Extraction of Lithium from Brine – Old and New Chemistry

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Abstract

Conventionally, lithium-bearing brines are processed via solar evaporation, chemical purification and either electrolysis to lithium hydroxide or precipitation of lithium carbonate. Lithium-ion battery technology and electric vehicles are forecast to greatly increase the demand for lithium, but not all lithium-bearing brines are amenable to the conventional extraction process and new approaches are being developed. The chemistry associated with conventional lithium extraction is outlined and two new approaches are discussed.

Introduction

The drive towards renewable energy and the lithium-ion battery technology that is enabling the rise of the electric vehicle have made lithium an element of great current interest. Garrett [1] lists known reserves of lithium in brines and ore deposits, as summarised in Table 1.

Table 1 – Estimated lithium quantities [1]

Region	Thousand tonnes Li	
	Brine	Ore
South America	8800	4
North America	2588	327
China	2000	500
Australia		160
Europe/Middle East	2000	10
Russia		130
Africa		368

The annual demand for lithium, expressed as lithium carbonate equivalent (LCE - the lithium content of a lithium product expressed as lithium carbonate), is forecast to be over five million tonnes by 2025 [2]. The numbers in Table 1 add up to a total of 90 million tonnes of LCE, about 90 percent of which is contained in the various brine resources. This would be enough to sustain an annual demand of five million tonnes for 45 years before we exhaust the reserves, assuming no more are found, leaving us plenty of time in which to develop a robust recycling industry once the quantity of lithium in spent lithium-ion batteries becomes large enough. On the face of it, that would appear to make the supply of lithium less of a problem than is actually the case. The reality is that the established technology cannot economically process all of the known brine reserves.

Brine

Table 2 lists composition ranges found in different brine types [1]. The only one being exploited commercially at present is salar brine. The usual lithium product from salar brines is lithium carbonate, but lithium hydroxide can also be produced.

Table 2 – Brine compositions [1]

Assay	Geothermal brine	Salar brine	Oilfield brine
Fe	1200 - 3700	-	35 -41
Mn	1000 - 2000	-	25 - 30
Zn	800 - 700	-	-
Mg	700 - 5700	2 - 9650	2900 - 3500
Ca	22600 – 39000	300 - 530	29100 - 34500
Na	50000 - 70000	65000 - 910000	54900 - 67000
K	13000 - 34200	18500 - 31300	2400 - 5900
Li	100 - 400	1500 - 2420	146 - 386
Cl	142000 – 209000	159000 - 189500	144500 - 171700
SO$_4$	42 - 50	8000 - 19000	375 - 450
B	400 - 500	400 - 685	123 - 366
Si	40	-	90

Current chemistry

Established technology for extracting lithium from salar brines uses solar evaporation, in which most of the water in the brine is lost to the atmosphere. Various salts are precipitated during this process [1]:

Halite (NaCl);
Halite and sylvite (KCl) as a mixture of NaCl and KCl called sylvinite;
Halite, sylvite and potassium lithium sulphate (KLiSO₄);
Halite, kainite (KCl•MgSO₄•2¾H₂O) and lithium sulphate (Li₂SO₄•H₂O);
Halite, carnallite (KCl•MgCl₂•6H₂O) and lithium sulphate;
Bischoffite (MgCl₂•6H₂O);
Bischoffite and lithium carnallite (LiCl•MgCl₂•7H₂O).

Precipitation of salts containing lithium would reduce the ultimate recovery of lithium. In cases in which the incoming brine contains enough magnesium or enough sulphate for lithium losses to precipitating salts to occur, the magnesium can be precipitated as magnesium hydroxide via the addition of lime, either before solar evaporation or at some point in the evaporation sequence.

When lime is added to a brine to precipitate magnesium, if the brine also contains sulphate, at least some of the added calcium can be removed from the liquid phase as gypsum or anhydrite, depending on the exact conditions. However, the solubility of gypsum or anhydrite is governed by the relevant solubility product, therefore decreasing the concentration of sulphate by precipitating gypsum or anhydrite requires the concentration of calcium to increase, simply due to the equilibrium:

$$Ca^{2+} + SO_4^{2-} \leftrightarrow CaSO_4 \qquad \text{or} \qquad Ca^{2+} + SO_4^{2-} + 2H_2O \leftrightarrow CaSO_4 \bullet 2H_2O$$

Adding lime to a salar brine, therefore, does not reduce the concentration of cations in the brine; it merely replaces whatever ions are precipitated with divalent calcium ions.

Some salar brines also contain boron, which needs to be removed before the recovery of lithium because lithium metal is made by electrolysis in a eutectic bath of LiCl-KCl [3]. Non-volatile
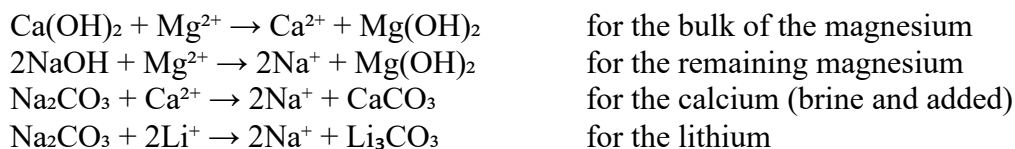
anions such as sulphate and borate accumulate in the electrolyte, resulting in rapid short-circuiting of the electrolysis cells [4]. When the level of calcium is sufficient, much of the boron in the brine precipitates as calcium borate salts as the evaporation proceeds [4]. Whatever boron is not precipitated can be removed by solvent extraction and ion exchange [5,6].

Divalent cations, particularly Ca^{2+}, precipitate ahead of lithium when carbonate is added to the system. This is exploited to purify the concentrated brine ex solar evaporation. The pH is raised with sodium hydroxide to above the maximum level (about pH 10) that $Mg(OH)_2$ can achieve and a slight stoichiometric excess (based on the Ca^{2+} in the solution) of sodium hydroxide is added. This causes most of the Mg^{2+} in the brine at that point to be precipitated as magnesium hydroxide and most of the Ca^{2+} to be precipitated as calcium carbonate.

The solution ex this step can be treated by ion exchange using a sodium-loaded strong acid resin to polish out essentially all of the residual divalent cations, and then again using a boron-specific weak base anion exchange resin to remove essentially all the boron. The chemistry of these two ion exchange steps would depend on the resins selected.

The purified solution can be further concentrated by evaporation or reverse osmosis (or a combination) if required. Then sodium carbonate can be added to precipitate lithium carbonate. In Figure 1, the left-hand graph shows the solubility of sodium carbonate and lithium carbonate in water. The vertical axis is logarithmic. The higher the concentration of lithium in the purified solution, the higher the per-pass recovery of lithium to the precipitated lithium carbonate.

An overall stoichiometric sequence covering the chemistry would be:

$$Ca(OH)_2 + Mg^{2+} \rightarrow Ca^{2+} + Mg(OH)_2 \qquad \text{for the bulk of the magnesium}$$
$$2NaOH + Mg^{2+} \rightarrow 2Na^+ + Mg(OH)_2 \qquad \text{for the remaining magnesium}$$
$$Na_2CO_3 + Ca^{2+} \rightarrow 2Na^+ + CaCO_3 \qquad \text{for the calcium (brine and added)}$$
$$Na_2CO_3 + 2Li^+ \rightarrow 2Na^+ + Li_3CO_3 \qquad \text{for the lithium}$$

If the resulting lithium carbonate is not pure enough, it can be purified by re-dissolution in water and carbon dioxide [7]. The carbon dioxide converts the carbonate to bicarbonate, thereby dissolving the lithium carbonate. In Figure 1, right-hand graph shows the solubility of lithium in water over a range of pressures of carbon dioxide at ambient temperature.
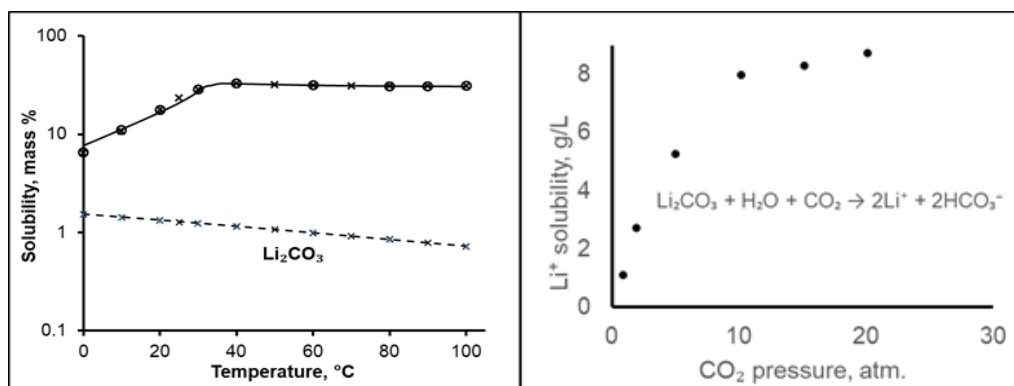

Figure 1 – Solubility in water and in water/CO₂

Calcium carbonate does not re-dissolve and can be filtered out before the solution of lithium bicarbonate is depressurised and heated, causing it to release CO_2 and re-precipitate purified lithium carbonate.

The ion exchange steps would also consume small amounts of HCl and NaOH for elution and regeneration. As an overall approximation, though, every mole of divalent cation in the brine is replaced with two moles of sodium, from NaOH or Na_2CO_3. The amounts of NaOH and Na_2CO_3 required are therefore set by the composition of the salar brine, which needs to carry enough lithium relative to the other cations to more than carry the cost of the NaOH and Na_2CO_3 needed to displace the other cations from the brine. This approximation does ignore the other reagents and utilities (such as hydrochloric acid, power, water) required by the process.

Major reagent costs – established chemistry

Using this approach and assuming the mid-points for the analyses of each brine shown in Table 2 leads to the major reagent requirements and costs listed in Table 3.

Table 3 – Calculated major reagent requirements

Reagent		Requirement, kg/kg LCE			Cost, $/kg LCE		
Reagent	US$/t	Geothermal	Salar	Oilfield	Geothermal	Salar	Oilfield
CaO	150	9.0	1.1	5.3	1.4	0.2	0.8
NaOH	560	0.1	0.02	0.1	0.1	0.0	0.2
Na_2CO_3	370	69.5	1.8	61.2	25.7	0.7	22.6
				Sub-total	27.1	0.8	23.5

The unit costs for CaO, NaOH and Na_2CO_3 in Table 3 were taken from the NI 43-101 technical report on the Cauchari-Olaroz project [8], rounded two significant figures. The reagent costs calculated for the other two brines are more than an order of magnitude greater than that of the salar brine because of the amount of Ca^{2+} that has to be replaced with Na^+ from Na_2CO_3.

Figure 3 is an image taken from The Statistics Portal [9], showing the annual average price of battery grade lithium carbonate.
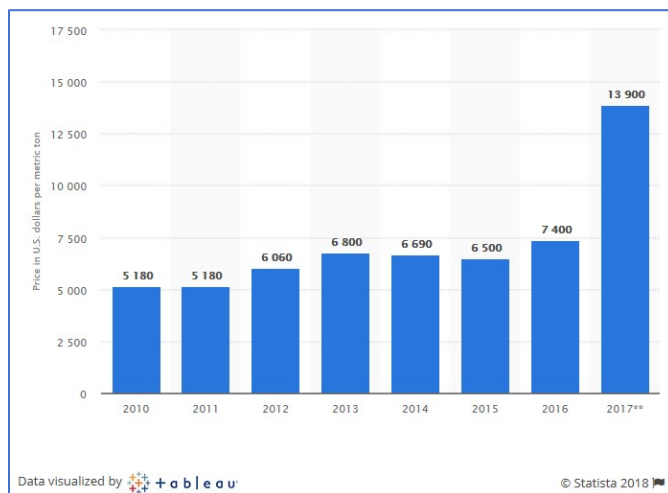

Figure 2 – Price of lithium carbonate, $/tonne LCE

Prior to 2016 the price was below $7.5/kg and in 2017 it was $13.9/kg. Unless and until the price of lithium carbonate rises substantially higher than about $30/kg, the established chemistry used to extract lithium from salar brines will not be applicable to the other brines.

While established, the chemistry outlined above also has these drawbacks:

- Solar evaporation loses most of the water in the brine to the atmosphere, thus the aquifer is depleted of its water. While it could be argued that this does not matter because the water will return as rain, that rain is unlikely to occur at the salar concerned, because salars are by nature found in arid regions.
- Solar evaporation of the brine generates large amounts of chloride salt that must be disposed of on large dumps, precluding other uses for the land area concerned. Again, this may not matter because the salar is in a sparsely populated, arid region. Even so, increasingly stringent environmental constraints could mitigate against new projects using the established chemistry to extract lithium from salar brines.
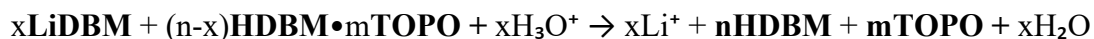
Chemistry using lithium-selective solvent extraction

An approach that does not require solar evaporation, and therefore will not deplete the aquifer of water or generate large dumps of salt, is enabled by solvent extraction technology that very selectively extracts lithium away from other monovalent cations. The Clayton Valley Lithium Project [10] uses this solvent extraction to very selectively extract lithium from a feed brine of the composition shown in Table 4. A facet of the solvent extraction system used is that it is only selective for lithium against other monovalent cations, and higher-valent cations are extracted ahead of lithium. Therefore, higher-valent cations (Ca^{2+}, Mg^{2+}, etc.) need to be fully removed from the brine ahead of the solvent extraction step. The Clayton Valley Lithium Project uses membrane technology, the membrane selected for its ability to allow monovalent cations to pass while blocking the passage of higher-valent ions. The composition of the permeate obtained is shown in Table 4.

Table 4 – Clayton Valley feed brine and permeate, mg/L

Brine	Mg	Ca	Na	K	Li	SO₄	B
Feed brine	409	796	38400	3850	209	4740	26
Permeate	<3	<3	35900	3670	210	<3	21

Lee et al. [11] give the following stoichiometry for the selective solvent extraction of lithium, the bold print denoting the organic phase:

$$xLi^+ + xOH^- + \mathbf{nHDBM} + \mathbf{mTOPO} \rightarrow x\mathbf{LiDBM} + (n\text{-}x)\mathbf{HDBM} \bullet \mathbf{mTOPO} + xH_2O$$

$$x\mathbf{LiDBM} + (n\text{-}x)\mathbf{HDBM} \bullet \mathbf{mTOPO} + xH_3O^+ \rightarrow xLi^+ + \mathbf{nHDBM} + \mathbf{mTOPO} + xH_2O$$

TOPO means trioctylphosphine oxide and HDBM means dibenzoylmethane (1,3-diphenyl-1,3-propanedione). The above stoichiometry could equally well have been written without the OH⁻ ion on the left and with a proton on the right instead of water. The proton released by the extraction has to be neutralised, and sodium hydroxide is the most convenient base. That means that the selective solvent extraction of lithium replaces each Li^+ cation extracted with one Na^+ cation. The membrane separation ahead of the solvent extraction stage removes the need for other reagents ahead of solvent extraction. Anions are not extracted, therefore there is no need to remove boron or sulphate from the feed to the solvent extraction step, although the membrane step ahead of that does reject sulphate.

In the chemistry selected for the Clayton Valley Project, the loaded organic phase is stripped with sulphuric acid in the anolyte from electrochemical cells with cation-selective membranes between the anode and cathode compartments. The stripping step, of course, removes the lithium from the loaded organic phase, replacing it with protons from the anolyte. The stripped organic phase and the lithium-replenished anolyte are recycled.

Minor amounts of sodium hydroxide and sodium carbonate are used to precipitate the very small amounts of divalent cations leaking through the membranes in the preceding step, plus a polishing ion exchange step between the stripping and electrochemical steps. The only reagent used in significant quantity in the overall chemistry is sodium hydroxide.

Using the same logic as was used in developing the overall stoichiometry for the established chemistry leads to the results shown in Table 5. The electricity cost is for the electrolysis of lithium sulphate to sulphuric acid and lithium hydroxide. This number was taken directly from the operating costs given for the Clayton Valley Project [10]. The chemistry selected for the Clayton Valley Project would appear to have an appreciable cost advantage over applying the established chemistry to that feed brine.

Table 5 – Established and new chemistry applied to Clayton Valley brine, $/kg LCE

Reagent	Cost, $/t	Established chemistry	New chemistry
CaO	150	0.1	0
NaOH	560	0	0.6
Na_2CO_3	370	1.3	0
Electricity		-	0.4
Sub-total		1.5	1.1

Chemistry using lithium-ion sieves

Another approach, that has not yet been part of any published work on project feasibility, also does not require solar evaporation. This approach is based on a class of materials referred to as lithium-ion sieves (LIS) [12,13]. One of these materials is made from titanium dioxide and lithium carbonate or lithium hydroxide, forming Li_2TiO_3 that is then contacted with dilute acid which converts it to H_2TiO_3. When the H_2TiO_3 is contacted with lithium-bearing solution under alkaline conditions, a solid-state exchange reaction takes place, with protons leaving the solid phase and being replaced by lithium ions from the liquid phase. Lithium and protons are the only cations small enough to penetrate the crystal structure of the solid phase. The magnesium cation is similar in size to the lithium cation, but is much more strongly hydrated, which prevents it from being able to shed its hydration sheath and enter the solid phase. Once loaded, the material is recovered, washed to remove entrained brine and stripped with dilute acid, giving a strip solution greatly purified in lithium and also regenerating the H_2TiO_3, which is recycled. Limjuco et al. [14] published the data shown in Table 6.

The literature reports that protons expelled from the H_2TiO_3 in the loading step limit the amount of Li^+ that can be loaded, and that a high pH needs to be maintained for the maximum loading. If sodium hydroxide is used to maintain a high pH in the loading step, the loading chemistry exchanges lithium ions for protons that are in turn neutralised with NaOH, effectively replacing Li^+ with Na^+ in the feed solution. The great advantage of the LIS materials is that, unlike the lithium-selective solvent extraction, lithium can be selectively removed from solutions that also

contain divalent cations such as Ca^{2+}, Mg^{2+}, etc. That removes any need to remove those ions ahead of the lithium extraction step. Anions like sulphate and borate are not extracted, therefore sulphate and boron do not need to be removed from the feed brine.

Table 6 – Published selectivity values for of LIS materials

Sea water		mmol/kg		Selectivity
Ion	mg/kg	Dissolved	Adsorbed	Li/Other
Li^+	0.18	0.02593	1982.4	-
Na^+	10561	459.38	235.3	149242
K^+	380	9.72	135.3	5491
Mg^{2+}	1272	52.33	94.1	85012
Ca^2	400	9.98	94.1	16212

Simplistically, stripping the loaded LIS with HCl would require one mole of HCl per mole of lithium stripped. If the resulting strip solution is used to precipitate lithium carbonate, that would consume one mole of sodium carbonate per mole of lithium carbonate produced. Copying the logic used for the other chemistry and assuming that the levels of divalent cations in the strip solution are low enough that precipitating them as hydroxide or carbonate requires amounts of sodium hydroxide and carbonate too small to register in these overall calculations, this leads to the results shown in Table 7. The reagent cost calculated for making lithium carbonate via this new lithium-ion sieve chemistry is slightly below the number calculated for applying established chemistry to the Clayton Valley Project, and the same as for producing lithium hydroxide in the Clayton Valley Project.

Table 7 – Lithium-ion sieve chemistry producing Li_2CO_3 or LiOH, \$/kg LCE

Reagent	Cost, \$/t	Li_2CO_3	LiOH
HCl	240	0.1	0
NaOH	560	0.6	0.6
Na_2CO_3	370	0.5	0
Power		-	0.5
Sub-total		1.3	1.1

At this level of analysis, the LIS-based chemistry gives the same calculated major reagent (and power, in the case of making lithium hydroxide) costs, regardless of the type of brine, thus this approach would seem to be applicable to high-calcium brines that are not amenable to the established chemistry.

Conclusion

The established chemistry for producing lithium carbonate from salar brines would appear to be applicable only to salar brines. Extracting lithium from other brines will need new chemistry, two variations of which have been presented.

At the calculated reagent cost of about \$0.8/kg LCE, the established chemistry appears to have an economic edge over the other two, but only for salar brines. As can be seem from Table 3, the

non-salar brines, because they carry so much more calcium, are clearly not accessible to the established chemistry.

This paper presents an extremely "high-level" overview of the technology for extracting lithium from brines. Minor reagent costs, utility costs, fixed operating and maintenance costs etc., have been ignored. While it does uncover some differences between the established and the new chemistry and indicates that the new chemistry may well be amenable to brines tat the established chemistry cannot process economically, this paper is not meant to denigrate or endorse either the established or the emerging chemistry for lithium extraction from brine.

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Presented at the Critical Materials Symposium, EXTRACTION 2018, Ottawa, August 26-29