

Salting Out Process for Lithium Recovery

Donald E. Garrett and Martin Laborde

Saline Processors, Inc.

*Ojai, California, U.S.A. and Corporación Nacional del Cobre (CODELCO)
Santiago, Chile*

ABSTRACT

Lithium sulfate monohydrate may be recovered from certain brines by means of a "salting out" technique. For brines of the Na-K-Mg-Li-SO₄-Cl system, or others, that may be concentrated by solar or plant evaporation beyond a certain concentration,

lithium may be selectively partially removed by the addition of sulfate compounds such as sodium sulfate, magnesium sulfate and sulfuric acid. A process is described for simply obtaining this sulfate salt, concentrating the brine, and recovering the lithium.

INTRODUCTION

There are a few locations in the world where lithium occurs in relatively high concentration in brines and a few industrial liquids or other materials in which similar lithium concentrations or mixtures can exist. Many of these brines, such as the ones occurring in the Salar de Atacama, Chile, are concentrated in sequential flow solar ponds to first remove halite (NaCl), and then to crystallize their potash values as sylvinites (NaCl plus KCl) or potash double salts. During this concentration process even with high-lithium brines, lithium would not start to crystallize until near the end of the potash crystallizing period when lithium sulfate monohydrate comes down with the carnallite (KCl·MgCl₂·6H₂O) and other salts. At what would normally be the end of the potash crystallization sequence, 70 to 100 percent of the lithium is generally still in solution.

Lithium is currently recovered from one naturally occurring brine by adding a base, such as lime, to the weak or partially concentrated brine to precipitate the magnesium and the sulfate. This requires a large amount of lime but does leave the brine in a state where it can be concentrated by solar and plant evaporation to yield a concentrated lithium chloride solution. This is then taken to the plant and the lithium precipitated with soda ash to produce the less soluble lithium carbonate.

Another industrial process precipitates lithium sodium phosphate during plant evaporation of brine and then separates and processes it in a multistep process. Development work has been done on a similar co-precipitation with aluminum hydroxide, but this also involves considerable base and much auxiliary processing.

Other development work has been done on the solar evaporation of brine to its maximum concentration and then bringing it to the plant where MgCl₂·6H₂O is crystallized and removed from the solution. The concentrated brine is treated with lime, followed by Li₂CO₃ precipitation. As a final method, a liquid-liquid extraction process¹ has been studied where ferric chloride is added to the brine and a FeCl₃—LiCl complex extracted. This mixture can be separated later into its two components.

It is apparent from the above discussion that each of the present methods is expensive and involves complex processing.

DISCUSSION

It has been discovered that lithium may be simply recovered from brines by a salting out procedure with a soluble sulfate salt.² In the sequence of solar evaporation discussed in the Introduction section, if magnesium sulfate, sodium sulfate or sulfuric acid were added to the strong brine, i.e., after potash recovery, a reasonable yield of Li₂SO₄·H₂O would be crystallized. An example of this is shown in Table I.

In a strong magnesium brine it is seen that the most effective sulfate salt for salting out is magnesium sulfate, since the magnesium is most soluble in the solution. When sodium sulfate is added, some sodium chloride or magnesium sulfate (epsomite) also precipitates with the lithium sulfate. When sulfuric acid is added beyond a certain concentration much of the borate that is present

¹U.S. Patent 3,537,813.

²U.S. Patent pending.

TABLE I
Salting Out Lithium—Experimental Results

	Additive					
	Na ₂ SO ₄		MgSO ₄ *		H ₂ SO ₄	HCl
Amount, wt. %	5	20	8.9	9.22	0.69†	1.08†
Brine	A	A	A	B	B	B
Residual Solution, g/l						
Cl	20.22	14.74	20.48	25.45	26.55	26.3
SO ₄	4.65	9.27	3.95	1.52	0.05	0.35
Mg	5.90	5.00	6.65	7.98	7.95	7.68
K	0.41	0.43	0.40	0.06		
Li	0.985	1.00	0.696	0.54	0.60	0.70
H ₃ BO ₃	2.74	2.84	2.61	3.60	1.38	1.34
Product, wt. %						
Amount	2.05	28.26	3.27	4.66	3.94	
NaCl	57.15	46.7				
Na ₂ SO ₄	18.53	4.07				
MgSO ₄ ·6H ₂ O		44.2				
MgSO ₄ ·H ₂ O			4.5	4.5		
Li ₂ SO ₄ ·H ₂ O	24.32	5.0	96.5	95.5	22.8	
H ₃ BO ₃					77.2	100
Li Recovery, %	6.3	14.3	32.0	49.0	13.9	0
H ₃ BO ₃ Recovery, %					72.6	49.9

*35.5% water present as a hydrate.

†pH = 0.

Initial Feed Brine (from the Salar de Atacama, Chile)				
Brine A	Density = 1.294 at 25°C	pH = 3.95 at 25°C (approx. brine 7 Charts 7 and 8)		
Brine B	Density = 1.342	pH = 2.0		
Ion	Composition, wt. %		Brine A	
	Brine A	Brine B	Moles per 1000	Moles H ₂ O
Cl	21.63	26.50	MgCl ₂	66.46
SO ₄	2.21	0.39	K ₂ Cl ₂	1.40
Mg	5.91	7.24	Li ₂ Cl ₂	14.49
K	0.41	0.06	Li ₂ SO ₄	6.18
Li	1.077	1.057	Na ₂ B ₁₀ O ₁₆	1.18
B ₁₀ O ₁₆	1.58			
B as H ₃ BO ₃	2.74	3.80		

converts to boric acid and also crystallizes. Because of this, in a sequential salting out process, both lithium and boron can be recovered from certain brines.

PHASE CHEMISTRY

Due to the huge size of the body containing the brine under study, its composition showed large variations. This required that a general process, technically flexible and economically feasible, had to be developed in order to recover the most valuable compounds present in the brine.

The brines have the following composition (grams/liter):

Li	1.3–2.0
Mg	10–20

K	17–24
Na	94–102
Ca	0.2–0.4
B*	3.5–4.8
Cl	195–240
SO ₄	5–27

*as boric acid.

One of the many occurring brines, the most representative of the reservoir has the following composition (grams/liter):

Cations	Anions
Li = 1.34	SO ₄ = 17
K = 20	Cl = 196
Na = 100	H ₃ BO ₃ = 4.4
Kg = 11	

There is no literature available for this system, so different assumptions had to be conceived followed by empirical tests.

Two different phase charts were basically utilized. The first, provided by Autenrieth, was of the following quinary system (at 25°C): K, Na, Mg, Cl, SO_4 ; expressed as moles of MgCl_2 (abscissa) per 1,000 moles of water versus moles of MgSO_4 (ordinate) per 1,000 moles of water (see Chart 1). All the sulfate present in the brine is expressed as MgSO_4 .

This diagram was used as a first approximation to explain the behaviour of the brines during their earlier stages of concentration in the process of concentration by solar evaporation.

Later on, as lithium became saturated as lithium sulphate, the phase diagram $\text{MgSO}_4\text{--Li}_2\text{Cl}_2$ was utilized (Chart 2). In this case it was assumed that the boron components would not alter substantially the behaviour of the other four ions.

The brines were slowly and carefully concentrated, in the lab as well as at the brine sites, at different temperatures, in order to study the pattern (behaviour) of the evaporation path. Evaporation studies, during a period of four years, were conducted both in summer and winter

and later on at the corresponding seasonally prevailing medium temperatures repeated in the lab (Chart 3).

It was discovered that the brines followed, with only a minor bias, the Autenrieth diagram during the first three stages of concentration (seven fold). As predicted by the literature, sodium and potassium chlorides were the major salts crystallizing during the concentration path.

When lithium reached a concentration over eight grams per liter in winter, and slightly below eight in summer, it began to crystallize. This behaviour complied with the $\text{MgSO}_4\text{--Li}_2\text{Cl}_2$ phase diagram.

In order to keep lithium in the brine, it was then necessary to remove the sulphate in the early stages of concentration.

Autenrieth has also provided the solubility locus of epsomite for the quinary system $\text{Na--K--Mg--SO}_4\text{--Cl}$, which was used extensively for brines containing less than eight grams per liter of lithium. Some lines of data, specifically Na_2Cl_2 and K_2Cl_2 have been blurred in order to highlight data. (Chart 4). Tests were conducted in order to correlate the epsomite solubility locus as provided by Autenrieth and the one pertaining to the brine system. (Chart 5).

It was shown that the solubility at 5, -5, -10 and

Chart 1. K—Mg—Na—Cl— SO_4 phase diagram.

(Saturated with NaCl and KCl)
25°C

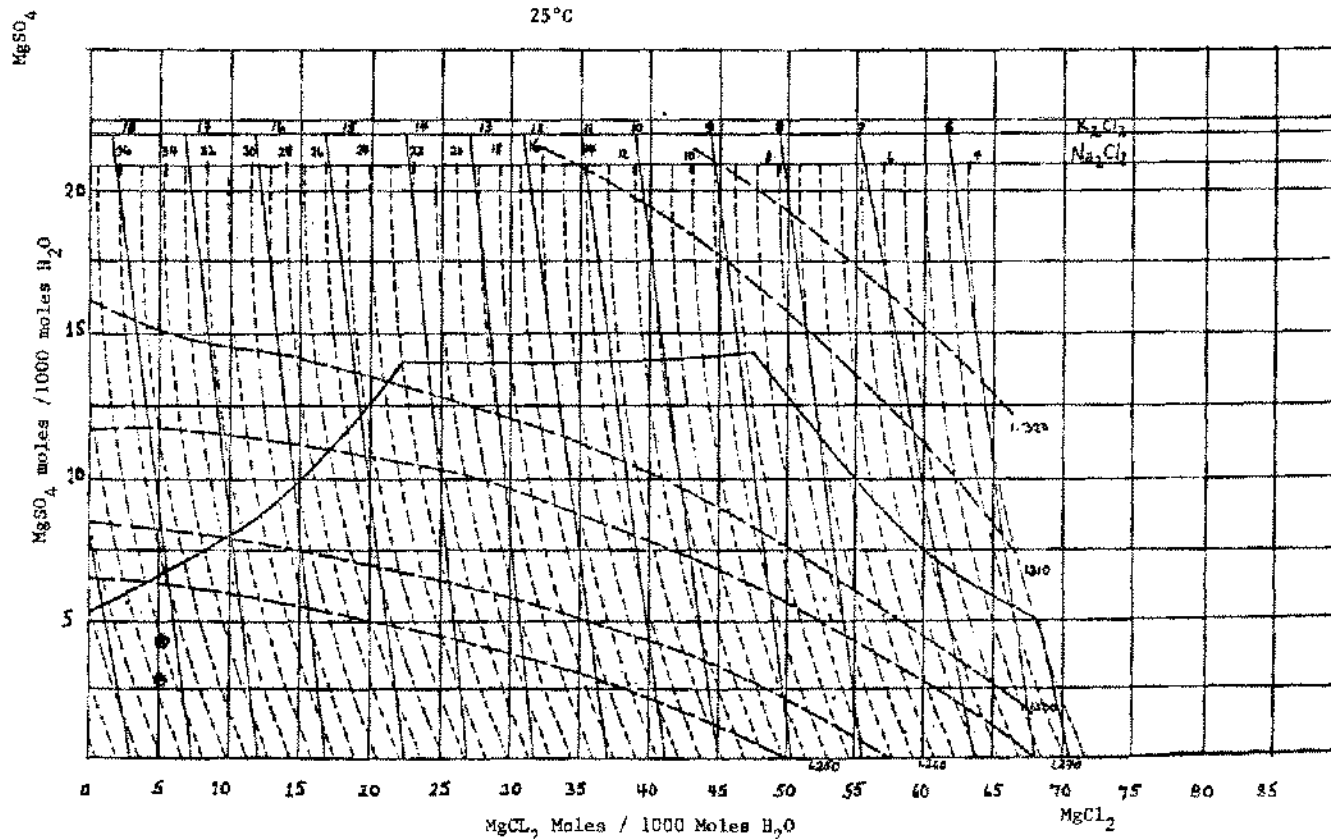
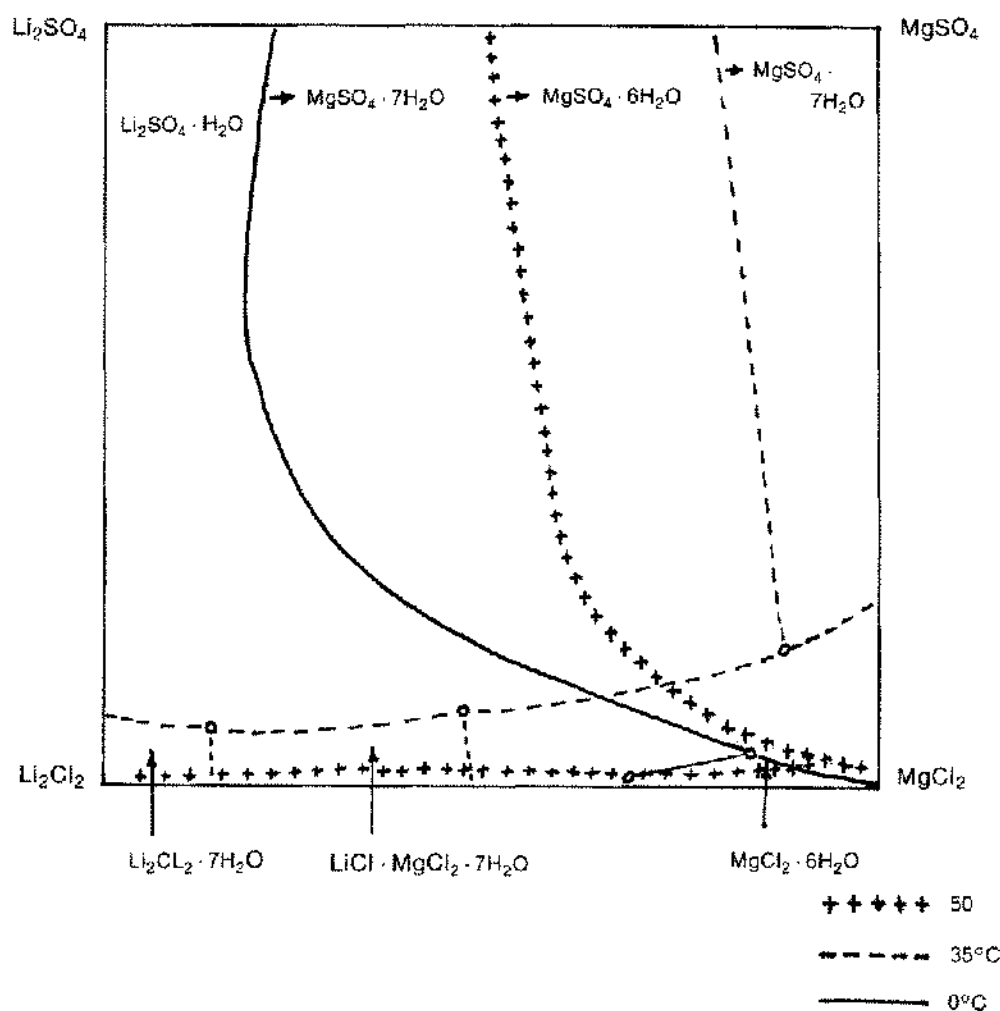


Chart 2. Phase diagram at 0°, 35° and 50°C of Li, Mg, Cl, SO₄—H₂O.

—15°C of epsomite for the brine system under study correlated fairly well with the above mentioned quinary system, for the brines tested with a concentration no greater than 14 grams per liter in lithium. Finally for brines highly concentrated in lithium and magnesium (and low in sodium and potassium) it was observed that lithium sulfate has a reverse solubility in the range of 30° to 40°C; at temperatures below 0°C epsomite would be the less soluble salt, whereas in the range of 30° to 40°C, the situation reverses and Li₂SO₄·H₂O has the lower solubility.

In Chart 6, using the MgSO₄·Li₂Cl₂ phase diagram, it is shown that during the concentration process the brine composition tends to reach the congruent point (A) at 25°C, and then, of course, MgCl₂ and Li₂SO₄ would crystallize upon further concentration. So if epsomite is removed by cooling the brine to temperatures under —10°C, sulfate is eliminated and the brine composition deviates from the congruent point A. The brine can be

further evaporated, and again upon reaching lithium sulfate saturation concentration is stopped. At this stage temperature is increased to 30° to 40°C and epsomite added, resulting in a salting out of lithium sulfate (for example, from point 7 to 8, Charts 7 and 8).

The filtered brine is later cooled and under —10°C to remove epsomite (SO₄) and further concentrated until Li₂SO₄·H₂O again reaches saturation at room, or pond, temperature. A new salting out step follows.

Successive cooling stages (epsomite removal from the brine), followed by brine concentration (mainly by solar evaporation) and salting out will yield Li₂SO₄·H₂O in the crystallizers and MgCl₂·6H₂O in the ponds.

Also if desired, at any given level sulfate can be removed by liming. This brings down the sulfate concentration to under 4 grams/liter and allows lithium to concentrate in the ponds to over 50 grams per liter. In the brines under study liming can take place with practically no formation

Chart 3. K—Mg—Na—Cl—SO₄ phase diagram.

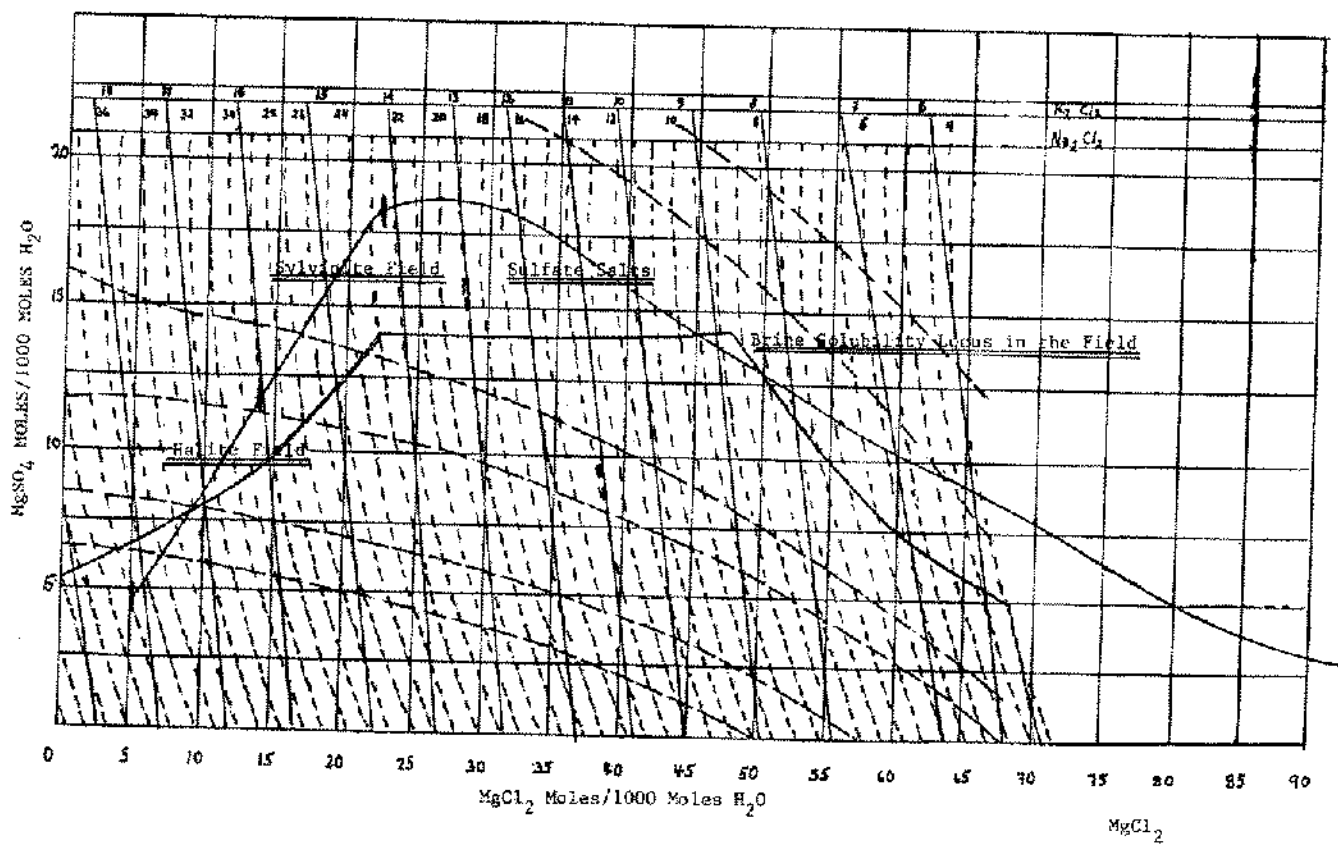
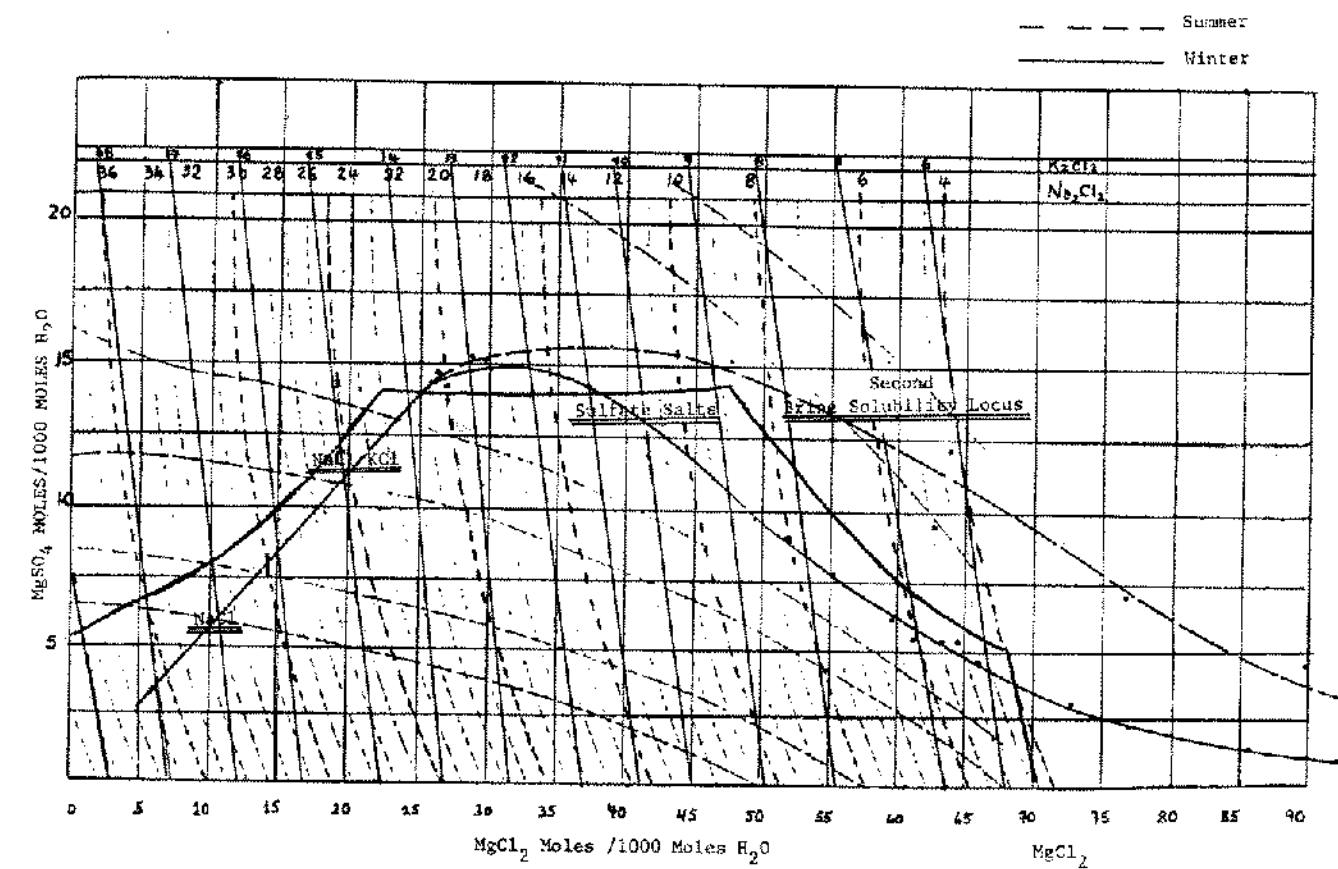
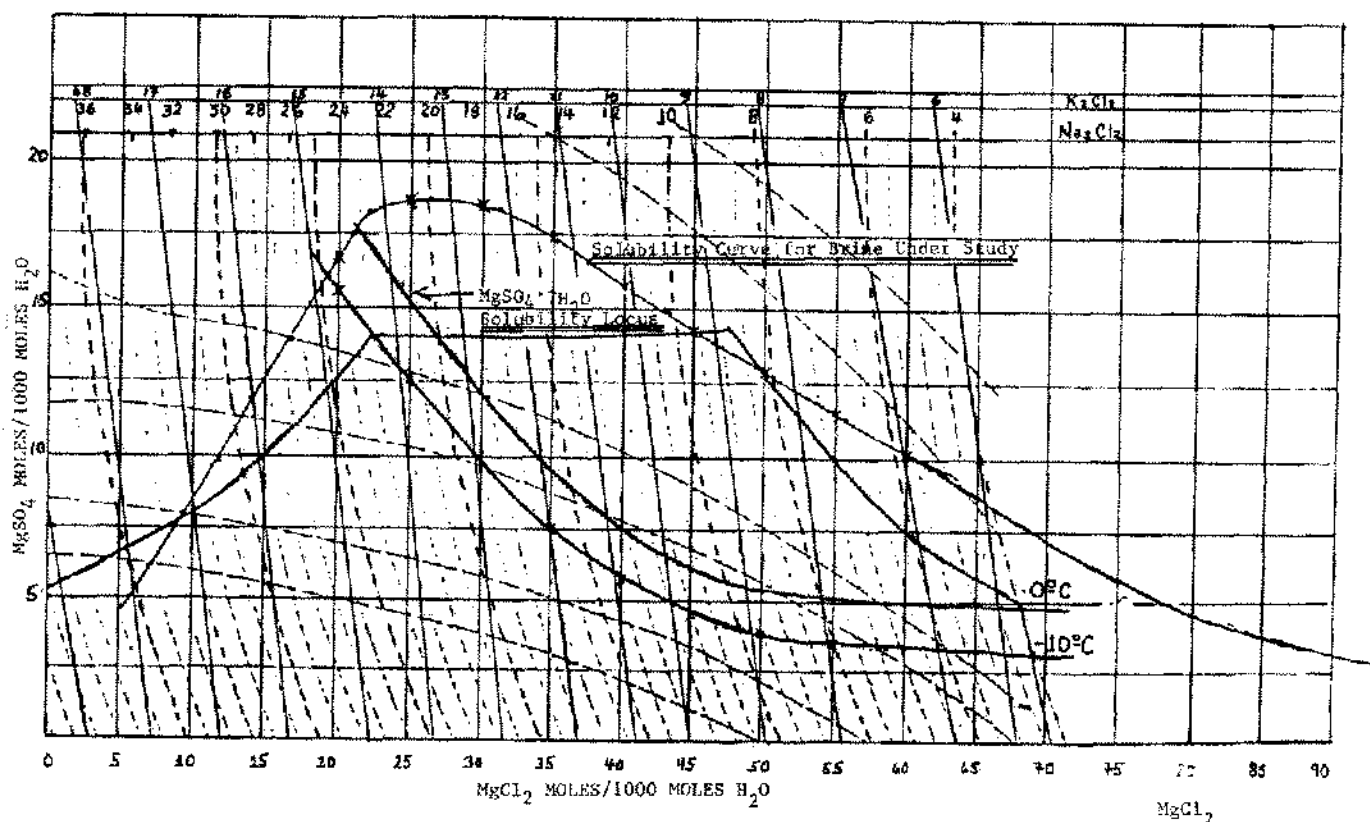


Chart 4. Solubility curve of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ (Autenrieth). K—Mg—Na—Cl— SO_4 phase diagram.

of magnesium hydroxide because of the low pH of the concentrated brines (in the order of 3) due to the influence of boric acid, which acts as a buffer.

EXAMPLE

An example of a flow sheet for this salting out process is given in Chart 8 (and 7). Several initial steps of solar evaporation and cooling are shown to illustrate what might occur in feed brine preparation. Epsomite, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ is easily crystallized from fairly strong brines (i.e., greater than 20 and preferably 30 to 65 moles MgCl_2 /1000 moles water) at lower temperatures, such as below 0°C , and preferably about -10°C . This can serve as the salting out agent directly, or it could be partially or totally dehydrated to avoid the slight dilution caused by its water content. For the brines under study the best MgSO_4 yields take place at 30 to 32 moles of MgCl_2 per 1,000 moles of water for the first cooling stage.

Brines of this type are generally evaporated to recover the potash (points 1 to 2) (KCl) or potassium sulfate (from point 2 to 3). If this is the case, any lithium that crystallizes before the salting out step can be redissolved in the potash processing and ultimately returned to the final brine. In most cases with these types of brines,

when reached a concentration greater than about 30 moles MgCl_2 /1,000 moles water they can be taken to a plant and cooled below 0°C to crystallize epsomite ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$). (Chart 8, point 3).

The resulting brine leaving the first cooling stage (point 4, Chart 8) can be concentrated again in solar ponds as far as 45 moles MgCl_2 per 1,000 moles H_2O (point 5). This stage must be carefully watched, otherwise upon further concentration lithium sulfate crystallizes.

The major salts crystallizing between 4 and 5 are halite and sylvite. The brines pertaining to point 5 are again cooled to -10°C , (45 to 50 moles of MgCl_2) and again epsomite is removed from the brine by a subsequent cooling stage. The yields of epsomite removal are 50% to 55% of the sulfate present in brines 3 and 5, respectively. Thus, approximately 80% of the original sulfate can be eliminated with two cooling stages for the feed brine under study.

Brine 6 is again concentrated in solar ponds up to point 7, just below a stage where lithium sulfate becomes saturated again. Brine 7 is then heated to 35 to 40°C and then the salting out agent added. As epsomite crystallizes with salt and potash, these can be removed by a mild leaching process. The salting out agent is added under strong agitation, yielding Brine 8 and a solid fraction, mainly lithium

Chart 5. Laboratory tests to check $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ solubility with salar brines K—Mg—Na—Cl— SO_4 phase diagram.

(Saturated with NaCl and KCl)

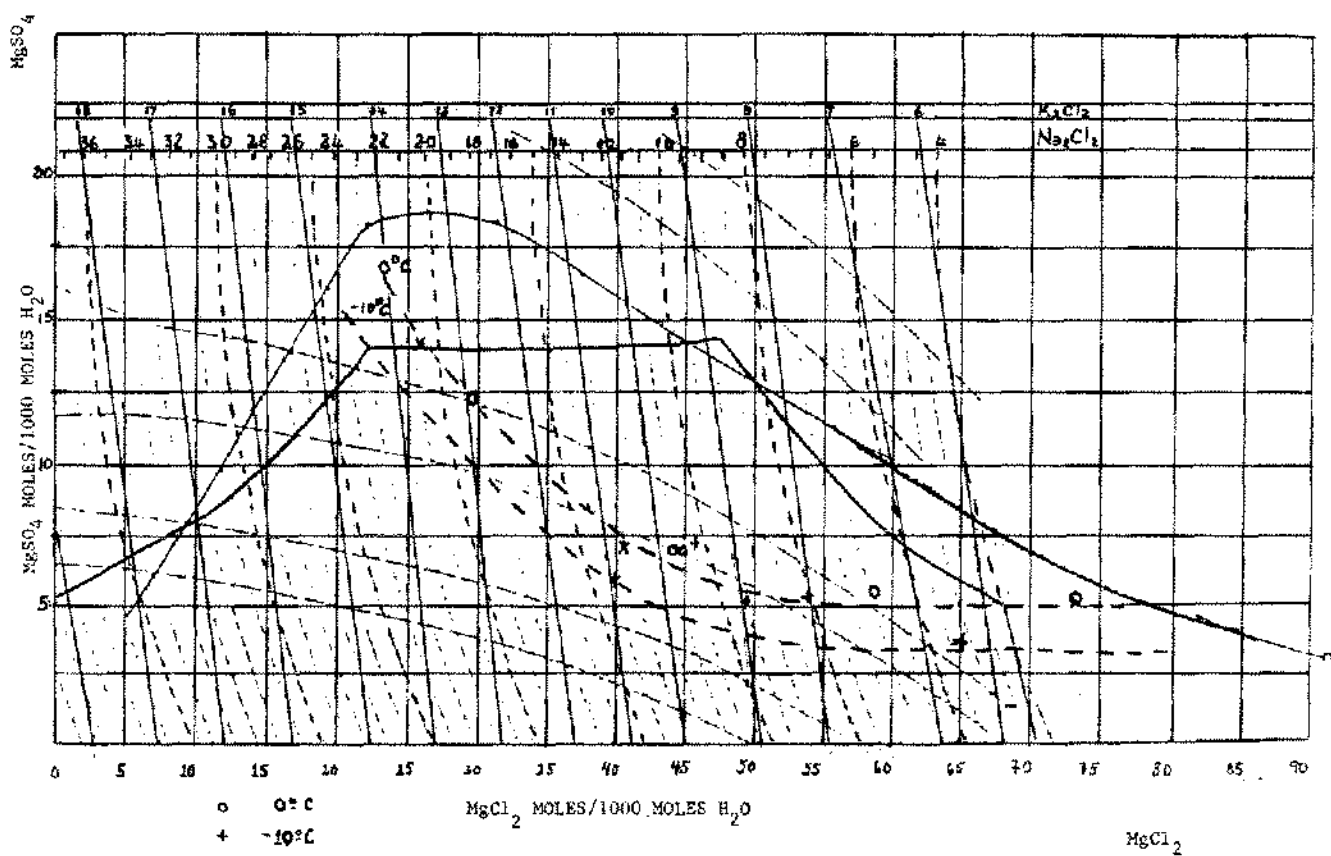


Chart 6. Evaporation path of brine under study.

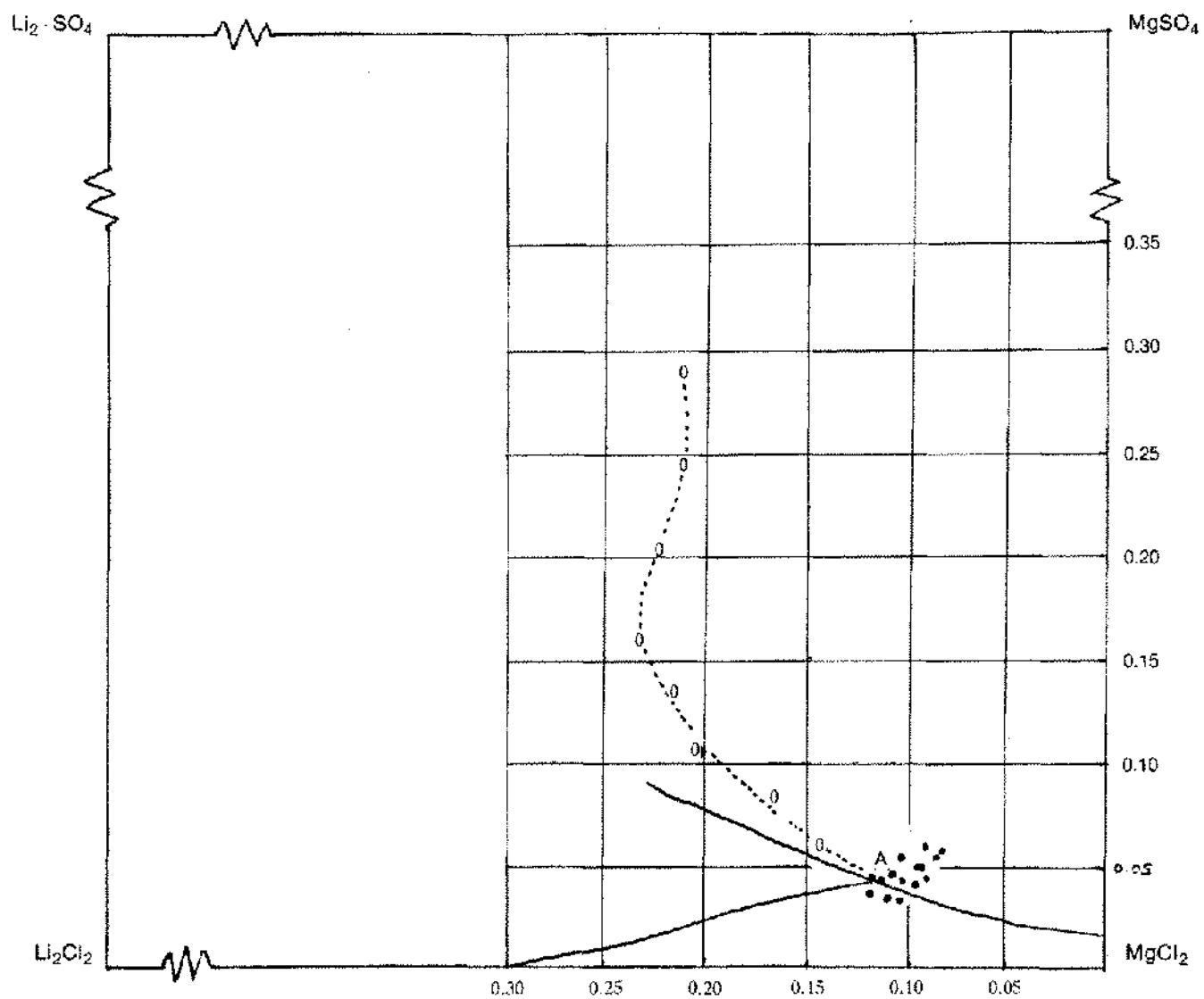


Chart 7.

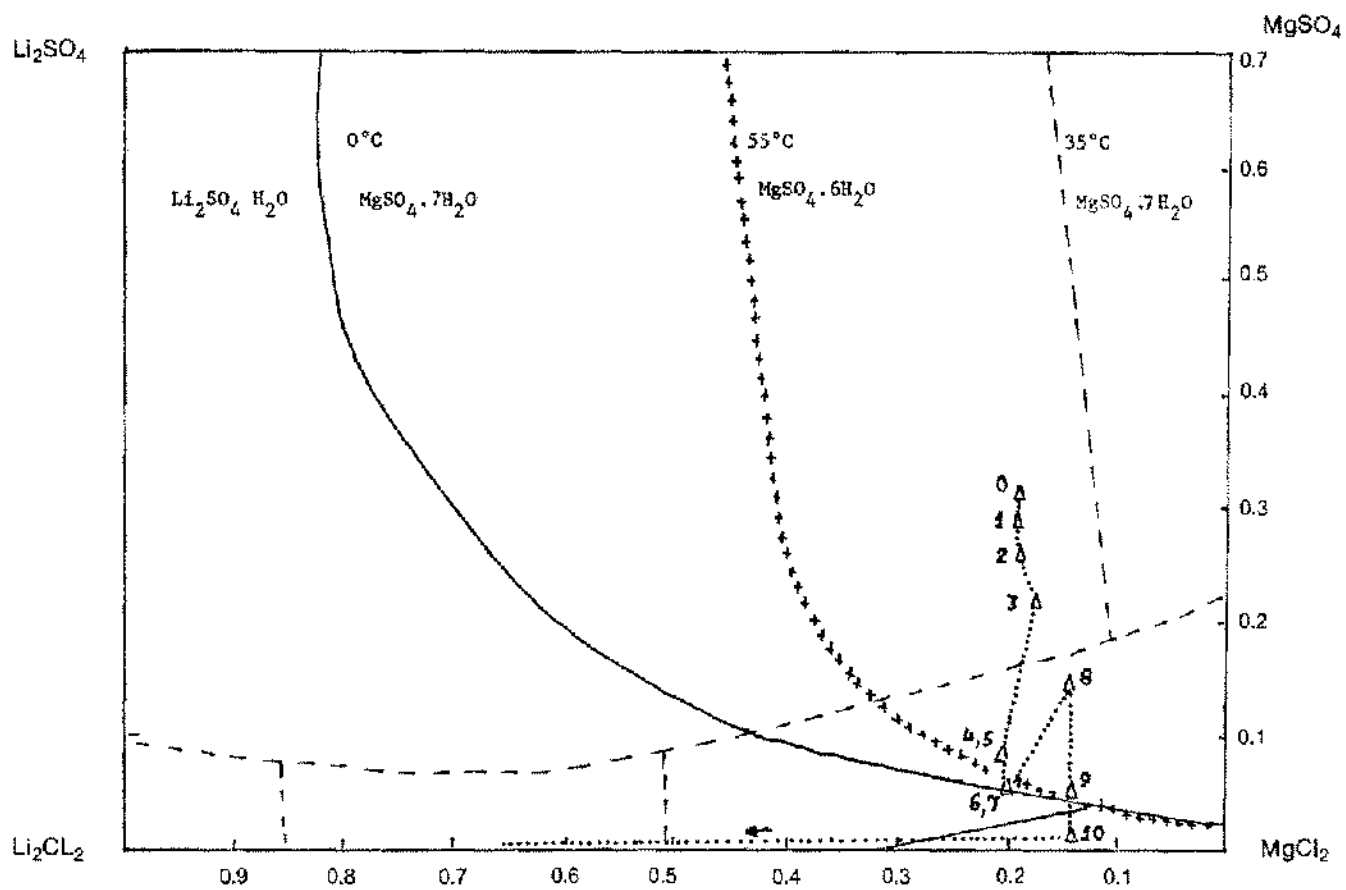
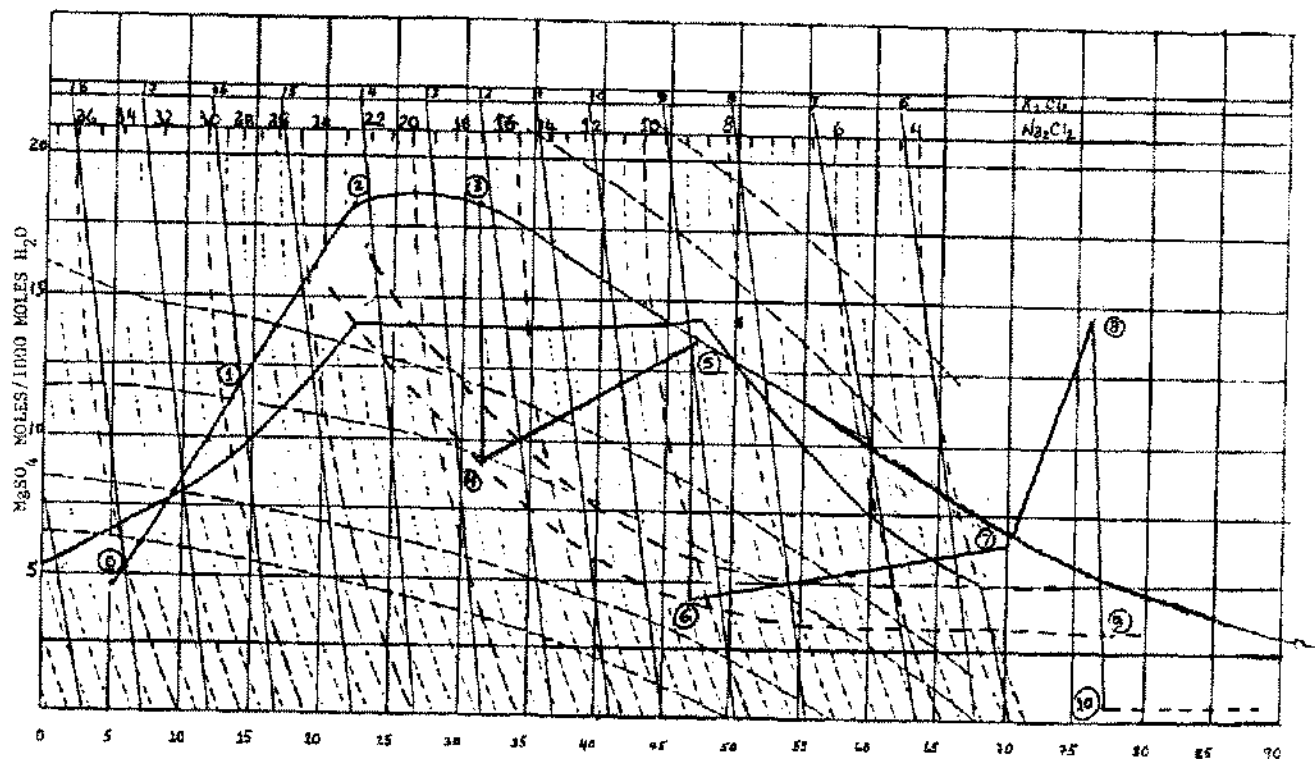


Chart 8. K—Mg—Na—Cl—SO₄ phase diagram.

(Saturated with NaCl and KCl)

25°C



sulfate monohydrate (see Table 1), which was separated. Filtered Brine 8 is then cooled to -10°C to eliminate epsomite, and Brine 9 is obtained.

At this stage a liming process is recommended, as pH is in the order of 3, thus 50% to 60% to the remaining sulfate is removed. Brine 10 may follow a subsequent concentration process to recover lithium by traditional methods as well as boric acid (when its concentration reaches 50 grams/liter) by the addition of hydrochloric acid.

A second means of representing the phase relationships of the salting out process is by a LiCl—MgSO₄ reciprocal salt pair diagram (Chart 7) where all other ions are ignored. Just as the Autenrieth diagram is reasonably accurate during the early stages of evaporation when the lithium concentration is low, near the end of the evaporation when magnesium chloride is the major component, lithium on a molar basis becomes by far the second major cation (see Table 1), and this diagram is reasonably accurate. Three different temperature isotherms are shown,

along with a typical evaporation path for this brine. The epsomite cooling operation is represented by lines 3-4 and 5-6, the salting out process by line 7-8, the last cooling stage by line 8-9, liming by line 8-10 and subsequent evaporation by 10 and beyond.

Summary

In summary, a process has been developed to rather simply recover lithium from brines by means of a salting out technique. The magnesium sulfate salting agent can be obtained from cooling the same brine at an early stage of evaporation. Enhanced evaporation techniques can be used to force the solar evaporation to a point where the lithium concentration is high enough to yield maximum recovery.

In Table 1 some experimental results are given for the salting out process, where it is shown that lithium sulfate (95.5%) is obtained with entrained epsomite.