

## Parasitic Crystalline Occlusions in Solar Salt

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### ABSTRACT

*Study of the metastable equilibria at different temperatures from 15°C to 55°C makes it possible, for a specified composition of sea-water, to establish the solubility of the compound (or compounds) which may crystallize at the same time as sodium chloride, either in the form of independent crystals or in the form of occlusions. From this one can deduce what rules should be applied (factors of concentration, temperature) in order to control salt crystallization precisely and to avoid parasitic occlusions.*

*Solar salts may contain large quantities of magnesium, even after complete washing and centrifuging. Analysis by polarised light clearly displays the presence of other crystals within the salt which differ greatly from those of calcium sulphate (gypsum, hemihydrate or anhydrite).*

### RESEARCH BASED ON THE QUINARY SYSTEM DIAGRAM AT 25°C.

In brine saturated with NaCl (solar) reciprocal proportions of  $Mg^{++}$ ,  $K^+$  and  $SO_4^{--}$  remain constant during evaporation as long as no precipitation of compounds containing  $Mg^{++}$ ,  $K^+$  and/or  $SO_4^{--}$  occurs. The triangular diagrams (Fig 1) show the reciprocal solubility, at 25°C, for different salts according to the system ( $Na^+K^+Mg^{++}$ ) ( $Cl^-SO_4^{--}H_2O$ ). The diagram presents the crystalline conditions of magnesium and potash compounds developing from brine saturated with NaCl. Table I and II show the crystallization limits of different compounds which could precipitate according to the molecular concentration of  $Mg^{++}$ ,  $SO_4^{--}$ ,  $K^+$  for 100 moles of these compounds. The tables also indicate composition at specific points on the diagram (Fig 1).

Reciprocal proportions of  $Mg^{++}$ ,  $K^+$  and  $SO_4^{--}$  are constant and depend only of the type of sea-water used. If brine is taken with the following composition:

sp. gravity	= 1.263
$Cl^-$	= 186 g/l
MgO	= 79.4 g/l
$SO_3$	= 52.4 g/l
CaO	= 0.114 g/l
KCl	= 25.4 g/l
$MgCl_2 \cdot 6H_2O$	= 270 g/l
$MgSO_4 \cdot 7H_2O$	= 161 g/l

Weight of crystallized salt: 592 g/l

Weight of water in g/l: 671 g/l

The representative plot of this brine is indicated on Figure 1 by SW, corresponding to a temperature of 25°C. In order to avoid parasitic crystallization, the quantity of water in this brine must be greater than that which corresponds to the composition of the various plots located on the line limiting the involved area.

From this one notes that:

1. Brine from salt works contain relatively high quantities of potash and magnesium. These brines are plotted in the upper portion of the Figure 1. Thus it is evident that different compounds are susceptible to crystallization, (for example bloedite, leonite, kainite, epsomite and even picromerite).

2. The mother brine saturated with NaCl can be defined by the reciprocal proportions of Mg,  $SO_4$  and K, which in turn determine the limits of the possible parasitic crystallization range.

3. If plot of point SW represents the composition of a mother brine from the Mediterranean Sea at 25°C, then this plot will be found within the crystallization limits of bloedite. But because this range will change according to temperature, SW will be then situated within the zone 1 2 3 5 and J, which fact accounts for the generation of different compounds. It is possible to determine the quan-

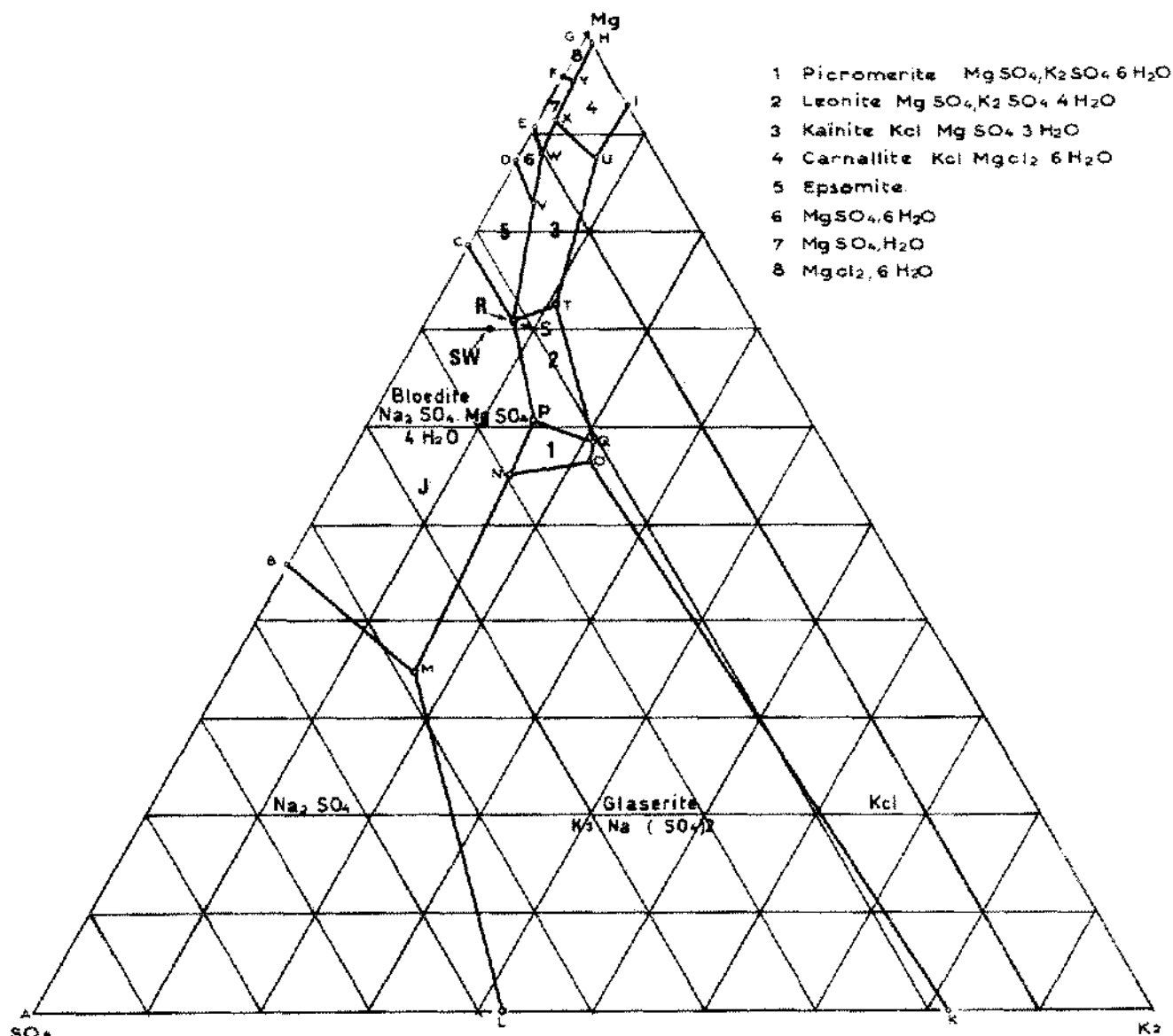


Figure 1. Triangular diagram showing the system  $(\text{Na}^+ \text{Mg}^{++}) (\text{Cl}^- \text{SO}_4^{--}) \text{H}_2\text{O}$  at  $25^\circ\text{C}$ .

TABLE I

System:  $(\text{Na}^+, \text{K}^+, \text{Mg}^{++}) (\text{Cl}^-, \text{SO}_4^{--}) \text{H}_2\text{O}$  at  $25^\circ\text{C}$

Solid phases in addition to NaCl	Liquid Phase — M per 1000 M $\text{H}_2\text{O}$				
	NaCl	KCL	$1/2\text{MgCl}_2$	$1/2\text{MgSO}_4$	$1/2\text{Na}_2\text{SO}_4$
A. $\text{Na}_2\text{SO}_4$	101.0				24.9
B. $\text{Na}_2\text{SO}_4$ + Bloédite	92.6			33.4	6.4
C. Bloédite + $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	34.6		91.8	34.6	
D. $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ + $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$	8.4		135.0	24.0	
E. $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$ + $\text{MgSO}_4 \cdot \text{H}_2\text{O}$	5.0		158.0	19.0	
F. $\text{MgSO}_4 \cdot \text{H}_2\text{O}$ + $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$	1.8		203.8	10.2	
G. $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$	2.0		212.0		
H. $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ + Carnallite	2.0	1.0	210.0		
I. Carnallite + KCl	4.0	11.0	141.0		
J. KCl	89.0	39.0			
K. KCl + Glasérite	88.0	40.0			9.0

TABLE I (Continued)

Solid phases in addition to NaCl	NaCl	KCl	Liquid Phase — M per 1000 M H <sub>2</sub> O		
			1/2MgCl <sub>2</sub>	1/2MgSO <sub>4</sub>	1/2Na <sub>2</sub> SO <sub>4</sub>
L. Glasérite + Na <sub>2</sub> SO <sub>4</sub>	88.0	21.0			29.0
M. Glasérite + Bloédite + Na <sub>2</sub> SO <sub>4</sub>	84.0	16.0		32.0	12.0
N. Glasérite + Picromérite + Bloédite	55.0	21.0	33.0	37.0	
O. Glasérite + KCl + Picromérite	46.0	28.0	43.0	28.0	
P. Bloédite + Picromérite + Léonite	44.0	21.0	46.0	38.0	
Q. Picromérite + Léonite + KCl	39.0	29.0	51.0	29.0	
R. Bloédite + Léonite + MgSO <sub>4</sub> · 7 H <sub>2</sub> O	21.0	15.0	84.0	38.0	
S. MgSO <sub>4</sub> · 7 H <sub>2</sub> O + Léonite + Kaïnite	18.0	15.0	90.0	39.0	
T. Léonite + KCl + Kaïnite	19.0	19.0	94.0	29.0	
U. Kaïnite + KCl + Carnallite	5.0	12.0	136.0	10.0	
V. MgSO <sub>4</sub> · 7 H <sub>2</sub> O + MgSO <sub>4</sub> · 6 H <sub>2</sub> O + Kaïnite	7.0	8.0	131.0	26.0	
W. MgSO <sub>4</sub> · 6 H <sub>2</sub> O + MgSO <sub>4</sub> · H <sub>2</sub> O + Kaïnite	3.0	4.0	154.0	20.0	
X. MgSO <sub>4</sub> · H <sub>2</sub> O + Kaïnite + Carnallite	2.0	2.0	171.0	16.0	
Y. MgSO <sub>4</sub> · H <sub>2</sub> O + Carnallite + MgCl <sub>2</sub> · 6 H <sub>2</sub> O	2.0	1.0	200.0	10.0	

Bloédite = Na<sub>2</sub>SO<sub>4</sub> · MgSO<sub>4</sub> · 4 H<sub>2</sub>O      Picromérite = MgSO<sub>4</sub> · K<sub>2</sub>SO<sub>4</sub> · 6 H<sub>2</sub>O  
 Glasérite = K<sub>3</sub>Na (SO<sub>4</sub>)<sub>2</sub>      Léonite = MgSO<sub>4</sub> · K<sub>2</sub>SO<sub>4</sub> · 4 H<sub>2</sub>O  
 Kaïnite = KCl · MgSO<sub>4</sub> · 3 H<sub>2</sub>O      Carnallite = KCl · MgCl<sub>2</sub> · 6 H<sub>2</sub>O

TABLE II

Calculation of the quantity of water contained in the brine representing different specific points on Figure 1 for 100 moles of the sum SO<sub>4</sub> + K + Mg

Specific Points	Moles				Solid Phases
	H <sub>2</sub> O	K	SO <sub>4</sub> (1/2 SO <sub>4</sub> )	Mg (1/2 Mg)	
A.	4.011,62		100		Na <sub>2</sub> SO <sub>4</sub>
B.	1.368,30		54,37	45,63	Na <sub>2</sub> SO <sub>4</sub> bloédite
C.	621		21,41	78,51	bloédite + MgSO <sub>4</sub> 7H <sub>2</sub> O
D.	285,56		13,10	86,89	MgSO <sub>4</sub> 7H <sub>2</sub> O + MgSO <sub>4</sub> 6H <sub>2</sub> O
E.	510,69		9,69	90,31	MgSO <sub>4</sub> 6H <sub>2</sub> O + MgSO <sub>4</sub> H <sub>2</sub> O
F.	446,44		4,55	95,45	MgSO <sub>4</sub> H <sub>2</sub> O + MgCl <sub>2</sub> 6H <sub>2</sub> O
G.	471,54			100	MgCl <sub>2</sub> 6H <sub>2</sub> O
H.	473,76	0,47		59,53	MgCl <sub>2</sub> 6H <sub>2</sub> O + canallite
I.	657,44	7,24		92,76	Canallite + KCl
J.	2.561,64	100			KCl
K.	2.038,83	81,63	18,37		KCl + glaserite
L.	2.001,66	42	58		glaserite + Na <sub>2</sub> SO <sub>4</sub>
M.	1.088,41	17,39	47,63	34,78	glaserite + bloédite + Na <sub>2</sub> SO <sub>4</sub>
N.	781,85	16,41	28,91	54,69	glaserite + bloédite + picromérite
O.	787,33	22,05	22,05	55,91	glaserite + KCl + picromérite
P.	699,06	14,69	26,57	58,74	bloédite + picromérite + léonite
Q.	725	21,01	21,01	57,97	picromérite + léonite + KCl
R.	570,69	8,57	21,71	69,71	bloédite + léonite + MgSO <sub>4</sub> 7H <sub>2</sub> O
S.	545,80	8,20	21,31	70,49	MgSO <sub>4</sub> 7H <sub>2</sub> O + léonite + kaïnite
T.	584,84	11,11	16,96	71,93	léonite + KCl + kaïnite
U.	596,21	7,14	5,95	86,90	kaïnite + KCl + canallite
V.	523,31	4,19	13,61	82,20	MgSO <sub>4</sub> 7H <sub>2</sub> O + MgSO <sub>4</sub> 6H <sub>2</sub> O + kaïnite
W.	505,49	2,02	10,10	87,88	MgSO <sub>4</sub> 6H <sub>2</sub> O + MgSO <sub>4</sub> H <sub>2</sub> O + kaïnite
X.	487,98	0,98	7,80	91,22	MgSO <sub>4</sub> H <sub>2</sub> O + kaïnite + canallite
Y.	452,31	0,45	4,52	95,02	MgSO <sub>4</sub> H <sub>2</sub> O + canallite + MgCl <sub>2</sub> 6H <sub>2</sub> O

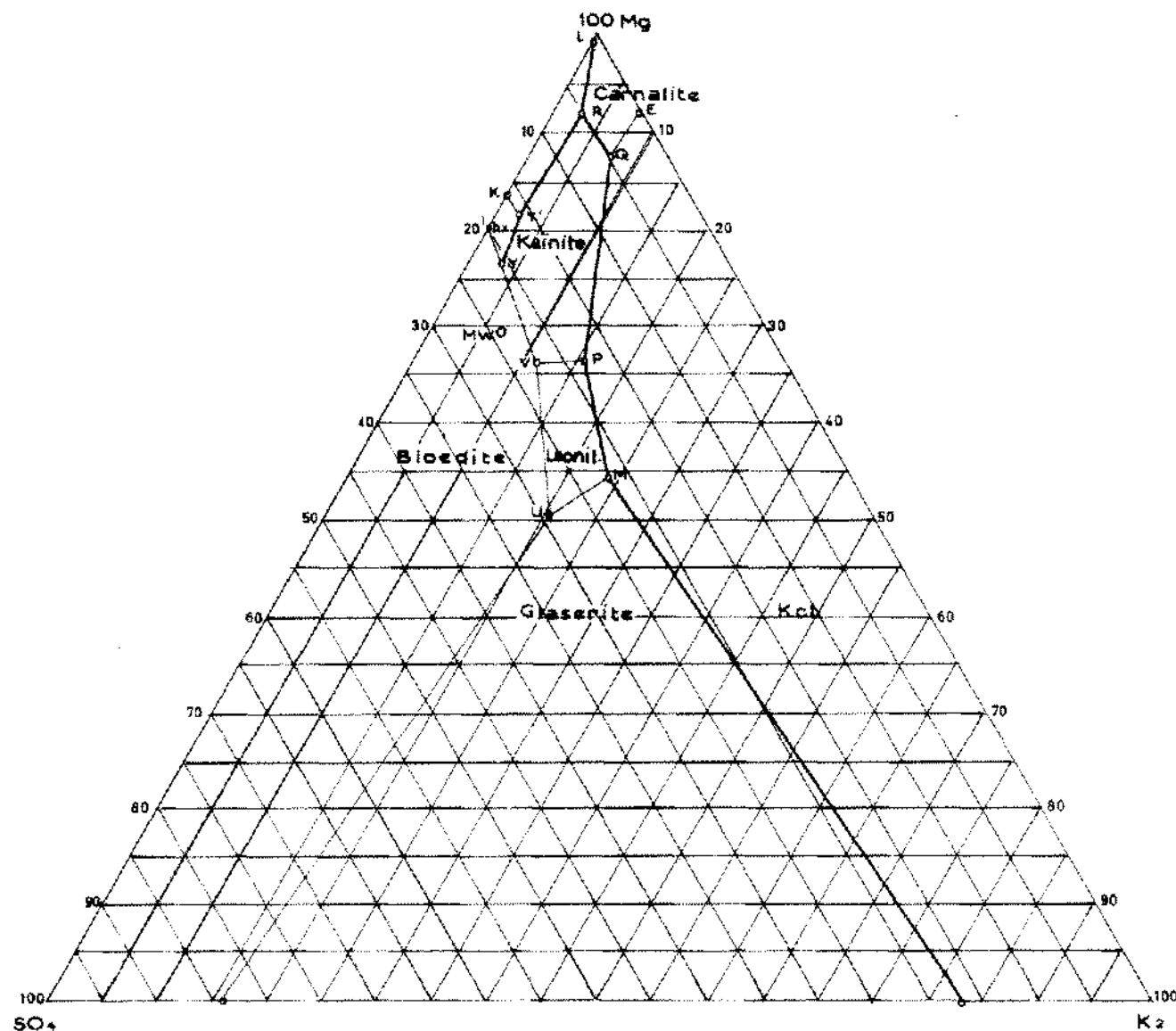


Figure 2. Triangular diagram showing the system  $[\text{Na}^+ \text{Mg}^{++} \text{K}^+] [\text{Cl}^- \text{SO}_4^{--}] \text{H}_2\text{O}$  at  $35^\circ\text{C}$ .

ties of water corresponding to different invariable borders at a given temperature. These quantities of water correspond to the limit of concentration of  $\text{Mg}^{++}$ ,  $\text{K}^+$  and  $\text{SO}_4^{--}$  which must not be exceeded. For example, in order to avoid parasitic crystallization, the quantity of water at plot SW must be greater than that represented by P, i.e. 700 moles of water for 100 moles of  $\Sigma (\frac{1}{2} \text{Mg} + \frac{1}{2} \text{SO}_4 + \text{K})$ . For a brine with sp.gr.=1.263, which contains 25.27 moles of  $\Sigma (\frac{1}{2} \text{Mg} + \frac{1}{2} \text{SO}_4 + \text{K})$  for 1000 moles of water, the quantity of water must be greater than

$$\frac{700 \times 25.27}{100} = 176.89 \text{ moles}$$

Note that if one takes point R into consideration, one obtains 144 moles of water.

The evaporation process can then proceed. This presupposes that the temperature is maintained at  $25^\circ\text{C}$  and that the composition of the brine does not exceed in Mg, K,  $\text{SO}_4$ , the ionic characteristics of a brine at point R.

### MICROSCOPIC ANALYSIS OF CRYSTALS

Microscopic analysis of sea salt crystals from Tunisia and Ethiopia demonstrates the presence of compounds which show the form of calcium sulphate crystals, gypsum, hemihydrate or anhydrite (Fig 3). Other occluded crystals take the form of either thick plates, solid grains or short prisms, (Fig 4 and 5—bloedite). These correspond to the characteristics of double sulphate of magnesium or sodium or potassium sulphates. The parasitic crystals of Tunisian salt seem to be made of bloedite. A more precise

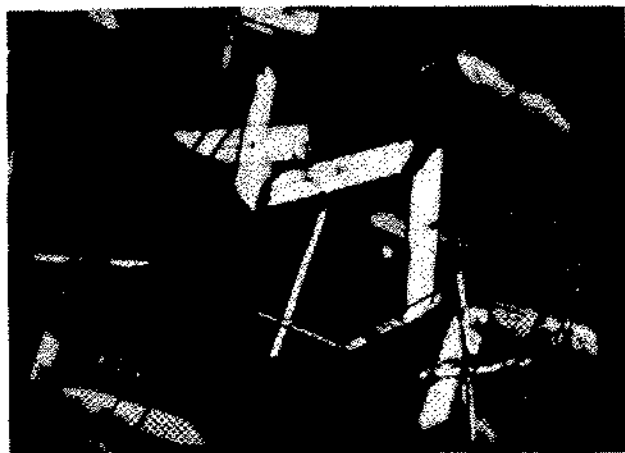


Figure 3. Tunisian salt. Calcium sulfate crystals (gypsum).



Figure 5. Tunisian salt. Crystalline occlusions of bloedite.



Figure 4. Crystalline occlusions of bloedite.

definition of the compound can be made by X-ray inspection.

Other microscopic analysis shows that deposits of magnesium sulphate crystals are on the surface of crystals of sodium chloride and that they are quite different from bloedite or calcium sulphate (Fig 6, 7).

### CONCLUSION

1. Brine saturated with NaCl by solar evaporation can be defined by reciprocal proportions of  $Mg^{++}$ ,  $K^+$  and  $SO_4^{--}$ , when these last remain during evaporation, and when no precipitation of compounds containing  $Mg^{++}$ ,  $K^+$ ,  $SO_4^{--}$  occurs. The triangular diagrams (Fig. 1, 2) define the crystallization zones of different compounds according to the temperature. At a given temperature and depending on amount of water contained in the saturated brine, the compound which will crystallize simultaneously with the salt can be defined.

It is always possible to know and to modify the compo-

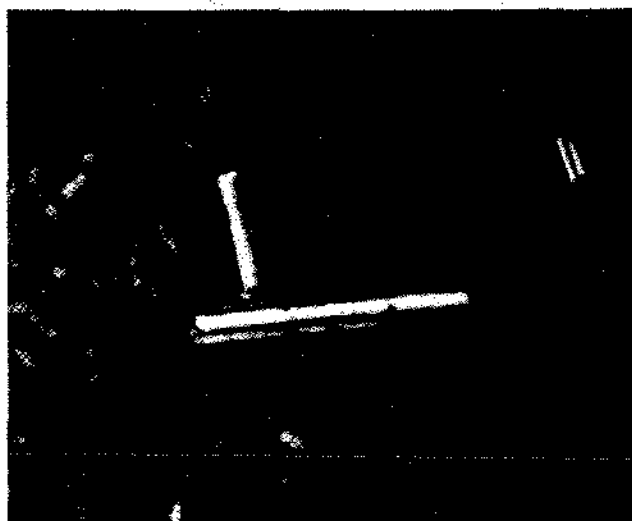


Figure 6. Crystals of  $MgSO_4 \cdot 7H_2O$  on the surface of NaCl crystals.



Figure 7. Crystals of  $MgSO_4 \cdot 7H_2O$ .

sition of the brine. But that is not possible regarding temperature and evaporation. Analysis of the triangular diagrams at 25°C and 35°C, (Fig 1, 2) demonstrates that the crystallization limits of different compounds are modified according to the temperature. Between 25 and 35°C, a brine with a specific gravity of 1.263 remains within the crystallization range of bloedite, but the quantities of water available for evaporation in order to avoid precipitation are very different. At 0°C, the plot representing this same brine is within the mirabilite range  $\text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O}$ , and the corresponding quantity which must be evaporated before crystallization is much smaller. Granted that the temperature of a brine of a higher specific gravity than 1.263 can vary between 10° and 40°C, the risk of parasitic

crystallization obviously appears. Moreover, it must also be pointed out that certain compounds have a negative solubility coefficient, and others a positive one, such that precipitation can occur either as a result of heating or cooling.

2. Triangular diagrams constructed for different temperatures (from 0° to 50°C, for example) and the corresponding tables can be used to calculate the limits of  $\text{SO}_4$ , K and Mg concentrations beyond which parasitic crystallization would occur. In this way, it is possible to modify the composition of the brine by the control of both inlet and outlet volumes in order to produce NaCl with the least quantity of occluded impurities.