + \%Mg^{2+} + \%SO_4^{2-}) = 100.$$

Table 2 Chemical analysis of liquid (concentrations in moles per 1000 moles of water)

Density	Na^+	K^+	Ca^{2+}	Mg^{2+}	Cl^-	SO_4^{2-}
1.1870	78.00	1.88	0.50	11.41	88.01	7.91
1.2000	83.26	2.25	0.40	12.40	94.26	8.51
1.2360	92.82	2.70	0.25	15.18	106.04	10.08
1.2400	89.22	3.36	0.05	17.51	104.10	11.84
1.2510	84.51	3.53	0	18.93	100.64	12.64
1.2610	78.73	3.82	0	24.30	100.00	15.59
1.2650	70.77	4.43	0	28.41	95.34	18.40
1.2740	70.45	6.07	0	36.05	98.64	25.00
1.2830	62.97	6.55	0	38.50	93.70	26.44
1.2910	53.18	6.46	0	40.97	88.79	26.42
1.2980	52.95	7.57	0	44.60	98.89	27.43
1.3030	48.07	10.95	0	54.34	114.98	26.44
1.3120	45.54	11.26	0	60.10	121.38	25.90
1.3105	37.21	11.43	0	62.46	122.43	25.63
1.3150	23.49	15.05	0	66.88	126.19	23.09
1.3230	10.11	10.46	0	69.80	120.68	19.80
1.3250	6.50	5.93	0	71.56	121.64	17.02

The percentages of K_2^{2+}, Mg^{2+} and SO_4^{2-} (Table 3) were calculated from the concentrations of the ions present in the brine (Table 1).

Under the experimental conditions adopted, the evaporation is not isothermal. Indeed, crystallisation and redissolution of the salts proceed constantly at the solid–liquid interface.

In accordance with the example of Berthon and Aubry [9], we consider that the quinary oceanic diagram at 25°C [10, 11] corresponds to the representation of the changes in the brine under the experimental conditions of this work.

At the beginning of the evaporation, the number of moles of water decreases without any precipitation and the brine becomes more concentrated. The salt which precipitates first is NaCl, and the majority of it crystallises.

In Fig. 2, the representative points below U relate to the experimental errors. NaCl is precipitated jointly with the other phases during the evaporation.

Starting from brine U (Fig. 2), which has a composition of 4.86% K_2, 59.88% Mg and 35.24% SO_4 and a density of 1.298, the composition of the brine changes according to UV.

The point V corresponds to brine with the composition 7.72% K_2, 68.59% Mg and 23.68% SO_4 and a density of 1.315. Extension of segment UV coincides with the representative point of astrakanite ($Na_2Mg(SO_4)_2 \cdot 4H_2O$). This interpretation is confirmed by the diffractograms of the salt deposits.

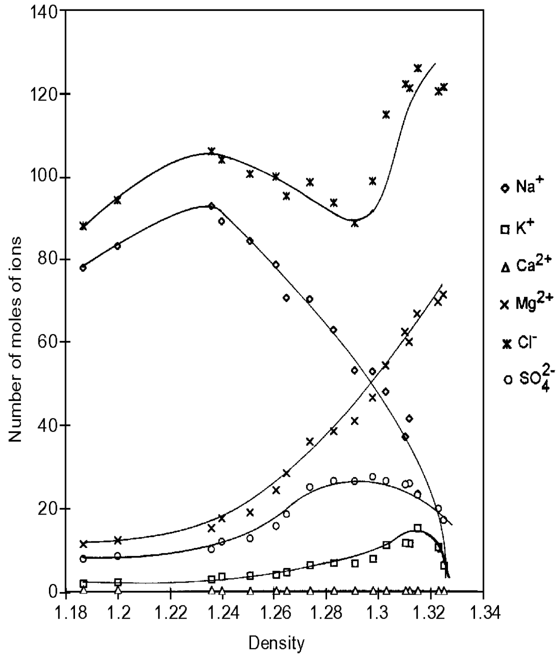

Fig. 1 Variations in numbers of moles of ions as a function of density

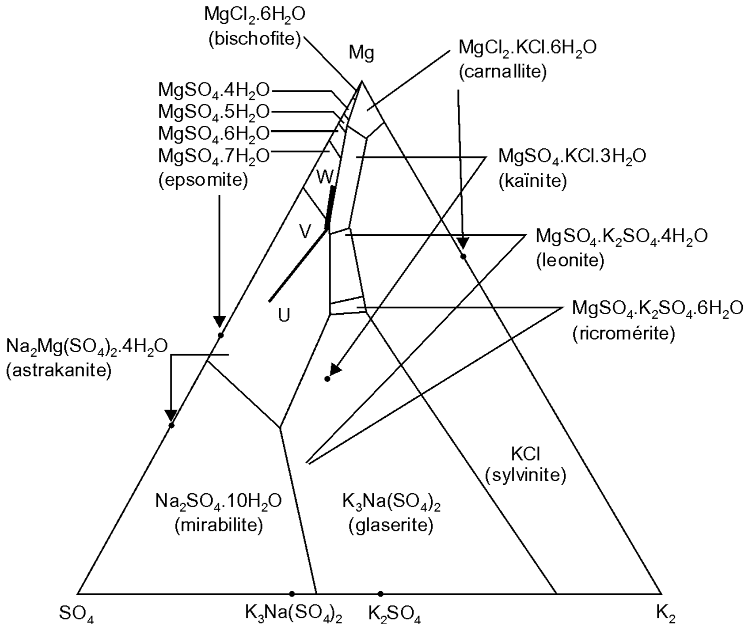

Fig. 2 Representation of changes in composition of the brine in the system Na^+, K^+, Mg^{2+}/Cl^-, SO_4^{2-}–H_2O

Brine V deposits a mixture of salts, among them astrakanite and epsomite.

Between points V and W, the progress follows a common line to the crystallisation domain of kaïnite ($MgSO_4{\cdot}KCl{\cdot}3H_2O$) and epsomite ($MgSO_4{\cdot}7H_2O$). This result is in agreement with the decrease in the number of moles of K^+.

All the results concerning the natural evaporation of the brine from sebkhat El Adhibat allowed us to establish the break densities corresponding to selective crystallisation of the different salts. This can be schematised as in Fig. 3.

Variation in the numbers of moles of different salts as a function of the number of moles of $MgCl_2$

In this section, we ascribe to each liquid sample a hypothetical mineralogical composition in which the components of the solution are simple salts such as $CaSO_4$, Na_2SO_4, $MgSO_4$, K_2SO_4 and $MgCl_2$. During the evolution of the brine, the variation in the numbers of moles of the different salts was studied as a function of the number of moles of $MgCl_2$, because this is the only salt which does not precipitate even at high densities.

When the residual solution is concentrated in $MgCl_2$, a decrease in the rate of evaporation is noted.

The numbers of moles of different salts were obtained as follows:

$n_{(X)}$=number of moles of X

$$n_{(\mathrm{Na_2Cl_2})}=\frac{n_{\mathrm{Na^+}}}{2} \tag{2}$$

$$n_{(\mathrm{MgSO_4})}=n_{(\mathrm{SO_4^{2-}})}-n_{(\mathrm{CaSO_4})} \tag{3}$$

$$n_{(\mathrm{K_2Cl_2})}=\frac{n_{\mathrm{K^+}}}{2} \tag{4}$$

$$n_{(\mathrm{MgCl_2})}=n_{(\mathrm{Mg^{2+}})}-n_{(\mathrm{MgSO_4})}=\frac{n_{\mathrm{Cl^-}}}{2}-n_{(\mathrm{Na_2Cl_2})}-\ n_{(\mathrm{K_2Cl_2})} \tag{5}$$

The variation in the numbers of moles of salts per 1000 moles of water, and the variation in the numbers of moles of salts relative to the number of moles of $MgCl_2$, are presented in Table 4 and Fig. 4.

The curves in Fig. 4 indicate three sequences corresponding to a succession of crystallisation of NaCl, $MgSO_4$ and K_2Cl_2. Due to the low quantity of Ca^{2+} in the brine, $CaSO_4$ disappears following the third liquid sampling during the evaporation.

Calculations relating to the deposited salts and the evaporated water

Sodium and potassium salts crystallised out in the forms NaCl, $Na_2Mg(SO_4)_2{\cdot}4H_2O$ and K_2SO_4.

As concerns the material balance of the deposited salts and the evaporated water, we presumed that the ions in solution were associated as simple salts: $CaSO_4$,

Table 3 Molar percentages of ions in the brine during evaporation

Density	%K_2	%Mg	%SO_4
1.1870	4.64	56.31	39.04
1.2000	5.11	56.25	38.63
1.2360	5.08	57.03	37.87
1.2400	5.42	56.42	38.15
1.2510	5.30	56.77	37.92
1.2610	4.56	58.13	37.29
1.2650	4.52	57.93	37.53
1.2740	4.73	56.24	39.01
1.2830	4.80	56.44	38.75
1.2910	4.57	58.00	37.41
1.2980	4.86	59.88	35.24
1.3030	6.34	62.99	30.65
1.3120	6.14	65.58	28.26
1.3105	6.09	66.58	27.32
1.3150	7.72	68.59	23.68
1.3230	5.51	73.06	20.87
1.3250	3.24	78.16	18.59

Na_2SO_4, $MgSO_4$, K_2SO_4 and $MgCl_2$. During the evaporation, these salts crystallise out successively as a function of their solubilities.

The curves in Fig. 4 can be divided into three parts, which can be used to determine the amounts of water and salts crystallised. These parts are separated by lines corresponding to the following brine compositions:

	Number of moles				
Brine	$CaSO_4$	Na_2Cl_2	$MgSO_4$	K_2Cl_2	$MgCl_2$
B_0	0.50	39.00	7.40	0.94	4.00
B_1	0.25	46.41	9.82	1.35	5.35
B_2	0.00	26.59	27.43	3.79	19.71
B_3	0.00	11.74	23.09	7.53	43.79

In order to simplify the writing of the expression of the material balance, the numbers of moles of H_2O, Na_2Cl_2, $MgSO_4$, K_2Cl_2 and $MgCl_2$ in relation to 1000 moles of water in the brine B_i are represented by H^i, N^i, M^i, K^i and Mc^i respectively. The number of moles of water evaporated and the numbers of moles of Na_2Cl_2, $MgSO_4$ and K_2Cl_2 crystallised between B_i and B_j are given by H^{i-j}, N^{i-j},

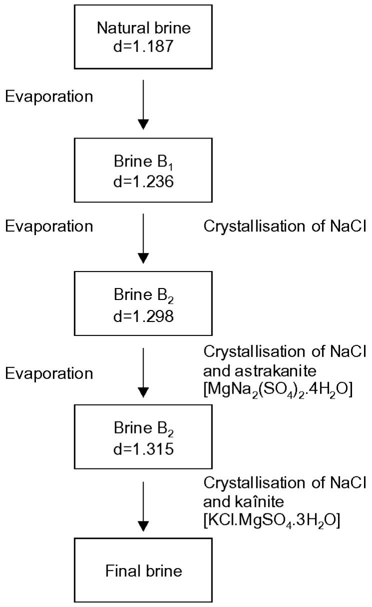

Fig. 3 Changes during evaporation of a brine from sebkhat El Adhibat

M^{i-j} and K^{i-j}, respectively. $MgCl_2$ does not precipitate and its mole number is conserved during evaporation.

The number of moles of water evaporated in the first part, H^{0-1} (Fig. 4), can be calculated via the following equation:

$$H^{0-1} = H^0(1-\alpha) \tag{6}$$

where $\alpha = Mc_o/Mc_1$.

The number of moles of water evaporated, H^{1-2}, and the number of moles of NaCl crystallised, N^{1-2}, in the second part (Fig. 4) can be calculated by using the following equations:

$$H^{1-2} = \alpha H^0(1-\beta) \tag{7}$$

$$N^{1-2} = 2N^1(1-\beta) \tag{8}$$

where $\beta = Mc_1/Mc_2$.

Finally, in the third part of Fig. 4, the number of moles of water evaporated, H^{2-3}, and the numbers of moles of NaCl, N^{2-3}, and $MgSO_4$, M^{2-3}, crystallised can be calculated by using the following equations:

$$H^{2-3} = \alpha\beta H^0(1-\gamma) \tag{9}$$

$$N^{2-3} = 2N^2(1-\gamma) \tag{10}$$

Table 4 Numbers of moles of different salts in relation to 1000 moles of water

Density	Na_2Cl_2	$CaSO_4$	$MgSO_4$	K_2Cl_2	$MgCl_2$
1.1870	39.00	0.50	7.40	0.94	4.00
1.2000	41.63	0.40	8.11	1.12	4.28
1.2360	46.41	0.25	9.82	1.35	5.35
1.2400	44.61	0.05	11.78	1.68	5.72
1.2510	42.25	0	12.64	1.76	6.28
1.2610	39.36	0	15.59	1.91	8.71
1.2650	35.38	0	18.40	2.21	10.00
1.2740	35.22	0	25.00	3.03	11.04
1.2830	31.48	0	26.44	3.27	12.06
1.2910	26.59	0	26.42	3.23	14.54
1.2980	26.47	0	27.43	3.78	19.17
1.3030	24.03	0	26.44	5.47	27.89
1.3120	20.77	0	25.90	5.63	34.20
1.3105	18.60	0	25.63	5.71	36.83
1.3150	11.74	0	23.09	7.52	43.78
1.3230	5.05	0	19.80	5.23	50.00
1.3250	3.25	0	17.02	2.96	54.54

$$M^{2-3} = M^{2}(1 - \gamma) \tag{11}$$

where $\gamma = Mc_2/Mc_3$.

For the studied Tunisian brine, calculations were performed for a quantity of the brine containing 1000 moles of water. The results are given in the following table:

First part	H^{0-1}=252.40 moles
Second part	H^{1-2}=538.94 moles
	N^{1-2}=66.91 moles
Third part	H^{2-3}=117.32 moles
	N^{2-3}=29.59 moles
	M^{2-3}=15.42 moles

Conclusions

In the present work, a study was made of the evaporation of a brine from a sebkat in the south of Tunisia. The brine was subjected to evaporation in the laboratory un-

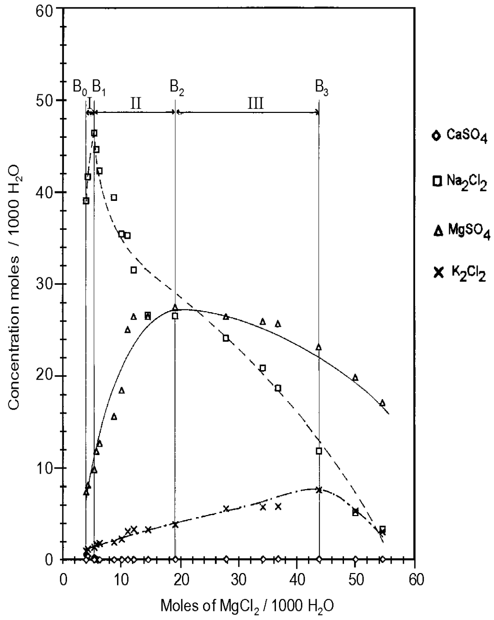

Fig. 4 Variations in numbers of moles of different salts as a function of the number of moles of MgCl$_2$

der conditions as close as possible to the natural conditions. The densities at the beginning of crystallisation of NaCl, astrakanite and potassium salts were determined.

The changes in density and in the diagram Na$^+$, K$^+$, Mg^{2+}/Cl$^-$, SO$_4^{2-}$–H$_2$O were followed. The amounts of evaporated water and of crystallised salts were determined in the various stages.

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