

Influence of The Evaporation Rate Over Lithium Recovery From Brines

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Abstract - The brines of the South American Puna contain a great amount of valuables ions. Among them, lithium has the highest economic value; therefore, its grade and recovery are of interest in the purification steps of the brine. The first step of the process is brine concentration by solar evaporation. This process involves the precipitation of the ions which form saturated brines and a mass of crystals impregnated with mother liquor is obtained. The first salt that precipitates is sodium chloride (NaCl) because of their high initial concentration. When approximately 60% of the water is evaporated, a mixture of NaCl and KCl (sylvite) is obtained. This by product is used as raw material to obtain potassium chloride (KCl). The others ions present in the brine such as magnesium, calcium, and sulphate precipitate by adding a specific reagent (chemical precipitation). Sulphate and calcium precipitate as CaSO₄, and magnesium as Mg(OH)₂. The purified solution is sent to a final evaporation stage where the concentration of Li⁺ increases to about 6%. At each evaporation step, the ionic concentrations of the brine increases. In contrast its volume decreases. Also, the crystals obtained are soaked with a brine which is increasingly concentrated in lithium. Thus, the limiting factor to a greater degree of evaporation is the loss of Li⁺ with the rich solution accompanying the mass of crystals. This liquor is the limiting factor in the evaporation level when a higher lithium grade is required. In this paper a progressive evaporation of brines from the North West of Argentina was performed and analyzed, focused in the lithium recovery from the concentrated brine. For a given brine, it is shown that when the 64.3% of evaporation in volume is reached, the lithium concentration increases from 900 to 7,200 ppm. In this case, it is obtained a brine yield of 33.5 % in volume and a lithium recovery of the 28.1%. On the other hand, when the evaporation reaches 40% in volume, lithium recovery is 74%.

Index Terms - brines, crystallization, evaporation rate, lithium recovery, purification

I. INTRODUCTION

Lithium has found application in many industries, from the manufacturing of glass, ceramics, rubbers and pharmaceuticals up to production of lithium-ion batteries. In 2012, batteries were the second most common use and rapidly increased until reaching the first place [1], [2].

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Nowadays, markets are estimated as follows: batteries 35%; ceramics and glass 32%, lubricating greases 9%; continuous casting mold flux powders 5%, air treatment 5%, polymer production 4%, primary aluminum production 1%, and other uses 9% [1]. Lithium is used in three basic forms: ore and concentrates, metal, and manufactured chemical compounds (Table I). Lithium ores and brines are the present sources of all commercial lithium exploitation [3]. The reserves of lithium were estimated as 40 million tones Li⁺ [1].

Table I: Properties and uses of lithium compounds.

Compound	Property	Use
Ores and concentrates (spodumene, petalite)	Mechanical strength and thermal shock resistance	Glass, ceramic, and porcelain enamel
Lithium chloride brine	Low vapor pressures	Absorption refrigeration systems
Metal form	High energy density Temperature strength, improves elasticity, and increases the tensile strength	Rechargeable battery Lithium aluminum and lithium magnesium alloys
Lithium carbonate	Conductivity of the molten bath Energy efficiency	Aluminum reduction cells Molten carbonate fuel cells Ceramic industry
Lithium fluoride	Flux	Enamels, glasses, and glazes
Lithium hydroxide	To retain viscosity	Lubricating greases

According to USGS [4], worldwide lithium production increased slightly in 2015 in response to increased lithium demand for battery applications. Production in Argentina increased by about 17% and production in Australia and Chile increased slightly. Major lithium producers expected worldwide consumption of lithium in 2015 to be approximately 32,500 tons, an increase of 5% from 31,000 tons in 2014 [4].

Today, brines are an important source of lithium carbonate in the world. Due to the growing lithium demand from China in the past several years mineral-sourced lithium regained market share and was estimated to account for one-half of the world's lithium supply in 2015 [4]. Two brine operations in Chile and a spodumene operation in Australia accounted for the majority of world production. Argentina produced lithium carbonate and lithium chloride from

brines. China produced lithium carbonate, lithium chloride, and lithium hydroxide, mostly from imported spodumene, but also from domestic brines and minerals. A new brine operation in Argentina began commercial production in 2015 [4].

Economical concentrations of lithium have been recorded in several salars throughout the Puna region of Chile, Argentina, Bolivia and Peru as seen in Table II, [5].

Usually, the brine is saturated with salt, and contains variable concentrations of lithium, potassium, magnesium,

sulfate and borate depending on different locations in the salar.

Because of the very dilute concentration of lithium, even in the most favorable brines, and the expense of a direct recovering of lithium in a processing plant, solar evaporation of the brine to further concentrate it has been the necessary first step in all the current lithium obtaining process. Intrinsically solar evaporation is a very simple and inexpensive operation.

Table II: Compositions of various brines of commercial value of South America, wt. %.

Salar	Brine Composition, % wt/wt								Ratio Mg/Li
	Na ⁺	K ⁺	Li ⁺	Mg ⁺⁺	Ca ⁺⁺	Cl ⁻	SO ₄ ⁼	B	
Hombre muerto, (A)	9.450	0.550	0.076	0.120	0.070	15.800	1.050	0.044	1.600
Olaroz, (A)	---	0.573	0.069	---	---	---	---	0.105	2.800
Diablillos ,(A)	---	0.620	0.056	---	---	---	---	0.065	---
Ratones ,(A)	9.300	0.880	0.054	0.220	0.047	15.300	0.500	---	4.100
Pozuelos, (A)	9.300	0.240	0.049	0.243	0.235	15.700	0.260	0.025	5.000
Pastos grandes,(A)	10.000	0.810	0.035	0.400	0.045	15.200	0.800	---	11.400
Pocitos,(A)	9.200	0.670	0.005	0.300	0.035	15.000	0.990	---	60.000
Rincón,(A)	9.200	0.920	0.037	0.370	0.040	15.300	1.700	---	10.000
Arizaro,(A)	9.990	0.680	0.002	0.280	0.063	16.000	0.410	---	140.000
Atacama, (C)	9.100	2.360	0.157	0.965	0.045	18.950	1.590	0.044	6.100
Uyuni,(B)	7.060	1.170	0.032	0.650	0.031	14.800	1.080	0.071	20.200

A: Argentina, B: Bolivia, C: Chile.

Because of the high altitude (over 3,500 meters over sea level), high solar radiation (sunlight), very low humidity (only 5–10%) and usually some-to moderate wind, the water evaporation rate at the Puna’s salars is relatively high, in the range of 1,500-3,000 mm/yr. Besides the area’s average rainfall is only 10–70 mm/yr and the brine is generally at 20–70 cm from the surface.

In order to precipitate lithium as lithium carbonate, the brine must be concentrated up to nearly the concentration of a saturated lithium chloride solution (6% Li⁺)[3].The sequence of salts crystallized during solar evaporation depends on the initial composition of the brine. In the solar ponds halite crystallizes immediately while the brine is evaporated, and if low-sulfate brine is used, much of the potassium will be crystallized as sylvinit (KCl).

Products of 99.5% to 99.99% lithium carbonate can now be manufactured from purified brines. Evaporation followed by precipitation of K and Mg and, finally, solvent extraction or ion exchange to remove other impurities are the steps to purify brines [6], [7].

The brine leaving the sylvinit ponds can contain about 1% Li⁺, and it can be sent to the lithium ponds to be concentrated up to 6% Li⁺ [3]. Then, the first step is the evaporation of the salar brine, with 200 to 600 ppm Li⁺, approximately, up to a value near to 10,000 ppm Li⁺.

Laboratory and solar pond studies must be carried out to determine the phase chemistry of the different brine types when being evaporated. To maximize the overall

evaporation rate (which decreases with the brine concentration), each one of the salts in the brine may crystallize in separate ponds, which may be taken out of service periodically to remove (harvest) these salts. Thus, when the brine in the halite ponds becomes saturated with potassium chloride it is pumped to sylvinit ponds, which also are periodically taken out of service, drained and harvested, and their salts are sent to the potash plant storage–drainage piles. A permanent 20-30 cm thick floor of crystals must be maintained in the ponds to protect the membrane during harvesting, and the thickness of the deposited crystals must built-up to a minimum of 35-40 cm before being removed [8].

Crystallized salts are soaked with concentrated brine. Hamzaoui et al. (2000) [9] demonstrate the existence of retention phenomenon by the crystallized salts and determine the retention mode (coating solution, adsorption and substitution). This impregnating liquor causes Li loss.

This paper describes the results of an experimental study focused on the evaporation of brine in several stages until its content reaches 6% Li⁺. The influence of evaporation level on grade and recovery of Li⁺ ions is analyzed. These results are useful to determine the best operating conditions in order to minimize lithium loss when sodium and potassium chlorides are removed as well as to maximize the recovery of brine from harvested salts.

II. EXPERIMENTAL

For all the assays it was used brine from the Hombre Muerto salar (Argentina). Tests were performed at laboratory scale (with 1,600 mL of brine) and at pilot scale (with 230 liters).

At laboratory scale, each sample was evaporated up to reach a 10, 20, 30, 40, 50, 55, 60, and 65% of weight diminution.

The pulp obtained was cooled up to room temperature and after solid-liquid separation and drying the crystals, the volume and weight of the evaporated water were calculated, as well as those of the overflow liquid, cake impregnated with the brine, and dried solid. Finally, solid and liquid samples were chemically analyzed and the recovery and yield of ions of interest were calculated. Also, it was measured the height of the impregnated cake (h_c), the level of brine to evaporate (h^0), and the level of pulp after evaporation (h_p). Then, it was calculated how much diminished the level of the pulp due to water evaporation (h_{Aev}) and the height of brine that could be recovered (h_{S^r}). These parameters allow evaluating the yield of the brine in the ponds (1), (2), and (3).

$$h_{Aev} = h^0 - h_p \quad (1)$$

$$h_{S^r} = h_p - h_c \quad (2)$$

$$\eta(\%) = h_{S^r} / 100 / h^0 \quad (3)$$

To study treatment cycles (as they occur at salt ponds) it was used 2,000mL of brine. Over the same sample were carried out consecutive evaporation-cooling and solid-liquid separations until were reached 20, 30, and 45 % of weight diminution.

The chemical analysis of liquids shows the evolution of ions concentration during evaporation.

Finally, a test at pilot scale was performed. The brine evaporation was conducted by continuous boiling in a heating coil agitated tank up to 30% of weight diminution. The concentrated liquors were separated from the precipitated solids by centrifuge filtration. Liquid samples were analyzed chemically in the same way as those of laboratory scale.

Concentrations of Ca^{2+} , Mg^{2+} , Na^+ , Li^+ and K^+ were determined by AAS (Shimadzu AA6051F). The SO_4^{2-} present was analyzed by gravimetry, where $BaSO_4$ precipitates because of the $BaCl_2$ added. The Cl^- was analyzed by Mohr method using a titrated solution of $AgNO_3$, and B_2O_3 was analyzed by a volumetric method based on the reaction between boric acid and manitol and titration with $Na(OH)$. The boric acid is a very weak acid, and the manitol is used to increase its acidity, allowing the titration using phenolphthalein as indicator.

III. RESULTS AND DISCUSSION

Chemical composition and yield (% wt) of liquids of laboratory scale test are shown in Table III.

Table III: Brines composition

Test N°	Evaporated water %	Brine Composition, wt%									Yield wt%
		Li^+	Na^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-	SO_4^{2-}	B	HCO_3^-	
1	0	0.09	9.00	0.57	0.27	0.23	16.09	0.20	0.04	0.46	100
2	13.9	0.11	8.23	0.71	0.33	0.27	16.09	0.20	0.05	0.55	80.8
3	22.5	0.13	8.14	0.81	0.39	0.32	15.73	0.18	0.06	0.63	69.0
4	34	0.17	7.78	1.09	0.58	0.41	16.20	0.16	0.08	0.79	52.8
5	41.2	0.20	7.37	1.27	0.70	0.45	16.84	0.16	0.09	0.91	43.2
6	47.7	0.24	6.92	1.61	0.86	0.56	17.06	0.11	0.12	1.20	33.7
7	55.9	0.35	5.90	2.38	1.21	0.78	17.34	0.09	0.17	1.74	22.6
8	61.3	0.50	4.35	3.54	1.76	1.13	18.96	0.07	0.25	2.46	15.3
9	64.3	0.72	3.14	3.18	2.36	1.44	19.98	0.07	0.30	3.39	10.0

As it was said before, height of every phase was measured. Fig. 1 shows the volumetric yield of each phase (evaporated water, concentrated brine to recover, and impregnated cake) expressed as meters of height refer to 1 meter of initial brine height.

It can be seen that when evaporation increases it also increases the fraction of pulp occupied by the impregnated cake and diminishes the volume of concentrated brine that can be recovered.

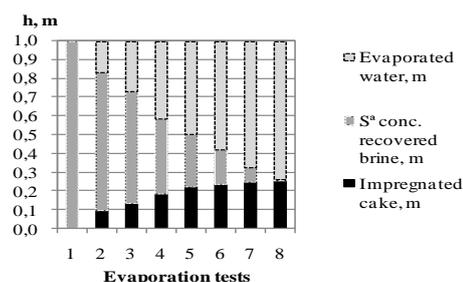


Figure 1: Volumetric yield after the evaporation.

At the salar, the solid obtained due evaporation is not filtered. It caused Li^+ losses with the brine which impregnated the cake. These Li^+ losses are shown in Fig.

2a and 2b. Two kind of Li⁺ recovery are defined and also shown. One of them is considering the Li⁺ contained in the original brine (maximum recovery). The other one (real recovery) considers the Li⁺ contained in the brine that can be industrially recovered.

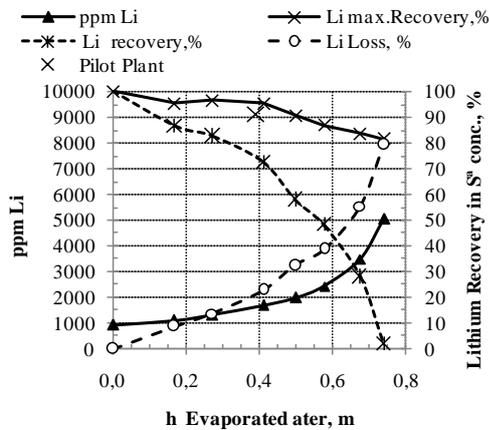


Figure 2a: Lithium recovery from the brine as function of height of evaporated water.

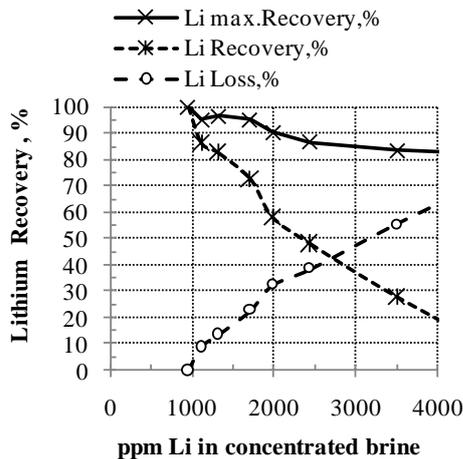


Figure 2b: Lithium recovery as function of Li⁺ content

The difference between these two recoveries corresponds to the Li⁺ losses with the liquor which impregnates the cake. Industrially to recover more than 80% of Li⁺ the pulp height must diminish no more than 0.32 m (Fig. 2a). Therefore, recovery is a limitation factor in the increase of the lithium grade in the concentrated brine.

Fig. 3 shows the relation between Li⁺ grade increase (ΔLi) and pulp height diminution (Δh) (4):

$$r = \Delta Li / \Delta h \quad (4)$$

From there, it grows exponentially. Concentration of Li⁺, K⁺, Mg²⁺, Ca²⁺ grows continuously and exponentially as evaporation increases, while Na⁺ and SO₄²⁻ concentration decreases due to their precipitation as NaCl and CaSO₄ (Fig.4a).

Every ion which remains in solution without crystallizing follows (5) while evaporation is less than 25% (Fig.4b).

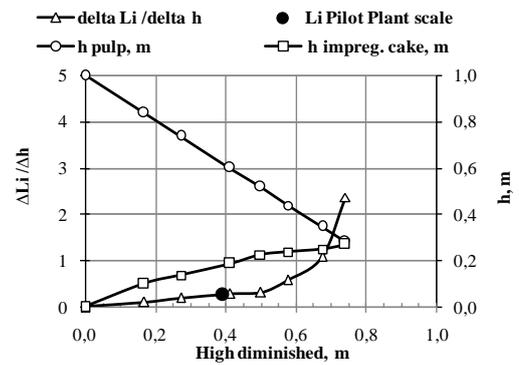


Figure 3: Lithium grade increase by evaporation.

The r increase is linear up to 0.5 m of pulp height diminution (equivalent to 0.5 m of evaporation).

$$C_f C_i = 1 / (1 - \% \text{ ev}). \quad (5)$$

In solution Ca²⁺ comes from CaCl₂ and its amount is greater than CaSO₄ solubility at room temperature; so, SO₄²⁻ concentration would be given by (6), less than CaSO₄ solubility in water.

$$[SO_4^{2-}] = k_{ps} [CaSO_4] / [Ca^{2+}] \quad (6)$$

In NaCl-KCl system, both solid phase coexist at 5.34% K⁺ and 7.88% Na⁺ [11].

Crystallization of KCl occurs when K⁺ is greater than 5.34% and Na⁺ is less than 7.88%. In our system, maximum values for K⁺ (see Table 3) are minor than 5.34% so we can assure that KCl does not precipitate along with NaCl.

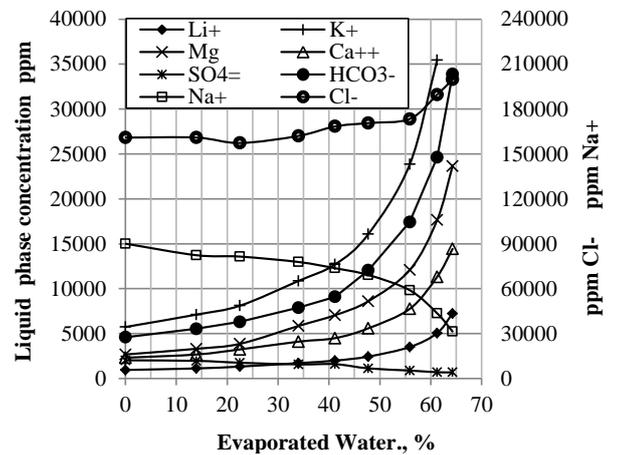


Figure 4a: Concentration ions for continue evaporation.

IV.CONCLUSIONS

When the brine is evaporated, the Li^+ grade and recovery is influenced by the evaporation ratio.

If evaporation is around 64% in volume, lithium concentration increases from 947 to 7,232 ppm, the brine yield is of 35.7% in volume, and Li^+ recovery is of 28.1%. The loss of Li^+ recovery is about 55%.

Industrially to recover more than 80% of Li^+ , the pulp height must diminish no more than 0.32 m. So, recovery is a limiting factor in the increase of the lithium grade in the concentrated brine. Height of pulp could be used as control tool.

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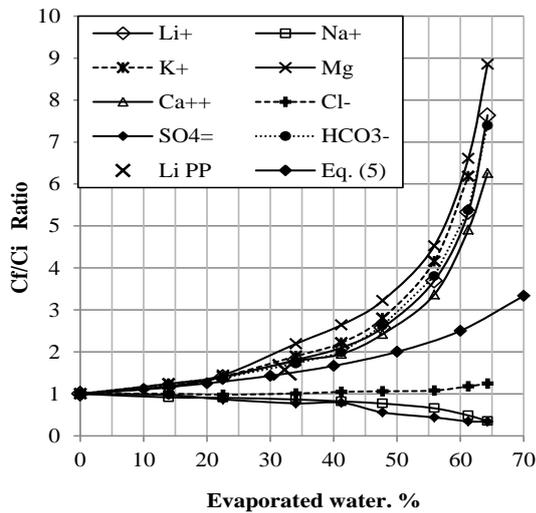


Figure 4b: Ions concentration for continue evaporation.

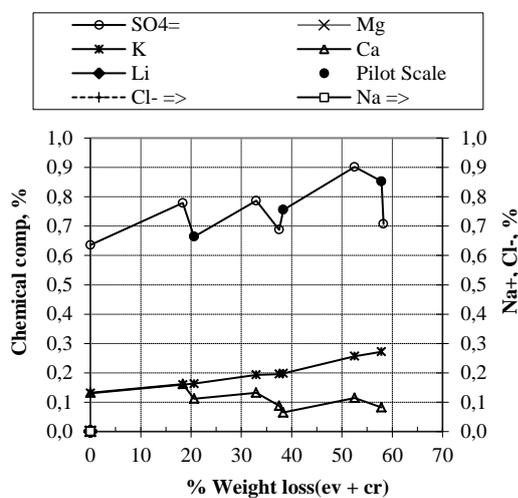


Figure 5: Concentration in liquid phase for evaporation in cycles.

For evaporations up to 61.3% the solid phase composition is 97.6% of NaCl and 1.4-1.6% of CaSO_4 . Other ions in this phase come from the impregnating liquor.

Fig. 5 shows the results of the test of evaporation-crystallization cycles. In this case the sample contains excess of SO_4^{2-} to precipitate CaSO_4 .

It can be seen from Fig. 5 that Li^+ , K^+ and Mg^{2+} concentration grow up continuously as in Fig. 4a. Na^+ , Ca^{2+} , Cl^- , and SO_4^{2-} increase their concentration while evaporating at 50°C and then decrease them after cooling and crystallizing at 16°C.

Pilot scale test was performed using 230 liters of pre-concentrated brine (1,857 mg Li^+ /L). After evaporating 32.3% of weight the height of pulp, impregnated cake, recoverable brine and evaporated pulp (Table III) are coincident with those obtained at laboratory scale (See Fig. 2a). The crystallized salt contains 97.44% of NaCl, with granular appearance, and 88.7% of crystals size are of 0.25 and 1.0 mm, the medium size is 0.43 mm.