

Study of the lithium retention by sodium chloride, crystallised from natural brines (South of Tunisia)

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

1. INTRODUCTION

The extraction of oceanic salts is often made in solar pans especially prepared to this purpose. During the evaporation process the concentration of the different ions changes and single or double salts crystallise [1, 2, 3].

Initially as trace element, the lithium concentrates but without crystallising. The Li content variations are bound to the phenomenon of concentration and possibly those of retention by the crystallised salts.

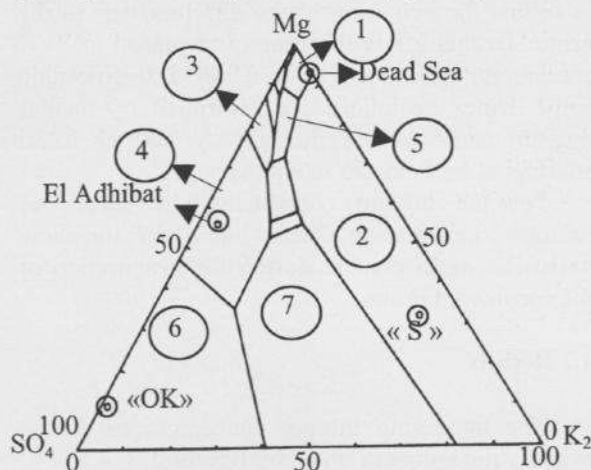
The extraction of lithium from natural brine puts the question when it is appropriate to recover it during the evaporation of the brine.

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

2. CHOICE OF THE BRINES

Brines are chosen in a manner to cover the area of the quinary diagram Na^+ , K^+ , Mg^{++} , Cl^- , SO_4^{--} / H_2O (figure 1). Consequently, two natural brines (El Adhibate and Dead Sea) and two synthetic brines

(Saumure "OK" and Saumure "S") are retained. The chemical compositions are mentioned on the table 1. The positions of these brines are reported on the quinary oceanic diagram at 25°C (figure 1).



① Carnallite, ② sylvine, ③ Epsomite,
④ Astrakanite, ⑤ Kainite, ⑥ Thénardite, ⑦
Glasérite

Figure 1. Positions of the brines on the diagram.

Table 1
Composition in (g/l) of studied brines

brines	Na	K	Mg	Cl	SO ₄	Li
S. Dead Sea	16.40	4.90	36.90	147.60	0.00	0.075
S. 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

3. SALTS CRISTALLISATION SEQUENCES

With regard to the compositions of studied brines and the quinary diagram (figure 1), the theoretical salt crystallisation sequences during isothermal evaporation are reported on table 2.

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 salts. The difference between the deposited salts, suggests an correlation between the nature of crystallising salt during brine evaporation and lithium concentration evolution.

4. EXPERIMENTAL STUDY

4.1. Procedure

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. Brines 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 versus liquid density show variations of Li content during the evaporation of the considered brines.

4.2 Results

The increasing lithium concentrations during evaporation are represented on figures 2, 3, 4 and 5.

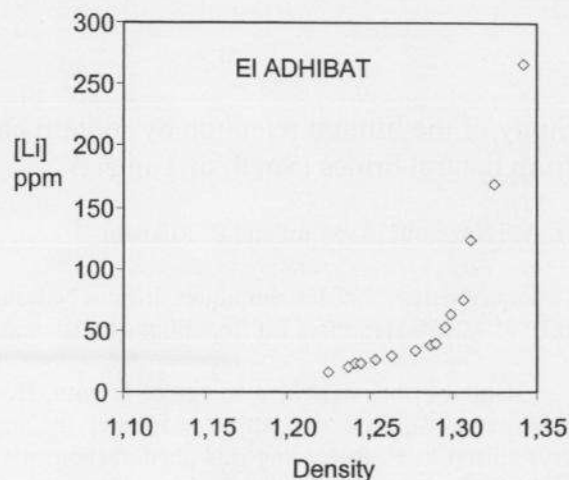


Figure 2. [Li] evolution in Sebkhate El Adhibate brine

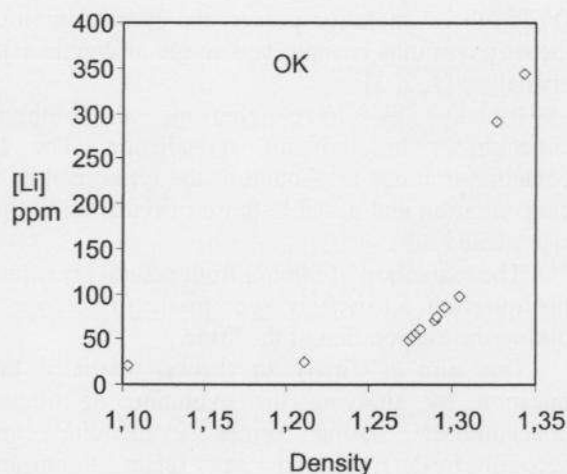


Figure 3. [Li] evolution in "Saumure OK" brine

Table 2
Theoretical crystallisation sequences

Sequences	El Adhibate Brine	OK Brine	Dead Sea Brine	S Brine
1	NaCl	NaCl	NaCl	NaCl
2	NaCl + Astrakanite	NaCl + thenardite	NaCl + Carnallite	NaCl + Sylvine
3	NaCl + Epsomite	NaCl + Astrakanite	NaCl + Kaïnite
4

Astrakanite = $\text{Na}_2\text{Mg}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$, thenardite = Na_2SO_4 , Carnallite = $\text{MgCl}_2\text{KCl} \cdot 6\text{H}_2\text{O}$, Epsomite = $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, Sylvine = KCl , Kaïnite = $\text{KClMgSO}_4 \cdot 3\text{H}_2\text{O}$.

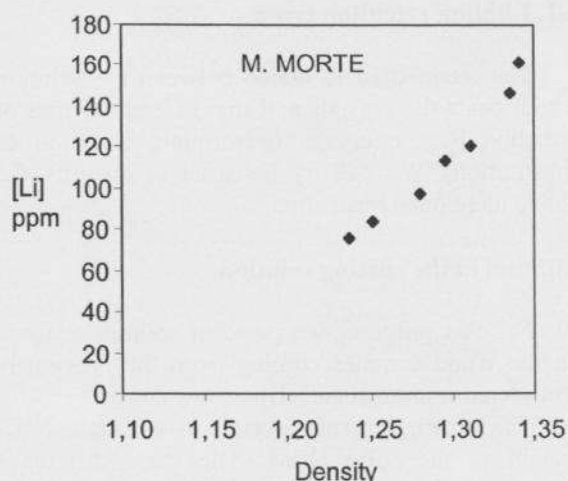


Figure 4. [Li] evolution in Dead Sea brine

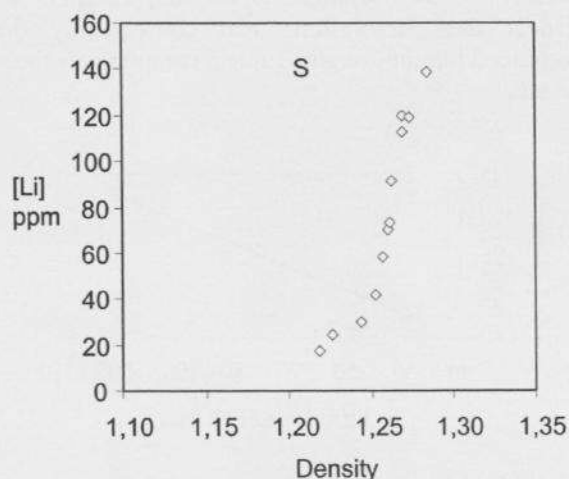


Figure 5. [Li] evolution in "saumure « S »" brine

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 pronounced and the lithium contents reach values of $250 \text{ ppm} > [\text{Li}] > 350 \text{ ppm}$.

In the second category, the increase of lithium content is monotonous. Also the lithium content does not exceed 170 ppm.

Considering this remarks and the characteristics of each brine group, it appears that the increase of Li content depend on the nature of the crystallised salt during the evaporation process. This is probably due to a retention mechanism of the lithium by the different salts.

To investigate the Li retention notion by the crystallised salts better, 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:

- deposit of NaCl ($1.225 < d < 1.290$).
- 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 $V_0 = 1500 \text{ ml}$ and $[\text{Li}]_0 = 16 \text{ ppm}$. For a density " d_i " the measured Li content is $[\text{Li}]_i$ 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.

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

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

Table 3
Li Retained by NaCl

i	d_i	(V_i) (ml)	[Li] measured	$(\text{Li})_i$ calculated (mg)	$(\text{Li})_i$ retained (mg)	$(\% \text{ Li})_i$ retained
0	1.2250	1500	16.00	24.00	/	/
1	1.2375	1162	20.00	23.24	0.759	3.161
2	1.2540	848	26.00	22.05	1.952	8.133
3	1.2630	728	29.00	21.11	2.890	12.041
4	1.2900	480	40.00	19.22	4.784	19.933
5	1.3150	91	136.33	12.45	11.554	48.143

5. STUDY OF THE LITHIUM RETENTION BY NaCl.

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

A better knowledge of the retention mode of Li by the salt could lead 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 having a density 1.3321. The lithium content (236-ppm) was chosen with regard to known Li concentrations in end brines.

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

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

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

Obtained results are reported in figure 6.

To be sure that this result is good a new mass balance based on solid phase for the same test indicates that the solid phase retains 21.95 % of total initial lithium in the solution, which concurs with the preceding results.

5.1. 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.

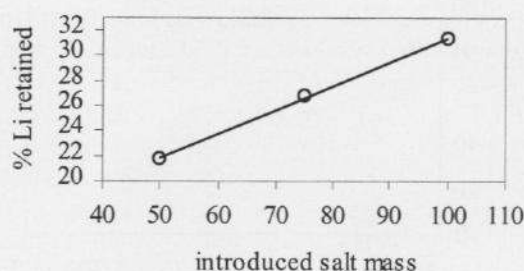


figure 6. % Li retained as function of NaCl introduced mass.

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

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 en (ppm)	1516.20	1516.20	1516.20
Volume du filtrate en (ml)	47.00	46.00	45.00
NaCl mass in the humid salt (g)	49.8187	74.8226	99.8265
Coating solution mass (g)	1.3813	1.8474	2.3235
Coating solution volume (ml)	1.0369	1.3868	1.7443
Li mass in the coating solution (mg)	0.2038	0.2606	0.3140
Total Li mass restrained by the solid (mg)	2.5626	3.1566	3.7000
% total Li restrained by the coating solution	7.9525	8.2553	8.4856

From this table, 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.

Other forms of lithium retention

We will try hereafter to distinguish between the above mentioned lithium 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. The system is stirred during 25 minutes. This washing process only removes the adsorbed lithium and the coating solution lithium. This option is dictated by the insolubility of NaCl [2, 3] and the solubility of LiCl in the washing agent.

Volume and Li content in the filtrate lead to the results reported on table 6.

Table 6
Lithium removed by HCl.

filtrate volume after HCl treatment (ml)	23.5
measured Li content in the filtrate (ppm)	6.62
lithium mass removed by HCl (mg)	0.15557

We notice that the removed quantity of Li by HCl is larger than the existing quantity in the coating solution ($0.1556 > 0.0995$). It's 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 on table 7.

Considering the geometrical vacant spaces in the NaCl crystal structure, It's more probably 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 calculate ones.

Table 7
Lithium distribution

Lithium retention types	% Li
Coating solution	7.86
Adsorbed lithium	4.43
substituted or possibly insert lithium	87.7

6. 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 respectively 20% and 28% 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 on the retention mode of Li by NaCl is developed. Three retention modes are identified: Coating solution, adsorption and substitution are 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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