

Study of the Lithium Retention by Salts Crystallised from Natural Brines

A. M'NIF, H.A. HAMZAOUÏ,† and R. ROKBANI*

*Laboratoire des procédés chimiques,
Institut National de recherche scientifique et Technique
B.P. 95-2050 Hammam Lif, République Tunisienne*

Natural brines may be a source of lithium. However the extraction of this element can be affected by solar evaporation. Indeed we put in evidence the existence of retention phenomenon of this element by the crystallized salts. Regarding this phenomenon, we determined the retention mode (coating solution, adsorption, and substitution) and establish relations between retention ratios and lithium concentrations in the solutions.

INTRODUCTION

The recovery of oceanic salts, from natural brines, is often made in solar pans especially built to this purpose. During the evaporation process the concentration of the different ions changes and single or double salts crystallise¹⁻³.

Initially as trace element, the lithium concentrates but without crystallising. The Li content variations are bound to lead to the phenomenon of concentration and possibly those of retention by the crystallised salts. The extraction of lithium from natural brine puts the question when it is appropriate to recover it during the evaporation of the brine.

Our aim is firstly to answer partially this question by studying the evolution of lithium concentration during brine's evaporation and secondly to determine how salts retain lithium and especially by NaCl.

Choice of the Brines

Brines are chosen with a manner to cover the area of the quinary diagram Na^+ , K^+ , Mg^{2+} , Cl^- , $\text{SO}_4^{2-}/\text{H}_2\text{O}$ (Figure 1). Consequently, two natural brines (El Adhibate and Dead Sea) and two synthetic ones (Saumure "OK" and Saumure "S") are retained. The chemical compositions are determined and mentioned in Table 1. The positions of these brines are reported on the quinary oceanic diagram at 25°C (Figure 1). The Jänacke coordinates of each position correspond to the molar percentage of each entity versus the total number of moles

and are calculated as follows: $\% \text{K}_2 = \frac{n[\text{K}_2] \times 100}{D}$, $\% \text{Mg} = \frac{n[\text{Mg}] \times 100}{D}$,

$\% \text{SO}_4 = \frac{n[\text{SO}_4] \times 100}{D}$, $D = n[\text{K}_2] + n[\text{Mg}] + n[\text{SO}_4]$, with $n[\text{X}] =$ mole number of the X entity.

†Faculté des sciences de Monastir

TABLE-1
COMPOSITION IN (g/L) OF STUDIED BRINES

Brines	Na	K	Mg	Cl	SO ₄	Li
Dead Sea	16.40	4.90	36.90	147.60	0.00	0.075
El Adhibate	88.00	3.60	12.60	150.00	37.00	0.016
Saumure "OK"	38.90	0.42	2.19	19.52	64.24	0.020
Saumure "S"	49.93	86.73	14.36	190.60	12.90	0.020

Salts Crystallisation Sequences: With regard to the compositions of studied brines and the quinary diagram (Figure 1), the theoretical salts crystallisation sequences during isothermal evaporation are reported in Table-2.

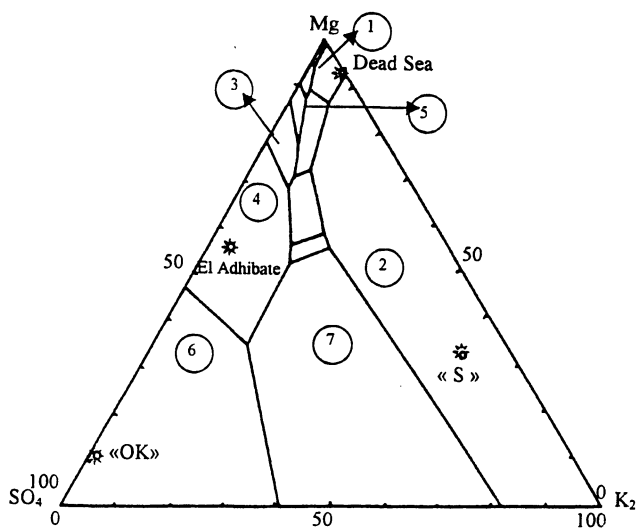


Fig. 1. Positions of the brines on the diagram.

① Carnallite, ② Sylvine, ③ Epsomite, ④ Astrakanite, ⑤ Kaïnite, ⑥ Thénardite, ⑦ Glaséite

We notice that the first crystallisation sequence is always sodium chloride. The constitution of the following sequences are: sulphated salts for the two first brines and chlorides for the two latest ones. The difference between the deposited salts: let us think of an eventual correlation between crystallising salt nature during brine evaporation and lithium concentration evolution.

TABLE-2
THEORETICAL CRYSTALLISATION SEQUENCES

Sequence	El Adhibate Brine	"OK" Brine	Dead Sea Brine	"S" Brine
1	NaCl	NaCl	NaCl	NaCl
2	NaCl + Astrakanite	NaCl + Thénardite	NaCl + Carnallite	NaCl + Sylvine
3	NaCl + Epsomite	NaCl + Astrakanite	—	NaCl + Kaïnite
4	—	—	—	—

Astrakanite = Na₂Mg(SO₄)₂·4H₂O, Thénardite = Na₂SO₄, Carnallite = MgCl₂KCl·6H₂O, Epsomite = MgSO₄·7H₂O, Sylvine = KCl, Kaïnite = KClMgSO₄·3H₂O

EXPERIMENTAL

Isothermal evaporation is used as a procedure to follow the evolution of the different ions in the brine. To this effect the brines are placed in PVC containers maintained at 25°C in a thermostatic bath. Brine evolutions are controlled by regular measurements of specific gravity and chemical analysis of both phases in equilibrium.

For the lithium component, the curves of lithium concentration vs. liquid density show variations of Li content during the evaporation of the considered brines.

RESULTS AND DISCUSSION

The increasing lithium concentrations (in ppm) during evaporation are represented in Figs. 2–5.

The examination of the precedent figures shows two subsets. The first one representing El Adhibate and “OK” brines and the second those of the Dead Sea and “S” brines.

In the first category, the slope of the curve is almost constant until a density of 1.280, then the slope increases progressively until $d \sim 1.320$; beyond this density the slope increase is more important and the lithium contents reach values of 250 ppm > [Li] > 350 ppm.

In the second category, the increase of lithium content is monotonous and presents some bearings which are not sufficiently perceptible. Also the lithium content does not exceed 170 ppm.

Considering these remarks and the characteristics of each brine group, it appears that the increase of Li content depends on the nature of the crystallised

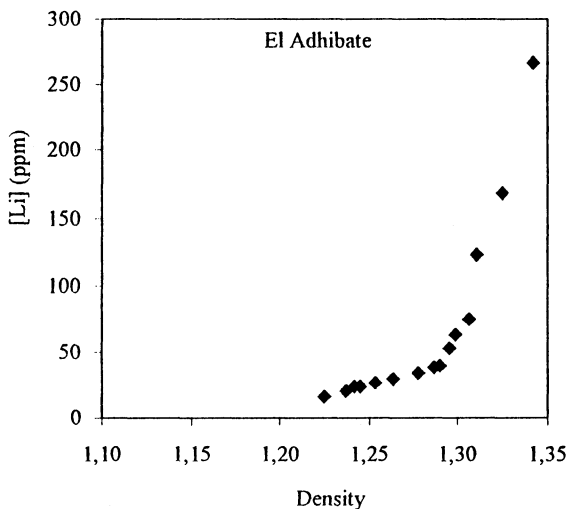


Fig. 2. [Li] evolution in Sebkhate El Adhibate brine.

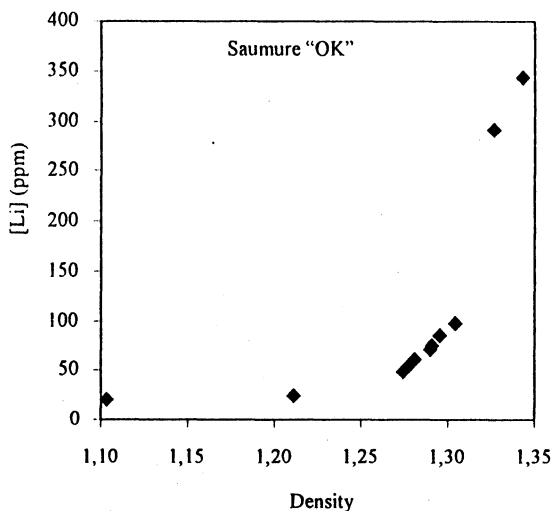


Fig. 3. [Li] evolution in "Saumure OK" brine.

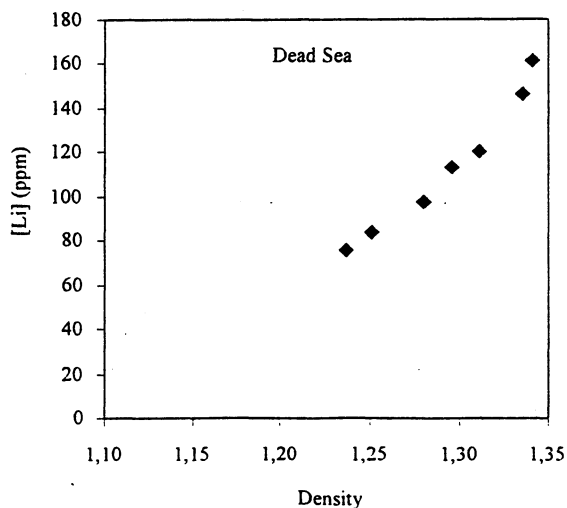


Fig. 4. [Li] evolution in Dead Sea brine.

salt during the evaporation process. This is probably due to a retention mechanism of the lithium by the different salts.

To better fear the Li retention notion by the crystallised salts, we studied the particular case of the El Adhibate brine. To this purpose we registered the evolution of the solution volume as a function of its density and the nature of the crystallised salt. Two sequences are retained:

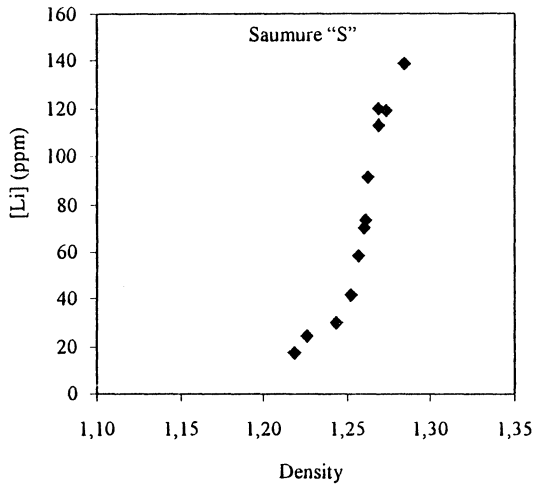


Fig. 5. [Li] evolution in saumure "S" brine.

(i) deposit of NaCl ($1.225 < d < 1.290$)

(ii) deposit of a mixture of two salts NaCl + Astrakanite ($1.290 < d < 1.3115$)

Table-3 recapitulates all the results. Initial volume and Li content are respectively $V_0 = 1500$ mL and $[Li]_0 = 16$ ppm. For a density " d_i " the measured Li content is $[Li]_i$ and the solution volume is V_i . A mass balance permits to deduct the lithium percentage retained by the crystallised solid at the considered density. The following equation is applied.

$$(\% Li)_i = \frac{([Li]_0 \times V_0 - [Li]_i \times V_i) \times 100}{[Li]_0 \times V_0}$$

We notice that the sodium chloride retains 20% of the total initial lithium and that the astrakanite sequence retains 28% of it.

Study of lithium retention by NaCl: Lithium retention by crystallising salts is a phenomenon that requires more investigations. To this effect, we studied NaCl salt case.

TABLE-3
Li RETAINED BY NaCl AND ASTRAKANITE

i	d_i	(V_i) (mL)	[Li] (ppm) measured	(Li) _i (mg) calculated	(Li) _i (mg) retained	(% Li) _i retained
0	1.225	1500	16.00	24.00	–	–
1	1.237	1162	20.00	23.24	0.759	3.161
2	1.254	848	26.00	22.05	1.952	8.133
3	1.263	728	29.00	21.11	2.890	12.041
4	1.290	480	40.00	19.22	4.784	19.933
5	1.315	91	136.33	12.45	11.554	48.143

A better knowledge of the retention mode of Li by the salt could conduct to its liberation from the solid. In order to reach this goal, three masses of pure (RP) NaCl (50–75 and 100 g) were treated each by a volume of 50 mL of saturated magnesium chloride solution (120 g/L at ambient temperature) containing 236 ppm of Li and has a density 1.3321. The lithium content (236 ppm) was chosen with regard to knowing Li concentrations in end brines.

The solid-liquid system is agitated during 30 min. After filtration, Li was measured in the two obtained phases. All results are reported in Table-4.

TABLE-4
REPARTITION OF LITHIUM BETWEEN NaCl AND THE SOLUTION

Designation	I	II	III
Initial salt mass (g)	50	75	100
Initial solution volume (mL)	50	50	50
[Li] ₀ initial lithium in the solution (ppm)	236	236	236
Filtrate volume (mL)	47	46	45
Humid salt mass (g)	51.2	76.67	102.15
Li content in the filtrate (ppm)	196.54	187.90	180
Li ratio in the humid salt in mg per 100 g	5.06	4.11	3.62

A mass balance permits to determine the Li portion retained by NaCl.

$$\% \text{Li}_{\text{retained}} = \frac{\{\text{initial Li Mass} - \text{Li Mass in filtrate}\} \times 100}{\text{initial Li mass}}$$

The obtained results are presented in Fig. 6.

To ensure that this result is accurate a new mass balance based on solid phase for the test number I (Table-5) indicates that the solid phase retains 21.95% of total initial lithium in the solution, which concurs with the precedent result (Table-3) which stipulates that the NaCl sequence retains 20% of initial lithium in the brine

Lithium Retention Types: The retained Li is shared between the solution which coats the crystals and the different shapes of retention by the crystal (adsorption, insertion or substitution). We will try hereafter to quantify the above mentioned repartition.

Lithium in the coating solution: For this purpose, we perform sodium analysis on the liquid samples coming from the previously considered tests (I, II and III).

The obtained results permit to calculate NaCl weight in the solid phase. The mass difference between the humid solid phase and calculated NaCl mass represents the coating solution mass. The density of this solution is known (1.3321); we deduct then its volume and consequently the restrained lithium weight. Table-5 recapitulates these results.

From Table-5, it appears that the coating solution retains 8 to 8.5% from the total retained lithium by the humid NaCl. The remaining lithium is consequently linked to the NaCl by adsorption, insertion or substitution.

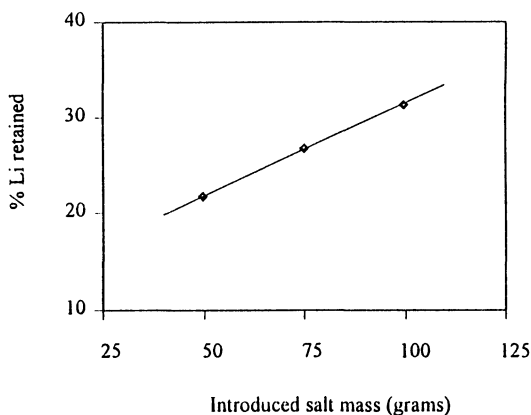


Fig. 6. % Li retained as function of NaCl introduced mass.

TABLE-5
RESTRAINED LITHIUM REPARTITION IN HUMID NaCl

Test	I	II	III
Humid solid mass (g)	51.20	76.67	102.15
Na concentration in the filtrate (in ppm)	1516.20	1516.20	1516.20
Volume of filtrate (in mL)	47.00	46.00	45.00
NaCl mass in the humid salt (g)	49.81	74.82	99.82
Coating solution mass (g)	1.38	1.84	2.32
Coating solution volume (mL)	1.03	1.38	1.74
Li mass in the coating solution (mg)	0.20	0.26	0.31
Total Li mass restrained by the solid (mg)	2.56	3.15	3.70
% total Li restrained by the coating solution	7.95	8.25	8.48

Other forms of lithium retention: We will try hereafter to dispatch lithium between the above mentioned retention forms. For this purpose, we achieve the following experimentation on the resulting products of the test I. A sample of 25 g of humid NaCl is treated with 25 mL of concentrated HCl and the system is stirred during 25 min. This washing process only removes the adsorbed lithium and the coating solution lithium. This option is dictated by the insolubility of NaCl^{4,5} and the solubility of LiCl in the washing agent. Volume and Li content in the filtrate lead to the results reported in Table-6.

TABLE-6
LITHIUM REMOVED BY HCl

Filtrate volume after HCl treatment (mL)	23.50000
Measured Li content in the filtrate (ppm)	6.62000
Calculated lithium mass removed by HCl (mg)	0.15557

We notice that the removed quantity of Li by HCl is superior to the existing quantity in the coating solution ($0.1556 > 0.0995$). It is consequently evident that the adsorbed quantity of lithium is at least equal to 0.0561 mg ($0.1556 - 0.0995$), which corresponds to 4.43% of the total restrained lithium by humid NaCl (1.265 mg). Similarly, the lithium distribution is reported in Table-7.

TABLE-7
LITHIUM DISTRIBUTION

Lithium retention types	% Li
Coating solution	7.86
Adsorbed lithium	4.43
Substituted or possibly insert lithium	87.70

Considering the geometrical vacant spaces in the NaCl crystal structure, it is more probable that Li substitutes Na rather than inserts in the void areas.

To make our results true we measure the lithium content in the treated NaCl. We find 81.5% of total initial lithium. Considering the analytical errors, this ratio confirms the above calculated ones.

Conclusion

The study of the lithium content evolution during the solar evaporation process of natural brine indicates that the crystallising salts retain the lithium component. A particular survey of El Adhibate natural brine shows that NaCl and Astrakanite retain 20% and 28% respectively of all initial lithium in the natural brine.

Consequently the total lithium content does not remain in the resultant solution after isothermal evaporation as it can be expected.

A study of the retention mode of Li by NaCl is developed. Three retention modes are identified: Coating solution, adsorption and substitution or insertion. The retained Li is shared as follows: 8% in the coating solution, 4.3% adsorption and 87.7% substitution or insertion.

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