Experimental Study Covering Production of Secondary Salts Extracted from Bitterns of Solar Salt Works

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ABSTRACT

Balard, the chemist who discovered bromine in the bitterns of the saltworks on the Mediterranean coast, led up to the extraction of secondary salts in our saltworks. Ever since that time, our Salin-de-Giraud plant has made use of the many possibilities of extraction of these salts compatible with the local climate. Depending on the technical and economical condition, we were brought to produce different combinations of salts.

D'Ans and Borchert's solubility diagrams for saturated solutions of sodium chloride constitute the main base of studies for the production of these salts. Precise examples show the results obtained. The obtention of epsomite, $MgSO_4 \cdot 7H_2O$, by precipitation in winter, starting from a brine with a well defined concentration, is explained. Also the study of a pilot plant, in a sub-tropical, semi-arid climate, has proved that at precisely fined temperatures and for specific concentration values it was possible to produce double potassium and magnesium salts and particularly kainite.

In conclusion, it is demonstrated that the possibilities of recuperation of salts from the bitterns of the saltworks are important and varied but that they depend on the climatological conditions of the production site.

INTRODUCTION

In the solar saltworks used to produce salt from seawater, salt is deposited on cristallizers. The bitterns which concentrate on these crystallizers must be discharged once a given density, generally 29 ant 30°B, is attained. If the concentration is continued by evaporation, these bitterns will deposit magnesium and potassium salts.

Research work made by d' Ans and Borchert has shown that changes in liquid temperature, at same ion concentration rates, changes crystallization. In practice, solar saltworks bitterns never reach a temperature beyond 50°C and they generally remain betwen 18° and 35°C.

The purpose of our tests was to compare the results recorded with bitterns from solar saltworks with the graphs plotted by d'Ans and Borchert and to set up the practical possibilities of producing certain salts from these bitterns.

BITTERNS CONCENTRATION CHART

We have built a square concrete basin, 1.5 m on the side, i.e. 2.25 m^2 in cross section, and of an approximate depth of 1 m. This basin has been filled with bitterns taken from the crystallizers, up to an approximate height of 0.60 m, measurement having been made accurately. Bitterns have been analyzed and density has been measured with precision and corrected according to temperature. We allowed evaporation to occur and every time the specific mass varied by 0.005 the following steps were carried out.

1. Accurate measurement was made of the corrected density "d" and as was analysis of bitterns.
2. Harvest of the salt deposited in the basin by means of a scraper, draining above the basin and measurement of the total weight of wet salt (P, kg).

3. Centrifugal drying down to 3% of 1 kg of this salt. Weight of the collected bitterns measured (p_1, kg).
4. Weight of brine for P kg of wet salt measured ($p_1 \cdot P$ kg).
5. Salt weight after centrifuging determined [$P(1 - p_1)$ kg].
6. Brine weight in the salt after centrifuging determined [$0.03\ P\ (1 - p_1)$ kg].
7. Brine weight removed by the samplings taken from the basin (p_2, kg).
8. Total brine weight removed from the basin [$p_{P1} + 0.03\ P\ (1 - P_1) + P_2$kg].
9. Total brine volume taken from the basin determined by:

$$V = \frac{P_{P1} + 0.03\ P\ (1 - P_1) + p_2}{d} dm^3$$

10. Drop of basin level due to brine which has been removed measured

$$\Delta h = \frac{V \times 100}{225} mm$$

11. Initial basin level measured h_0 mm.
12. Basin level after harvesting measured h_1 mm.
13. Basin level, as corrected for brine removal calculated $h_1 + \Delta h$ mm.
14. Level drop between two harvesting operations, due to evaporation calculated $h_0 - (h_1 + \Delta h)$ mm.
15. Evaporation on fresh water between two harvesting operations (measured with an evaporimeter) E mm.
16. Evaporation rate during the period considered

$$\alpha = \frac{h_0 - (h_1 + \Delta h)}{E}$$

17. Complete analysis made of the precipitated salt.
18. Maximum and minimum daily temperatures are recorded between two harvesting operations.

These experiments have been carried out three times. The duration of each experiment ranged between 6 months and 10 months. The average representative curves have been plotted, corresponding to ion content changes (SO_4^{--}, Mg^{++}, K^+, Cl^- ions) according to brine volume reduction (Fig. 1). We have also plotted a representative curve of the change in evaporation ration "α" (Fig. 2), where the $MgCl_2$ content is in abscissa.

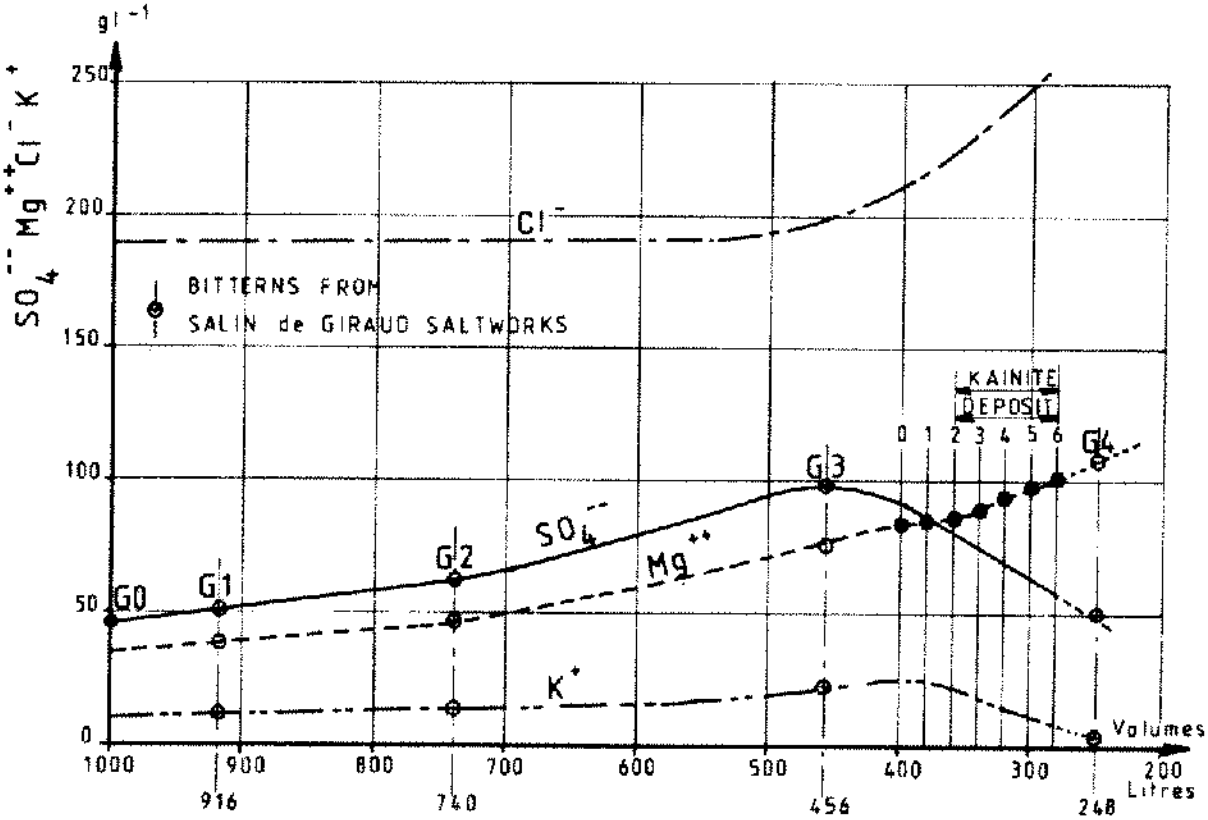

Figure 1. Composition and volumes of the bitterns during their concentration.

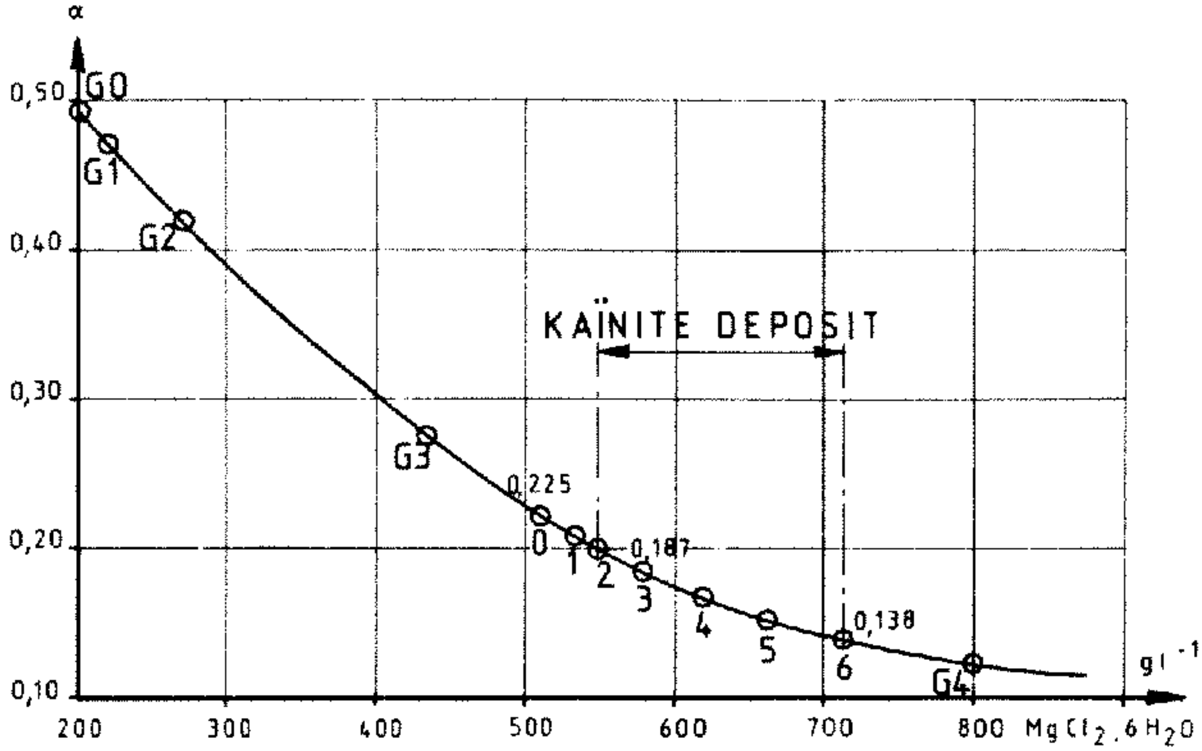

Figure 2. Brine evaporation ratio. Average curve of the three tests.

Analyses of crystallized salt have shown that kaïnite settles between certain given values. We have shown plots 0 to 6 on the concentration graph, points "0" and "6" limiting these salt deposits.

Temperatures ranged between 28°C and 35°C during these experiments. $MgSO_4$ and $MgCl_2$ solubilities vary considerably with temperature and increase with it. It has been noted that the maximum SO_4^{--} content might be slightly shifted. This explains the slight changes in $MgSO_4$ content of the crystallized salts.

Also shown on Figure 1 is the compositions of the bitterns from the Salin de Giraud, itemized as G_0, G_1, G_2, G_3, G_4 (Table 1 and 2) average statistical values recorded over a period of 50 years). It can be seen that they are found actually on the curves of Graph 1.

TABLE 1

Average Statistical Values of the Bitterns in Salin de Giraud

Brine Designation	Mg^{++} g.l^{-1}	SO_4^{--} g.l^{-1}	K g.l^{-1}
Point G_0	37.0	47.0	10.0
Point G_1	39.63	52.08	11.06
Point G_2	47.89	62.88	13.31
Point G_3	76.60	97.43	21.60
Point G_4	108.57	49.89	4.20

TABLE 2

Average Values of the Evaporation Rate of the Bitterns

Brine Designation	$MgCl_2 6H_2O$ g.l^{-1}	α
G_0 1000 l.	200	0.494
G_1	221	0.469
G_2	270	0.415
G_3	434	0.275
Point 0	511	0.225
Point 1	534	0.211
Point 2	554	0.199
Point 3	578	0.187
Point 4	618	0.170
Point 5	662	0.153
Point 6	714	0.138

SOLUBILITY DIAGRAMS AND CRYSTALLIZATION OBTAINED

Triangular diagram. If we plot on the diagrams (Figs. 3 and 4) corresponding to 25°C and 35°C the values representing the solutions on points 0 to 6 (Table 3), it can be seen that at 25°C there is practically no kaïnite while at 35°C one must be within the crystallization range of this salt.

In fact, the analyses of the salts crystallized in the basin have shown that, due to temperature changes, in the begin-

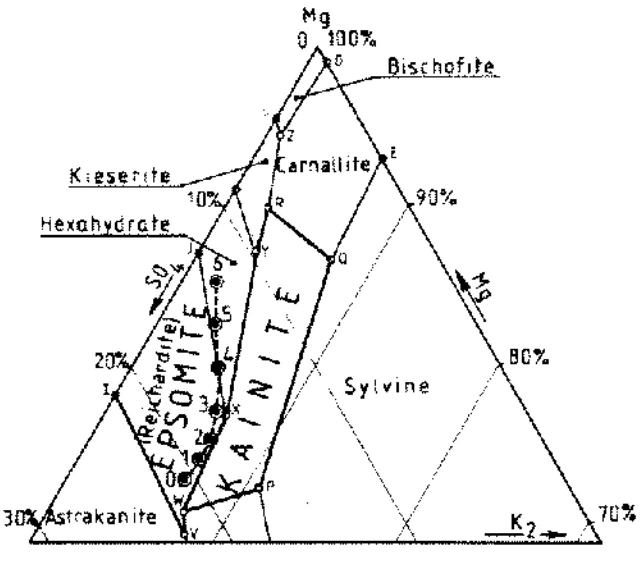

Figure 3. Solubility diagram. Solution stabilized at 25°C. Moles of K_2, Mg, SO_4 for 100 moles.

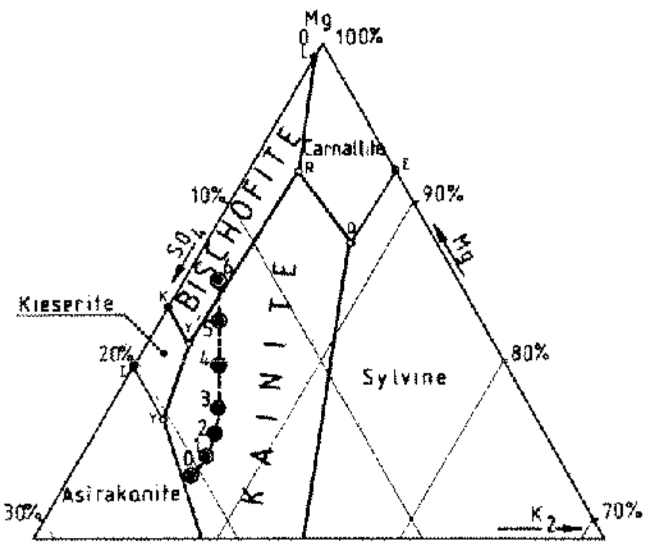

Figure 4. Solubility diagram. Solution stabilized at 35°C. Moles of K_2, Mg, SO_4 for 100 moles.

TABLE 3

Brines Plotted on Blochert's Chart

Brine Designation	Moles SO_4^{--}% Moles	Moles Mg^{++}% Moles	Moles $2K^+$% Moles
Point 0	20.39	73.15	6.46
Point 1	19.10	74.14	6.76
Point 2	17.88	75.38	6.74
Point 3	16.71	77.31	5.98
Point 4	15.48	79.90	4.62
Point 5	14.05	82.77	3.18
Point 6	12.67	85.47	1.86

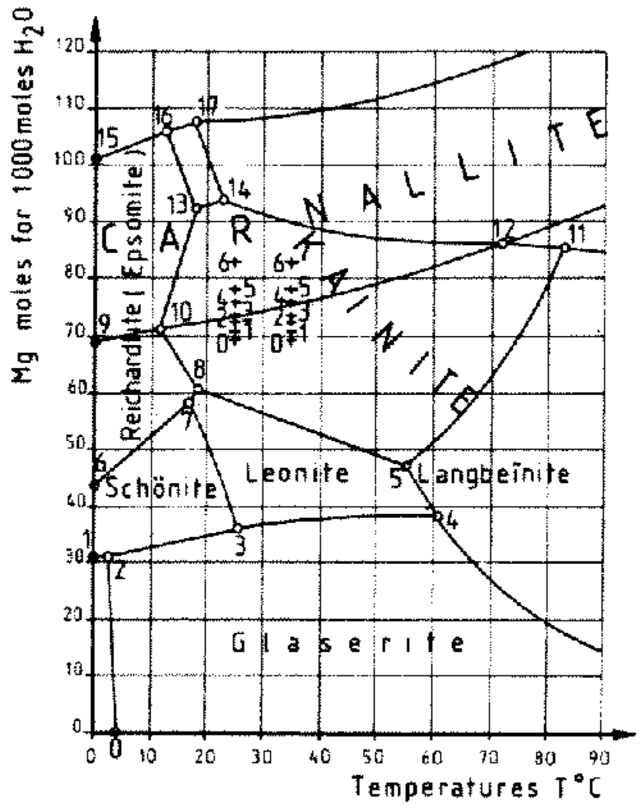

Figure 5. Solubility diagram (d'Ans) for saturated solution in KCl.

ning epsomite alone is deposited, then epsomite and kaïnite, then kaïnite and, finally, kaïnite in company of bischofite and/or carnalite.

Polythermic balance diagram. The diagrams (Figs. 5 and 6) have been established for KCl saturated solutions. The same points 0 to 6 have been plotted (according to Table 4). According to Graph 1, KCl saturation is reached between point 1 and point 2. If the solution were to be cooled below 15°C, epsomite might deposit. Beyond 70°C, lanbeïnite would then be produced. We found here a confirmation of the Borchert's diagrams on nature of the salts which crystallize.

PILOT SOLAR SALT PLANT

We built a pilot solar salt plant using the above data as bases. The plant has been divided up into two parallel rows in order to vary bitterns height, the first one operating with a level of about 0.30 m while the other one with 0.40 m. The area of each row was 14,475 m², divised up as follows: P_1, 1st crystallizer, 6,050 m², P_2, 2nd crystallizer, 4,000 m², P_3, 3rd crystallizer, 3,300 m² and P_4, 4th crystallizer, 1,125 m².

It has, however, been possible to note that bitterns height was not of a critical importance.

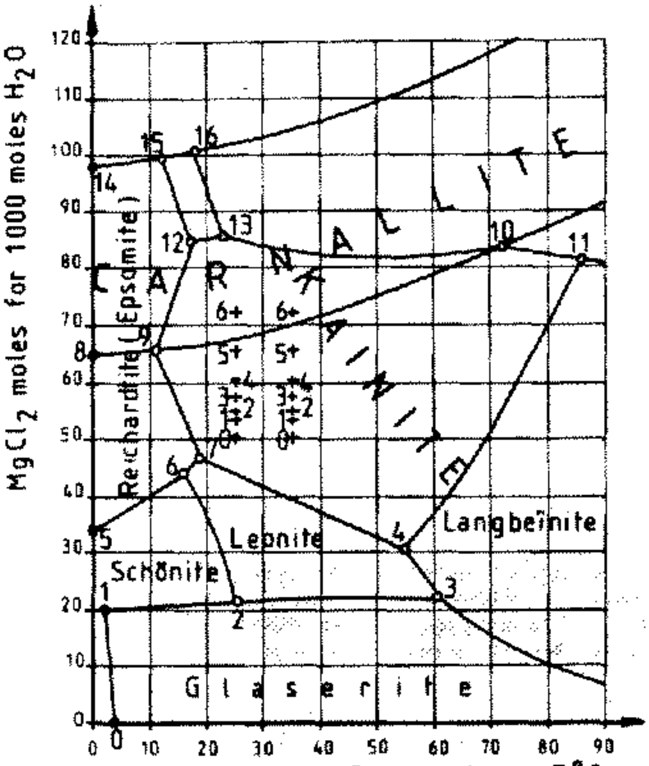

Figure 6. Solubility diagram (d'Ans) for saturated solution in KCl.

TABLE 4

Brines Plotted on d'Ans' Chart

Brine Designation	Mg^{++} Moles for 1000 Moles H_2O	$MgCl_2$ Moles for 1000 Moles H_2O
Point 0	69.80	50.34
Point 1	71.04	52.73
Point 2	71.87	54.81
Point 3	73.10	57.31
Point 4	75.58	60.93
Point 5	78.89	65.49
Point 6	82.60	72.35

We collected kaïnite on P_3 crystallizers (the input of P_3 corresponding to point "2" of the basin-made experiments). The average analysis of the raw product, as harvested, is as follows:

Mg^{++}	8.708%
SO_4^{--}	19.160%
K^+	7.415%
Cl^-	18.827%
Na^+	0.546%
H_2O	45.244%

The brine accompanying this salt harvested from P_3 had the following composition (corresponding to point "6"):

Mg^{++}	100.0 g.l^{-1}
SO_4^{--}	58.3 g.l^{-1}
K^+	7.3 g.l^{-1}
Cl^-	259.0 g.l^{-1}
H_2O	896.0 g.l^{-1}
Density	1.322

A simple calculation procedure (Appendix) provides a precise determination of the raw salt composition by distinguishing the crystallized salt from the accompanying brine. Thus:

Crystallized salt:	
kaïnite	44.22%
KCl	.39%
$MgCl_2$, $6H_2O$	6.57%
NaCl	1.18%
Accompanying brine:	
	47.64%
	100 %

One can note the presence of KCl and $MgCl_2$, $6H_2O$ which might be considered as carnallite and bischofite, according to the data taken from the solubility diagrams.

It was interesting (see concentration graph) to draw up the balance to see the quality of the salt deposited between point 1 and 6 (corresponding to saltworks operation, Table 5). The analysis of the salt theoretically deposited is as follows:

$MgSO_4$, KCl, $3H_2O$	88.73%
KCl	2.90%
$MgCl_2$, $6H_2O$	6.63%
NaCl	1.74%

If we compare this analysis with the one actually obtained (Table 6), one notices a slight difference, due to the following facts: 1) temperature changes during manufacture, 2) point 6 has sometimes been overstepped in the pilot saltworks. This caused an increase of $MgCl_2$, $6H_2O$ crystallization and a formation of carnallite.

It can be seen that our concentration chart is reliable and that for an input of 1 m^3 brine (analysis shown on the curve) we have 0.280 m^3 bitterns, having produced 0.0495 t kaïnitic salt (expressed without accompanying brine).

OPERATION OF THE SALIN DE GIRAUD SOLAR SALTWORKS (1,000,000 T/YEAR YIELD)

Once NaCl is produced, the brines discharged from the crystallizers (point G_2 on the graph) are processed in order to extract bromine. They are then circulated over evapora-

TABLE 5

Theoretical Calculation of the Salt Deposit Between Points 1 and 6

	$MgSO_4$	$MgCl_2$	KCl	NaCl	H_2O
Starting volume, point 1:380 l.					
Concentration rate, $g.l^{-1}$	109.67	250.19	48.65	6.58	896.00
Weight of the corresponding salts	41,674.60	95,072.20	18,487.00	2,500.40	340,480.00
Final volume, point 6: 280 l.					
Concentration rate, $g.l^{-1}$, P_3 tons	73.07	334.05	13.93	5.85	896.00
Weight of the corresponding salts	20,459.60	93,534.00	3,900.40	1,638.00	250,880.00
Salts deposited, g	21,215.00	1,538.20	14,586.60	862.40	89,600.00

TABLE 6

Salts Deposited Between Points 1 and 6

	Raw Salt Harvested With the Accompanying Brine %	Same Salt After a Centrifuging Down to 4% at the Industrial Scale %	Crystallized Salt (Without Accompanying Brine) %, as Dry	Salt to be Theoretically Obtained, %, as Dry
Kaïnite, $MgSO_4$, KCl, $3H_2O$	44.22	81.09	84.47	88.73
KCl	0.39	0.71	0.74	2.90
$MgCl_2$, $6H_2O$	6.57	12.04	12.54	6.63
NaCl	1.18	2.16	2.25	1.74
Accom. Brine	47.64	4.00	—	—

tion areas where they concentrate up to point G_3 and are then stored in deep basins. In winter, when temperature comes to about +5°C, concentration rates of these solutions are brought by water addition to such a value that epsomite crystallizes in a pure state, i.e. without driving NaCl along.

The brines remaining after this crystallization are slightly diluted by the rainfalls they receive. When the season favorable to evaporation comes again, they are allowed to flow over new surfaces where they are concentrated up to point G_4 to produce magnesium chloride.

Brine evolution has been plotted in Figure 7. The following features can be noted:

A) Evolution of SO_4—1–2, epsomite production, 2–3, rain dilution, 3–2–4, concentration with NaCl deposit, then NaCl + KCl deposit, and 4–5 kaïnite deposit, then kaïnite + carnallite deposit.

B) Evolution of Mg^{++}—6–7 epsomite deposit, 7–8 and 8–7–9 Mg ion concentrates, 9–10 kaïnite deposit, then kaïnite + carnallite deposit.

Points 1, 2, 3 and 5 and points 6, 7, 8 and 10 are average values obtained statistically over a period of 50 years or so. Points 4 and 9 are results of laboratory measurements.

CONCLUSION

The study of the reciprocal solubility diagrams, the tests made with the 2.25 m^2 basin and the experience gained from the operation of the pilot solar salt plant of 2.8 hectares enabled us to establish and confirm the enclosed concentration chart. This allows one to define the nature of the deposits, the concentration rates to be used and the areas necessary for this purpose for a given climate. In the specific case of the pilot solar salt plant (2.8 ha) we have organized, it is possible to produce 1,500 t raw kaïnite with 4% accompanying brine per hectare of crystallizer, per year. This kaïnite is a raw material which can be used for the production of sulphatized magnesian and potassic fertilizers.

It has been possible to carry out these experiments thanks to Concesion de Salinas, Colombia and we wish to express our thanks to its General Manager and all his assistants who helped us considerably due to their skill and their kind cooperation.

These results are compatible with the experience we gained at Salin de Giraud over a period of about a century.

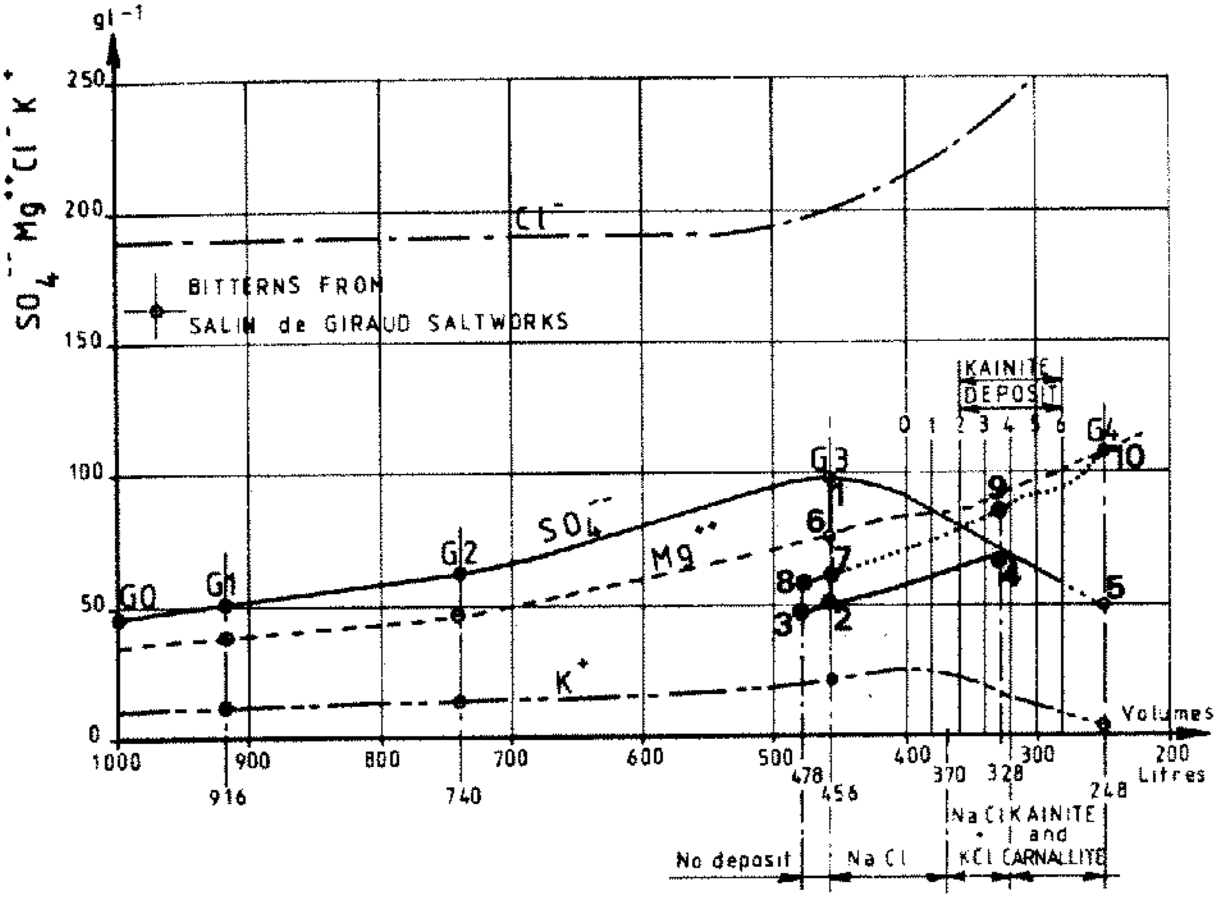

Figure 7. Composition and volumes of the bitterns during their concentration. Example from the Salin de Giraud saltworks.

APPENDIX

CALCULATION OF CHEMICAL ANALYSES

Materials analyzed. The crystallized salt and the accompanying brine.

AVERAGE ANALYSIS OF SALT HARVESTED

Mg^{++}	8,708%
SO_4^{--}	19,160%
K^+	7,415%
Cl^-	18,827%
Na^+	0,546%
H_2O	43,711%

$MgSO_4$	24,014%, 0,19958 mole of $MgSO_4$
$MgCl_2$	15,105%, 0,15847 mole of $MgCl_2$
KCl	14,147%, 0,09482 mole of K_2Cl_2
NaCl	1,389%, 0,01187 mole of Na_2Cl_2
H_2O	45,345%, 2,51917 mole of H_2O

ACCOMPANYING BRINE

SO_4^{--}	58,3 $g.l^{-1}$
Mg^{++}	100,0 $g.l^{-1}$
K^+	7,3 $g.l^{-1}$
Cl^-	259,0 $g.l^{-1}$
Na^+	2,3 $g.l^{-1}$

$MgSO_4$	73,07 $g.l^{-1}$, 0,60730 mole of $MgSO_4$
$MgCl_2$	334,05 $g.l^{-1}$, 3,50451 mole of $MgCl_2$
KCl	13,93 $g.l^{-1}$, 0,09336 mole of K_2Cl_2
NaCl	5,85 $g.l^{-1}$, 0,05000 mole of Na_2Cl_2
H_2O	896,00 $g.l^{-1}$, 49,77778 mole of H_2O
d =	1322,90

Calculations. Thus, for 1 mole H_2O, we have:

$MgSO_4$	0,01220 mole
$MgCl_2$	0,07040 mole
K_2Cl_2	0,00188 mole
Na_2Cl_2	0,00100 mole
H_2O	1,00000 mole

APPENDIX TABLE 1

Calculation Summary

Nature of Material	$MgSO_4$ mole	$MgCl_2$ mole	K_2Cl_2 mole	Na_2Cl_2 mole	H_2O mole
Brines S mole H_2O	0.01220 S	0.07040 S	0.00188 S	0.00100 S	S
Raw salt 100 g	0.19958	0.15847	0.09482	0.01187	2.51917
Kaïnite X g	0.00402 X		0.00201 X		0.01206 X
K Cl_2 Y g			0.0670 Y		
$MgCl_26H_2O$ Z g		0.00492 Z			0.02952 Z
Na_2Cl_2 A g				0.00855 A	

EQUATIONS

$$0.19958 = 0.01220\ S + 0.00402\ X \quad (1)$$

$$0.15847 = 0.07040\ S + 0.00492\ Z \quad (2)$$

$$0.09482 = 0.00188\ S + 0.00201\ X + 0.0670\ Y \quad (3)$$

$$0.01187 = 0.00100\ S + 0.00854\ A \quad (4)$$

$$2.51917 = S + 0.01206\ X + 0.02952\ Z \quad (5)$$

If we multiply (2) by 6, we thus have:

$$0.95082 = 0.42240\ S + 0.02952\ Z \quad (7)$$

If we calculate:

(5)−(7)

$$\begin{array}{rl} 2.51917 = & S + 0.01206\ X + 0.02952\ Z \\ -0.95082 = & -0.42240\ S - 0.02952\ Z \\ \hline 1.56835 = & 0.57760\ S + 0.01206\ X \end{array} \quad (8)$$

Multiplying (1) by 3, we have:

$$0{,}598874 = 0.03660\ S + 0.01206\ X \quad (9)$$

If we calculate:

(8)−(9)

$$\begin{array}{rl} 1.56835 = & 0.57760\ S + 0.01206\ X \\ -0.59874 = & -0.03660\ S - 0.01206\ X \\ \hline 0.96961 = & 0.54100\ S \end{array}$$

Thus,

$$S = 1.79226 \text{ mole of } H_2O$$

We draw, from (1)	X = 44.20758 g of kaïnite		44.222%
from (2)	Z = 6.56407 g of $MgCl_26H_2O$		6.566%
from (3)	Y = 0.38706 g of KCl		0.387%
from (4)	A = 1.17868 g of NaCl		1.179%
Brine weight	= 47.6307 g		47.646%
total	= 99.98320 g		100.00