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Crystallization Sequence of Brines–Geometrical Principles for a Computer Assisted Calculation

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Summary. A computer assisted calculation of the crystallization sequence of a brine is performed on the basis of the respective phase diagrams at 25°C. The nature of the solids and the mass balance are determined. The calculation gives immediate quantitative information of the brine behavior during evaporation. The calculation is performed assuming that *i)* the solids are always in equilibrium with the liquid, *i.e.* that some solid phases can be partially or completely redissolved during evaporation, or *ii)* the solids are separated from liquid by sedimentation and no redissolution is possible. The seasonal or day-night fluctuations of temperature and metastable equilibria have not been taken into account.

Keywords. Sea water; Brine; Crystallization sequence; Simulation.

Kristallisationsabfolge von Salzlösungen: geometrische Grundlagen für eine computerunterstützte Berechnung

Zusammenfassung. Die Kristallisationsabfolge beim Abdampfen von Salzsolen wurde bei 25°C auf der Basis der entsprechenden Phasendiagramme computerunterstützt berechnet. Dabei wurden sowohl die auskristallisierenden festen Phasen bestimmt als auch deren Massenbilanzen ermittelt. Um quantitative Information über das Abdampfverhalten von Salzsolen zu erhalten, wurden diesen Berechnungen zwei Grenzannahmen zugrunde gelegt: *i)* das Fest-flüssig-Gleichgewicht stellt sich laufend ein, sodaß sich feste Phasen während des Verdampfungsprozesses teilweise oder vollständig wieder auflösen können, bzw. *ii)* die festen Phasen sedimentieren und trennen sich von der flüssigen Phase, sodaß keine Wiederauflösung möglich ist. Tages- bzw. jahreszeitliche Temperaturschwankungen sowie metastabile Gleichgewichte wurden nicht berücksichtigt.

Introduction

An experimental determination of the crystallization sequence of brine during isothermal evaporation is very time consuming. It requires a lot of difficult, tedious,

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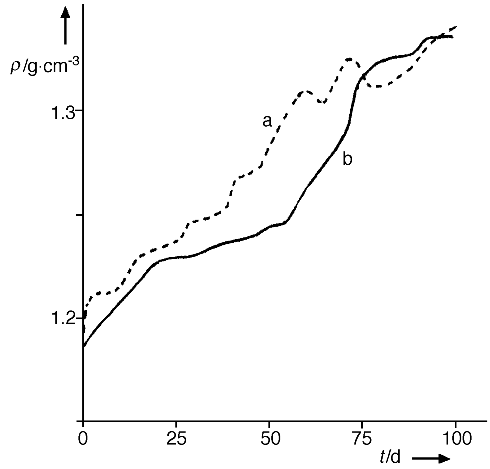

Fig. 1. Brine from Sebkhat El Adhibat; a: evaporation of natural brine, b: evaporation of synthetic brine

lengthy, and inaccurate analyses of liquid and solid phases. For example, Fig. 1 shows the variation *vs.* time of the density of the liquid phase during evaporation at 25°C of natural or synthetic solutions [1] from Sebkhat El Adhibat (south Tunisia). Computer programs have been used to perform a critical evaluation of solubility data [2–5] or to solve chemical and phase equilibria in multicomponent systems employing more or less user-friendly interfaces (EQ3/6, CHEMSAGE, THERMO-CALC, GEOCALC). They became generally accepted tools to simulate complex chemical systems including crystallization and dissolution processes. Given a thermodynamic data base, an engineer or geochemist can calculate species concentrations and phase amounts for arbitrary equilibrium processes.

However, if the phase diagram is known for a given system, application of the geometrical principles of the phase rule allows to develop simpler and faster codes to calculate equilibrium states. Also, the well-known problem of non-converging results in minimization routines does not exist using geometrical principles. Fast and simple codes are essential if the equilibrium calculations have to be performed within complex material transport algorithms or technical flow-sheet simulators. The present paper demonstrates the steps of calculation and its geometrical counter-part to obtain the crystallization sequence from sea-water brines. Furthermore it is shown how complex experimental results can be rationalized to draw far-reaching conclusions.

Results and Discussion

Expression of composition

Sea-water and natural brines are very complex media involving almost all known elements, and the expression of composition must take into account the particularities of such systems:

- They are reciprocal ion-pair salt systems.
- The major elements precipitate during evaporation or cooling, whereas the solubility product of minor and trace elements is not satisfied and they remain

quasi completely in the liquid phase except for small amounts being removed with the precipitate by adsorption or as impregnating solution. Consequently, the concentration of minor elements increases progressively during a crystallization sequence and must be taken into account in the determination of the thermodynamical properties of the system.

- An unsymmetrical expression of composition is desirable in order to get a suitable representation of evaporation phenomena.

For these reasons, the *Jänecke* expression has been found more convenient than the usual expressions (mole fraction, molality, *etc.*) and has been used in this work. The composition is related to the total amount of anions or cations, taking in account their charge:

$$X_i = \frac{z_i n_i}{D};\, Y_j = \frac{z_j n_j}{D};\, Z = \frac{n_H}{D};\, D = \sum_i z_i n_i = \sum_j z_j n_j \qquad (1)$$

i and *j* are related to all cations and anions (including minor and trace elements) and *H* to water, *n* and *z* are the amount of substance and the charge of a component, and *D* is the number of moles extended over all anions or cations of the solution, taking into account their charge in order to satisfy the electroneutrality condition of the medium.

Graphical representation of natural brine

The behavior of sea-water cannot be described by a single representative diagram. In dilute solutions the amount of minor and trace elements is negligible, and only the major elements Na^+, K^+, Mg^{2+}, Ca^{2+}, CO_3^{2-}, Cl^- and SO_4^{2-} have to be taken into account (7th order system). At the beginning of an evaporation process calcium carbonate and calcium sulfate precipitate as shown in Fig. 2 for the brine of Sebkhat

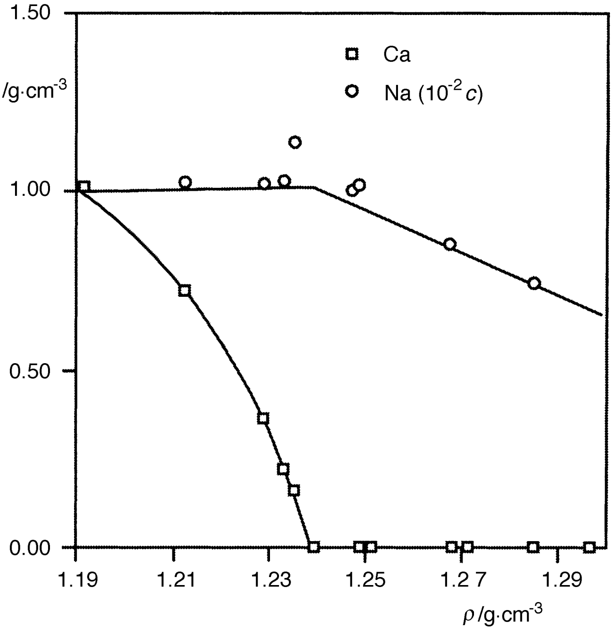

Fig. 2. Brine from Sebkhat El Adhibat; precipitation of NaCl and Ca salts at the beginning of evaporation

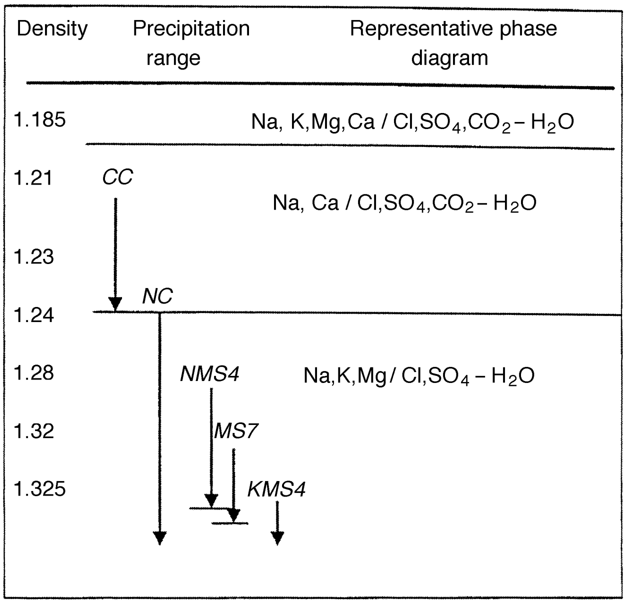

Fig. 3. Evolution of the representative phase diagram during evaporation

El Adhibat. During this step of evaporation K^+ and Mg^{2+} can be neglected; the representative system involves only Na^+, Ca^{2+}, CO_3^{2-}, Cl^-, and SO_4^{2-}. When the density reaches approximately $1.22\,g \cdot cm^{-3}$ the separation of calcium salts is almost complete, and NaCl begins to precipitate at about $\rho = 1.235\,g \cdot cm^{-3}$. During the crystallization sequence the system can be represented graphically as a 5th order phase diagram containing Na^+, K^+, Mg^{2+}, Cl^-, $SO_4{}^{2-}$ and H_2O (Fig. 3).

Under isothermal-isobaric conditions such systems imply four composition variables (X_K, X_M, Y_S, Z_H), and a graphical representation in a three-dimensional space requires two representative points, one for salts and one for the water content. A path through the diagram must be followed by the simultaneous displacements of the two representative points. At the end of the crystallization sequence the treatment of bittern requires new representative phase diagrams involving some of the minor elements.

Solubility field of NaCl

When the solution is saturated in NaCl, the number of independent variables is reduced to three under isobaric-isothermal conditions. Two volumes in three-dimensional spaces represent the solubility field of NaCl and a saturated solution corresponds to two conjugate points, one in each volume. Figure 4 shows the solubility domain of NaCl at 25°C. The volumes are limited by fifteen faces, 30 edges, and 25 apices.

Three faces (*obeza, obfgc, ochijkla*) are related to the limiting quaternary systems where an equilibrium between liquid and NaCl is observed; the others correspond to double saturation in salt (for example NaCl and KCl are in equilibrium with liquid along the face *bfmnpqe*). Three edges are situated on the axes and correspond to

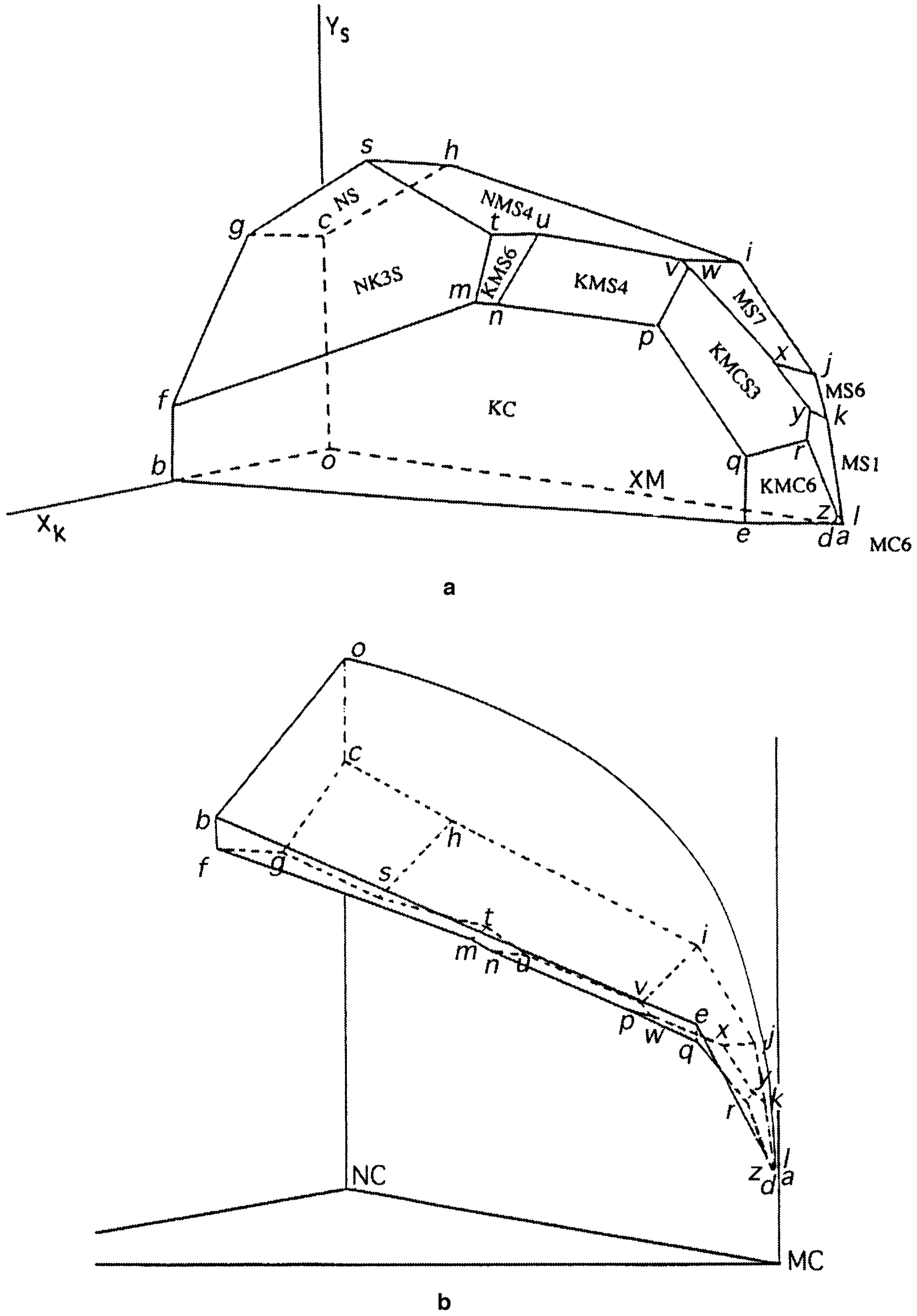

Fig. 4. Solubility domain of NaCl at 25°C; a: salt composition, b: water content

ternary subsystems (equilibrium liquid + NaCl), 11 are located on the faces (quaternary subsystems, double saturation in salts), and three solid phases are in equilibrium with liquid along the others. The apices correspond to an isothermal-isobaric invariant equilibrium (one solid phase for binary, two for ternary, three for

Table 1. Minerals observed at 25°C

Symbol	Name	Formula
H	Ice	H2O
NC	Halite	$NaCl$
KC	Sylvite	$KC1$
MC6	Bischofite	$MgCl_2 \cdot 6H_2O$
NS	Thenardite	Na_2SO_4
MS1	Kieserite	$MgSO_4 \cdot H_2O$
MS6	Hexahydrite (6)	$MgSO_4 \cdot 6H_2O$
MS7	Epsomite	$MgSO_4 \cdot 7H_2O$
NMS4	Astrakanite	$Na_2SO_4 \cdot MgSO_4 \cdot 4H_2O$
NK3S	Glaserite	$Na_2SO_4 \cdot 3K_2SO_4$
KMC6	Carnallite	$KC1 \cdot MgCl_2 \cdot 6H_2O$
KMS6	Schönite, picromerite (6)	$K_2SO_4 \cdot MgSO_4 \cdot 6H_2O$
KMS4	Leonite	$K_2SO_4 \cdot MgSO_4 \cdot 4H_2O$
KMCS3	Käinite	$KC1 \cdot MgSO_4 \cdot 11/4H_2O(6)$

quaternary subsystems, four in the quinary system. Their composition as collected from the literature is presented in Table 1.

As long as the brine is dilute the representative point of the brine is not located in the solubility domain of NaCl, and in three-dimensional projections the salt composition is inside the solubility domain of NaCl and the water amount is outside.

Geometrical determination of the crystallization sequence

In the determination of the crystallization sequence the faces of the NaCl solubility field are considered as planes and the edges as straight lines. This assumption introduces a small uncertainty in the calculations which will be evaluated during the modeling of the representative brine system.

Simulation of the crystallization sequence

The crystallization sequence is simulated by computer assisted calculations and determined step by step, each phase change corresponding to the end of a step and to the beginning of the next one. The mean composition of salts remains constant during each step so that the relative amounts of salts distributed between the phases in equilibrium can be evaluated by application of the lever rule. The water amount is not conservative and, at the present stage of modeling of the quinary system, its calculation cannot be directly performed at the end of the first step, *i.e.* when the solution is just saturated in NaCl. At the end of the second and further steps the representative points are located on the surface of the solubility field of NaCl so that the water content can easily be deduced from the salt composition. Two simulations have been done:

a) The sample is stirred during evaporation, and solid-liquid equilibrium is observed along the whole crystallization sequence; some solid phases can be partially or completely redissolved during evaporation.

b) The solid salts are separated from liquid by sedimentation (simulation of natural evaporation); redissolution of solid phases is not possible.

a) Stirring during evaporation

Step 1:

Saturation of the brine with NaCl, starting points $S_0S'_0(X_K^0, X_M^0, Y_S^0, Z^0)$, end points $S_1\,S'_1\,(X_K^1,\, X_M^1,\, Y_S^1,\, Z^1)$.

During evaporation of the dilute solution the representative point of the salt composition remains unchanged, whereas the water content decreases:

$$X_N^1 = X_N^0, X_K^1 = X_K^0, X_M^1 = X_M^0, Y_S^1 = Y_S^0, Z^1 < Z^0 \tag{2}$$

Step 2:

Saturated solution in NaCl, starting points $S_1S'_1(X_K^1, X_M^1, Y_S^1, Z^1)$, end points $S_2S'_2(X_K^2, X_M^2, Y_S^2, Z^2)$.

According to the lever rule the representative point of the starting mixture (S_1), the solid phase *NC* (point *O*)and the final solution (S_2) lie on a straight line in the salt composition space. A second solid phase appears at the end point S_2; it is located on a face of the NaCl solubility domain, and its composition is determined in two steps:

1) The intersection between the vertical plane OS_1 and the solubility field of NaCl is deduced from the projections of OS_1 and the NaCl solubility field on the base of the representative prism. As shown in Fig. 5, five edges (*hs*, *iv*, *wx*, *pq* and *eb*) are cut by the plane.
2) A projection on the vertical plane (Fig. 6) reveals that the intersection S_2 of the line OS_1 with the solubility field of NaCl is located between *sh* and *iv*. It corresponds to a double saturation in halite (NaCl) and astrakanite (*NMS4*) and its coordinates are given by the intersect of OS_1 and *sh-iv*.

Step 3:

Precipitation of *NC* and *NMS4*: starting point $S_2S'_2(X_K^2, X_M^2, Y_S^2, Z^2)$, end point $S_3S'_3(X_K^3, X_M^3, Y_S^3, Z^3)$.

During cocrystallization of halite and astrakanite, the end points S_3, S'_3 and the representative point of saturated solution move along the intersect between the limiting face of the solubility field of *NC* (face *ihstuv*) and the plane defined by S_2, the solid phase *NC*, and the representative point of astrakanite *AK* (Fig. 7). The end point S_3 is located on an edge of the diagram, and the calculation shows that it is a point of the line *uv*. The third salt observed by evaporation of the brine is *KMS4* (leonite).

Step 4:

Coprecipitation of *NC*, *NMS4* and *KMS4*; starting point $S_3S'_3(X_K^3, X_M^3, Y_S^3, Z^3)$, end points $S_4, S'_4(X_K^4, X_M^4, Y_S^4, Z^4)$

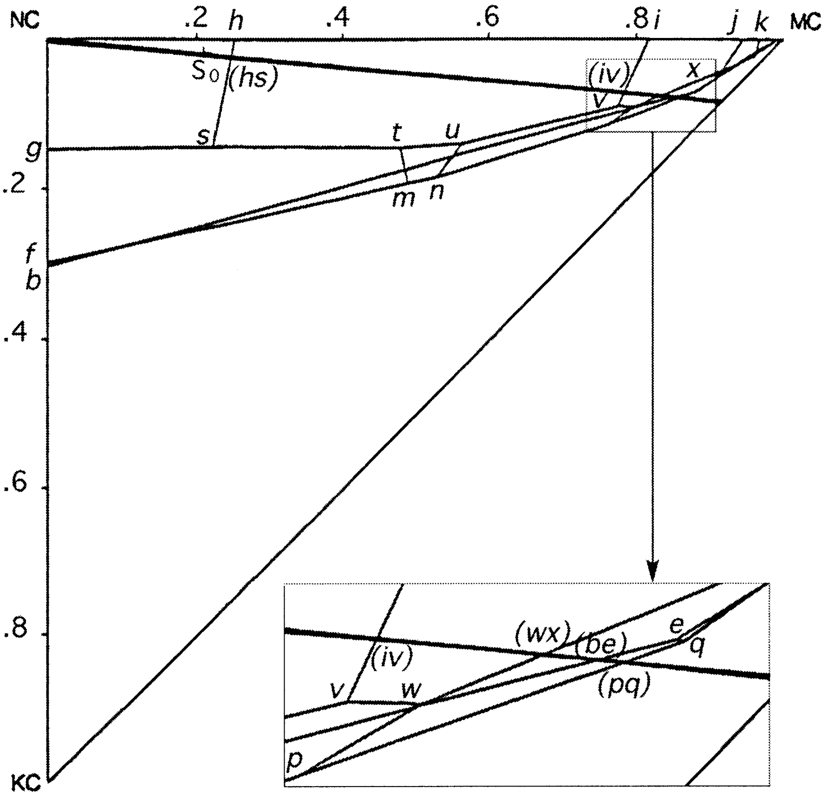

Fig. 5. Intersection of the solubility field of NaCl with the vertical plane of the brine; projection on the base of the reference prism

The representative point of the saturated solution moves along the edge *uv* until a new solid phase appears (point S_4) at an apex of the phase diagram. The fourth observed salt during evaporation of the brine is MS_7 (epsomite). S_3 is close to *v*; thus, the coprecipitation range of *NC*, *NMS4*, and *KMS4* is very short.

The representative point of the saturated solution is merged with *v*. According to the phase rule, the variance of the system is zero, and a phase (*KMS4*) must disappear during the precipitation of epsomite.

Following steps

The path through the diagram (Fig. 8a) follows the edges and apices limiting the solubility field of NaCl until disappearance of free water.

Mass balance

The start and end compositions of each step have been calculated using the phase diagram. The mass balance is deduced from the set of Eqs. (3). The quantities n_i^α and n_h^α of precipitated ion i and of evaporated water during the step α are given by.

$$X_i = \frac{z_i(N_i^{\alpha-1} - n_i^{\alpha})}{D^{\alpha-1} - \sum_i z_i n_i^{\alpha}} \quad Y_i^{\alpha} = \frac{z_{ji}(N_{ji}^{\alpha-1} - n_j^{\alpha})}{D^{\alpha-1} - \sum_i z_i n_i^{\alpha}} \quad Z_{iH}^{\alpha} = \frac{N_H^{\alpha-1} - n_H^{\alpha}}{D^{\alpha-1} - \sum_i z_i n_i^{\alpha}} \qquad (3)$$

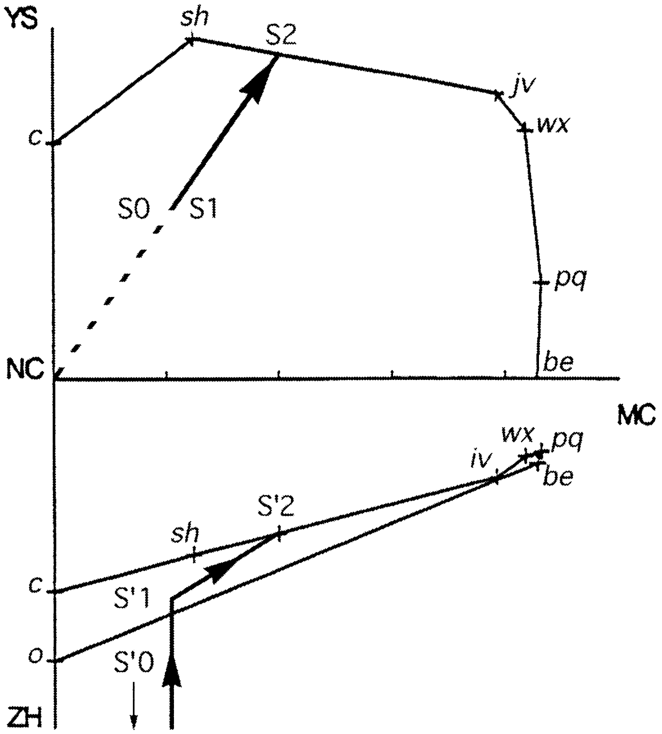

Fig. 6. Intersection of the solubility field of NaCl with the vertical plane of the brine, vertical section

As already mentioned, the amount of water evaporated during the first step of the sequence cannot be calculated graphically. For example, the relative quantities of sodium chloride and water remaining in the solution at the end of step 2 are given by

$$\frac{N_N^2}{N_N^0} = \frac{X_N^2(1 - X_N^0)}{X_N^0(1 - X_N^2)} \qquad \frac{N_H^2}{N_H^0} = \frac{Z_H^2(1 - X_N^2)}{Z_H^0(1 - X_N^0)} \tag{4}$$

The amount of precipitated NaCl is $n_N^2 = N_N^0 - N_N^2$, the amount of evaporated water is $n_H^2 = N_H^0 - N_H^2$; the balance of the evaporation process is presented in Table 2.

b) Simulation of natural brine

A simulation of natural evaporation is obtained if we suppose that there is no interaction between saturated solution and the solid precipitate. A comparison with the above calculations shows that steps 1–3 are identical. The fourth step will involve a coprecipitation of halite and epsomite, and the crystallization path is obtained by intersecting the plane NaCl – *MS7* – *S3* with the face *ivwxj* of the crystallization field of NaCl. The crystallization sequence is presented in Table 3 and Fig. 8b. At the end of step 7 the content of sodium chloride is very small. The representative point of the mixture leaves the solubility field of NaCl. The balance of the evaporation process is also given in Table 3.

A comparison between experience and calculation shows that the same sequence is found for Sebkhat El Adhibat, but the experimental determination

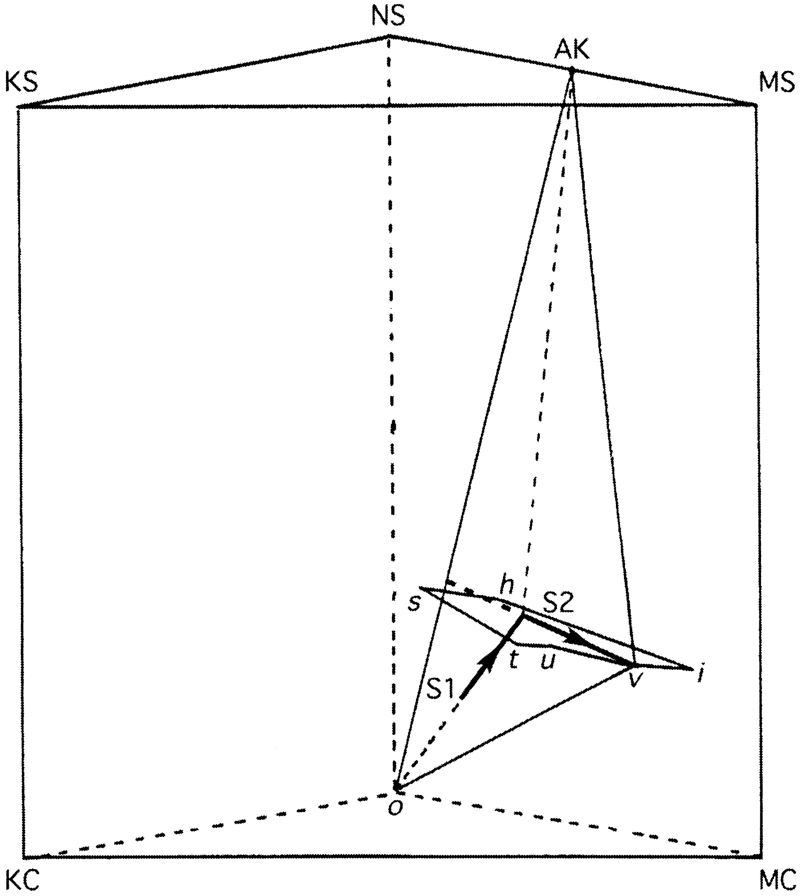

Fig. 7. Brine from Sebkhat El Adhibat, third step of evaporation; intersection of the solubility field of NaCl with the plane NC-Ak-S2

could not be carried out beyond the precipitation of hexahydrite, and experimental determination of the mass balance was not possible. In the case of concentrated Black Sea brine, experimental determination of the sequence shows that metastable or non-equilibrium states are observed, and epsomite precipitates instead of astrakanite.

Comparison of brines of various origin

The first and second step of the crystallization sequence, calculated for various brines (Tunisian Chotts and Sebkhats, Black Sea, Dead Sea) are presented in Fig.9. According to the origin of the brine, the second solid phase differs (astrakanite with Sebkhat El Adhibat and Black Sea, sylvite with Chott El Djerid, käinite for Sebkhat El Melah, carnallite with Dead Sea) A simple glimpse to the diagram shows that

- The theoretical behavior of concentrated Black Sea Water is similar to that of brine from Sebkhat El Adhibat.

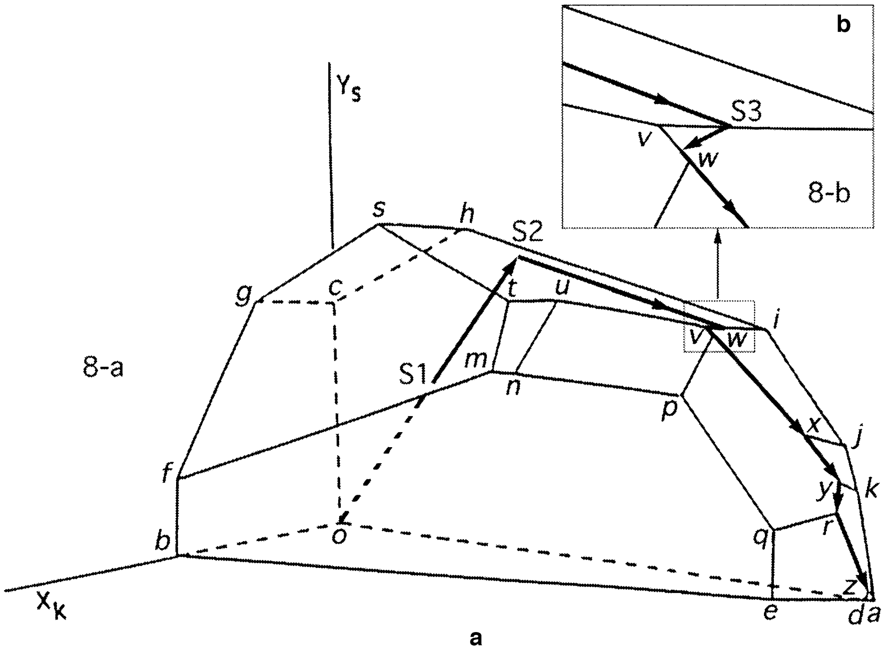

Fig. 8. Brine from Sebkhat El Adhibat, crystallization sequence; a: stirred sample, b: natural evaporation

Table 2. Mass balance of the crystallization sequence of a stirred brine from Sebkhat El Adhibat; S_0 (initial conditions): $XK = 0.0186$, $XM = 0.2091$, $YS = 0.2783$, $Z = 10.16$, dilute solution; S_1: $XK = 0.0186$, $XM = 0.2091$, $YS = 0.2783$, $Z < 8.0682$

	Evaporated water	Precipitated salts (mole) for $D = 100$ mol								
		NC	*NMS4*	*MS7*	*KMS4*	*SCMS3*	*MS6*	*MS1*	*KMC6*	*MC6*
S2	635.91	47.40								
S3	239.16	28.40	2.35							
S4	0.89	0.20	−0.78	0.19						
S5	20.40	5.54	−2.27	4.79	0.33					
S6	4.37	0.39		0.05	0.03					
S7	6.58	0.14		0.04	−0.36	0.83				
S8	18.74	0.93		0.08		0.68				
S9	5.14	0.00		−5.14		0.00	5.14			
S10	7.45	0.21				0.19	0.03			
S11	25.83	0.00				0.00	−5.17	5.17		
S12	1.84	−0.05				0.00		0.12		
S13	14.6	0.10				−1.70		1.86	1.79	
S14	3.82	0.06						0.11	0.06	
S15	4.90	0.02						0.01	0.01	1.32

Table 3. Mass balance of the crystallization sequence of brine from Sebkhat El Adhibat (simulation of natural evaporation); S_0 (initial conditions): $XK = 0.0186$, $XM = 0.2091$, $YS = 0.2783$, $Z = 10.16$, dilute solution; S_1: $XK = 0.0186$, $XM = 0.2091$, $YS = 0.2783$, $Z < 8.0682$

	Evaporated water	Precipitated salts (mol) for $D = 100$ mol					
		NC	NMS4	MS7	KMS4	KCMS3	MS6
S2	635.91	47.40					
S3	239.16	28.40	2.35				
S4	2.21	0.20	0.00	0.047			
S5	2.39	0.08		0.23	0.03		
S6	36.75	2.00		0.19		1.20	
S7	12.54	0.36				0.32	0.04
S8	The representative point is no longer in the solubility field on *NC*						

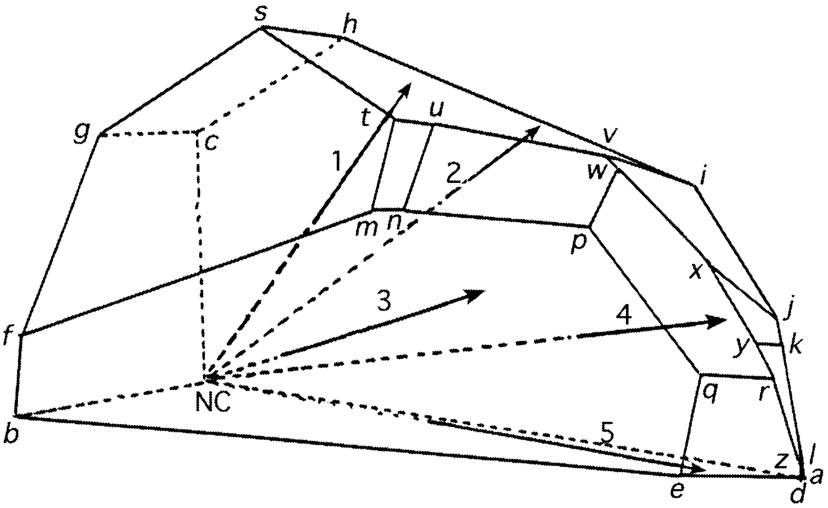

Fig. 9. Comparison of brines of various origin; 1: Sebkhat El Adhibat, 2: Black Sea, 3: Chott El Djerid, 4: Sebkhat El Melah, 5: Dead Sea

- The Sebkhat El Melah brine is rich in magnesium, and its second observed solid phase is sylvite. This brine seems quite suitable for the recovery of magnesium from bitterns.
- Water from Chott El Djerid is rich in potassium, and its second observed solid phase is käinite, making it convenient for the recovery of potassium from bitterns.
- The Dead Sea brine is very poor in sulfate; its second solid phase is carnallite.

Influence of sulfate on the yield of sodium chloride

As shown in Fig. 10 for brine of Sebkhat El Adhibat, the yield of pure NaCl can be correlated to the initial sulfate content of brine and increases by more than 30% when the sulfate composition Y_S decreases from 14.5 to 6.5%.

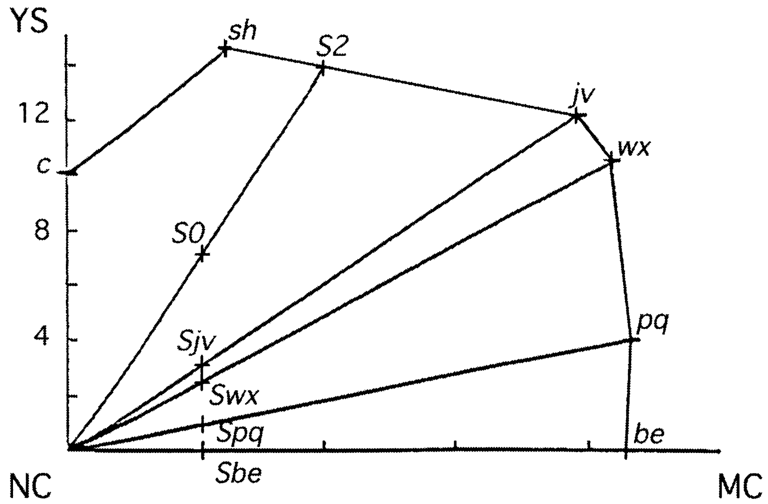

Fig. 10. Influence of sulfate content on the yield of NaCl

Comparison between calculation and experience

The crystallization sequence was compared to experimental determinations performed with brine from Sebkhat El Adhibat under various conditions (natural evaporation in pilot pools, laboratory investigation at constant temperature (25°C) with and without stirring) and concentrated Black Sea water. The same sequence was found for both brines under laboratory conditions, but the experimental determination could not be carried out beyond the precipitation of hexahydrite, and experimental determination of the mass balance was not possible. Without stirring, epsomite is observed instead of astrakanite. The calculation also gives the same sequence, but experience shows that no or metastable equilibria are observed with Black Sea water, and epsomite precipitates as second solid phase instead of astrakanite [7].

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