

AQUEOUS CHEMISTRY OF LITHIUM PRODUCTION

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ABSTRACT

This paper presents an overview of the aqueous chemistry found in lithium processing. The sulphate and chloride systems are examined via modelling of the relevant chemistry. Examples used are the purification and extraction of lithium from sulphate solutions arising from processing spodumene and clay, as well as concentrating, purifying and precipitating lithium carbonate from a generic salar brine.

The recovery of lithium from brine entails the solar evaporation of large volumes of chloride brine, with various salts crystallizing as evaporation proceeds. However, it is also necessary to pump the concentrated brine, and pumping a solution saturated in any given salt can suffer from scaling that blocks lines and foul pumps. For that reason, the saturated brine is usually diluted with fresh water before being pumped. This partially undoes the evaporation, so the amount of water added is important. This paper includes a study of scaling tendencies versus dilution at the various stages of solar evaporation.

Concentrated chloride brines are corrosive, and this paper presents a brief look at the effect of pH on the rates of corrosion on carbon steel and duplex stainless steel in chloride brine.

Keywords: Lithium, potassium, brine, aqueous chemistry, scaling, corrosion, potash.

INTRODUCTION

The rise of electric vehicles enabled by lithium-ion battery technology has made lithium an element of great interest^(1,2). Known resources of lithium are pegmatite deposits, lithium-bearing clays and lithium-bearing brines⁽³⁾. Lithium minerals of commercial significance are listed in Table 1. Lithium-bearing brines account for about 90 percent of the total known reserves of lithium⁽³⁾, and occur as geothermal, salar and oilfield brines. Table 2 lists examples of these; only salar brines are exploited at present.

Table 1 – Lithium minerals of commercial significance⁽³⁾

Spodumene	$\text{LiAlSi}_2\text{O}_6$
Petalite	$\text{LiAlSi}_4\text{O}_{10}$
Lepidolite	$\text{K}_2(\text{Li,Al})_{5-6}(\text{Si}_{6-7}\text{Al}_{1-2}\text{O}_{20})(\text{OH,F})_4$
Amblygonite	$\text{LiAlPO}_4(\text{OH,F})$
Eucryptite	LiAlSiO_4

Table 2 - Examples of brine analyses, mg/L¹

Element	Geothermal brine	Salar brine	Oilfield brine
Fe	1200 - 3700	-	35 - 41
Mn	1000 - 2000	-	25 - 30
Zn	800 - 700	-	-
Mg	700 - 5700	-	2900 - 3500
Ca	22600 – 39000	300 - 530	29100 - 34500
Na	50000 - 70000	65000 - 91000	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

Lithium carbonate and lithium hydroxide are traded as technical and battery grade products, the battery grade being relevant to the electric vehicle market. Table 3 shows a specification for battery grade lithium carbonate⁽⁴⁾ and **Error! Reference source not found.** shows a specification for battery grade lithium hydroxide⁽⁵⁾.

Table 3 – Battery grade lithium carbonate specification⁽⁴⁾

Li ₂ CO ₃	>99.9%	Na	<20 ppm	Mn	<5 ppm
Si	<40 ppm	Cl	<20 ppm	Al	<2 ppm
SO ₄	<30 ppm	Mg	<10 ppm	Cu	<2 ppm
Ca	<25 ppm	Pb	<5 ppm	Fe	<2 ppm

Table 4 – Battery grade lithium hydroxide monohydrate specification⁽⁵⁾

LiOH·H ₂ O	>99.3%	CO ₂	<0.30%
Na	<0.005%	Ca	<0.002%
K	<0.005%	Fe	<0.0007%
Cl ⁻	<0.003%	Insol (HCl)	<0.005%
SO ₄ ²⁻	<0.01%	Insol (H ₂ O)	<0.005%

PROCESSING

Conventional processing of salar brines entails solar evaporation to raise the concentration of lithium and to remove a large part of the sodium and potassium chloride, removal of boron if necessary, chemical precipitation of divalent cations and then the precipitation of lithium carbonate. Conventional processing of aluminosilicate minerals containing lithium entails calcination to convert less reactive minerals to minerals that are more reactive to acid^(6,7,8), (for example α -spodumene to β -spodumene) then digestion with concentrated sulphuric acid followed by leaching with water. Leaching of lithium-bearing clay⁽⁹⁾, with and without various types of roasting, has been shown to generate sulphate- and chloride-based solutions containing lithium. Mixtures of sulphuric and hydrofluoric acid⁽¹⁰⁾ have also been found to leach α -spodumene directly. Work has also been published on the leaching of spent active cathode material from Li-ion batteries in sulphuric and hydrochloric acid⁽¹¹⁾.

The established technology for extracting lithium from ores takes the lithium into solution, purifies the solution and then recovers lithium carbonate or lithium hydroxide from the purified solution. Extracting lithium from brine entails concentrating the brine, purifying it and recovering lithium carbonate or lithium hydroxide from the purified brine. Regardless of whether the source is ore or brine, therefore, the production of lithium entails the recovery of lithium carbonate or lithium hydroxide from purified aqueous solutions of lithium. The aqueous chemistry of lithium is, therefore, very important in the production of purified lithium compounds such as lithium carbonate and lithium hydroxide for the lithium-ion battery market.

MODELLING AQUEOUS CHEMISTRY

Process modelling is numerical calculation simulating chemistry and unit operations. There are levels at which it can be applied, from fairly simple spreadsheet calculations around stoichiometry to much more detailed modelling of complex chemistry. The level at which a process should be modelled depends on the situation in question and on the available tools. As with most things, there are ways and better ways of doing process modelling.

A simple example illustrating the pitfalls awaiting the unwary in modelling aqueous chemistry can be found in the chemistry of calcium hydroxide in water. A common approach to modelling this system is to assume the following equilibrium reaction, the downward arrow indicating a precipitated solid:



This assumption gives the results shown in Figure 1. The model arising from this assumption fits the data⁽¹⁴⁾ on pH versus temperature quite adequately, for saturated solutions of lime in water. However, the model appreciably underestimates the total solubility of lime in water.

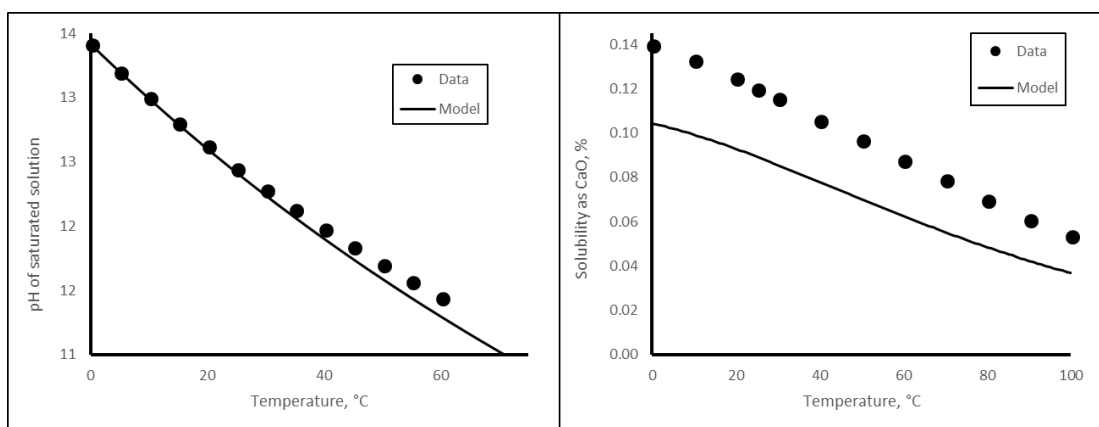


Figure 1 – Modelling predictions using reaction 1

The literature tells us that the following equilibrium reactions exist in this system, which leads to the results shown in Figure 2:

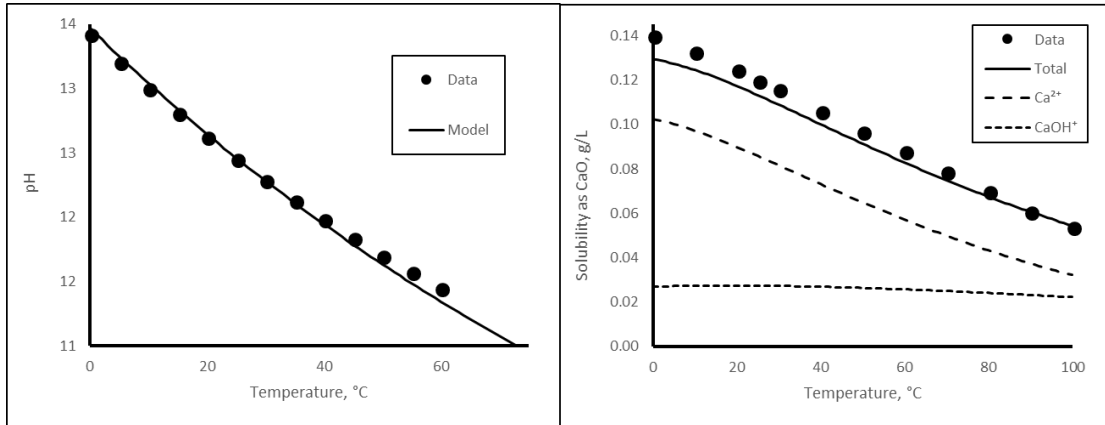
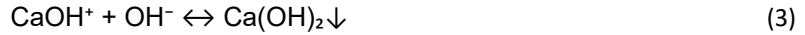


Figure 2 – Lime-water predictions using equations 2 and 3

This time, the model gets the predicted solubility of lime in water much closer to the data, while also predicting the pH slightly better than the simpler model. The point of this illustration is that even for common systems that might arguably be said to be well known, not all is always obvious. Whether or not such nuances are significant in any particular modelling exercise depends on the exercise in question, but wherever possible, better modelling is preferable.

Major requirements for a detailed understanding of the chemistry are appropriate theory fitted to measured data and the correct extrapolation/interpolation of the data to the various situations found in processing circuits. Research by people too numerous to list has given us a very substantial body of data. That alone, though, leaves us with a huge challenge – first finding relevant data, then screening out the contradictions and applying what remains to whatever is being examined.

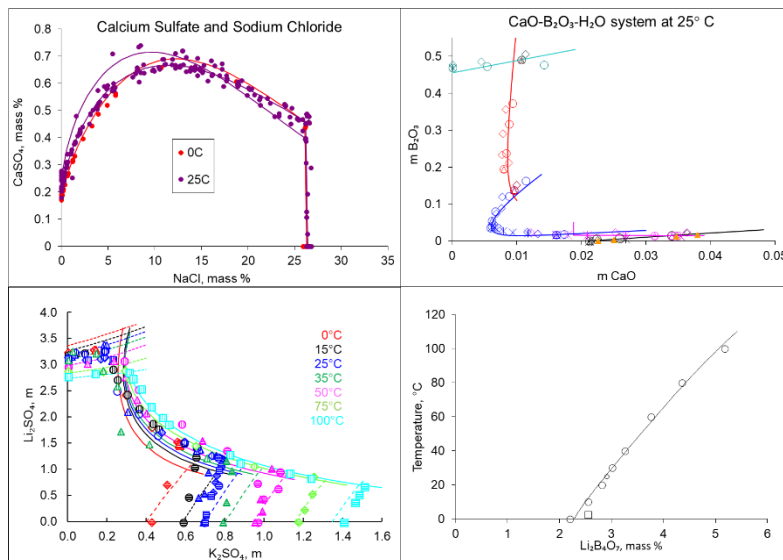


Figure 3 – Examples of aqueous chemistry modelling

This is where modelling using commercial software is a very powerful approach. The vendors of good software have done much of the hard work of finding and translating data into the parameters needed for the relevant theory to fit the data. One very convenient approach to modelling aqueous chemistry uses software commercially known as OLI Studio⁽¹⁵⁾. A vast amount of measured data is embedded into this software, together with sophisticated thermodynamic theory spanning a concentration range from pure water to molten salts^(16,17). A few examples of theory fitted to data via modelling of the aqueous chemistry, using OLI Studio[®], are shown in Figure 3. These examples

were picked from many because they are relevant to the theme of this paper and are presented here to show that complex systems can be modelled to reasonable levels of accuracy.

SULPHATE SYSTEMS IN LITHIUM CHEMISTRY

Table 5 lists published analyses of some sulphate solutions produced in the production of lithium. The standard approach to purification of these solutions is the adjustment of pH in stages. For example, trivalent cations such as Al^{3+} , Cr^{3+} and Fe^{3+} can be precipitated using lime. Figure 4 shows the results of modelling the associated chemistry, assuming the solution from spodumene in Table 5, oxidation with air and neutralization with lime. As found in the experimental work⁽⁷⁾, an end pH of six is quite sufficient for removing all the iron and aluminium from this solution. Divalent cations (Fe^{2+} , Ca^{2+} , Mg^{2+} , Mn^{2+} , Zn^{2+} , etc.) can be precipitated as hydroxides or carbonates via the addition of sodium hydroxide and sodium carbonate. Table 6 lists the results of some published experimental work⁽⁷⁾ in which the stoichiometric amount of sodium carbonate, based on the total divalent cations, was added and sodium hydroxide was used to raise the pH to 10. About half of the calcium and less than five percent of the magnesium were removed from the solution. There was a small loss of lithium, possibly due to entrainment of solution in the solids after filtration.

Table 5 – Sulphate leach solutions, g/L

Element	Spodumene ⁽⁷⁾	Clay ⁽⁹⁾	Petalite ⁽⁸⁾
Al	4	6	<0.001
Fe	0.4	4	<0.001
Mg	0.02	15	<0.001
Ca	0.3	0.4	0.007
Na	2		5
K	0.1	4	0.5
Li	24	1	12
pH	1.8		8

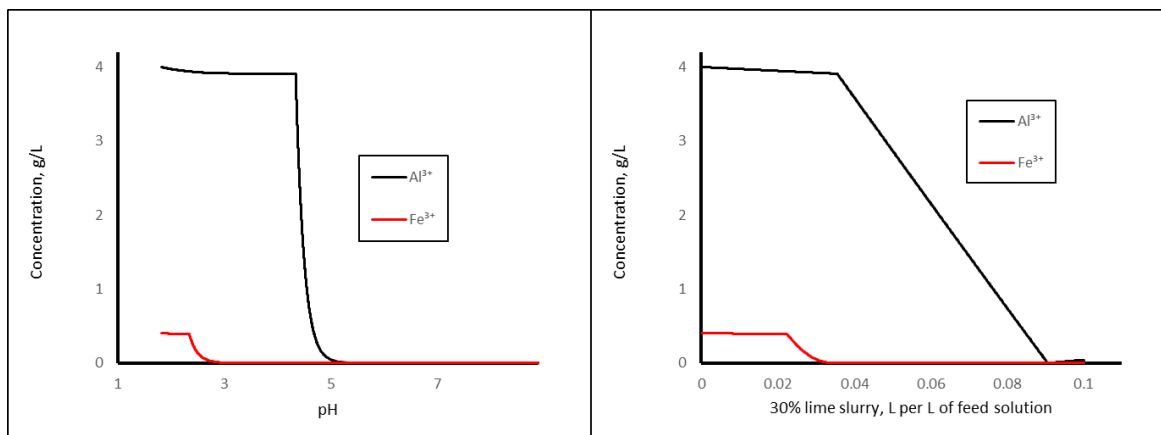


Figure 4 – Al and Fe removal by pH adjustment with lime

Table 6 – Secondary purification data⁽⁷⁾, mg/L

Cation	Feed solution	Product solution
Ca^{2+}	470	253
Mg^{2+}	100	81
Mn^{2+}	130	1

Figure 5 shows the results of modelling this step. Essentially complete removal of the Mg^{2+} requires the pH to be about 10.5 or higher. At the dosages of sodium hydroxide (to pH 10.5) and sodium carbonate (the stoichiometric requirement for Ca^{2+}) used, the residual calcium is predicted to remain at about 10 mg/L, regardless of the pH. The model predicts better removal of calcium and magnesium from solution than was achieved in the published work. The reason for that is not clear

but the model predicts the concentration of calcium to fall sharply in the range of stoichiometric addition of sodium carbonate and to depend quite strongly on the pH. Had that experimental work been done at half a pH unit higher, the removals of calcium and magnesium would probably have been better.

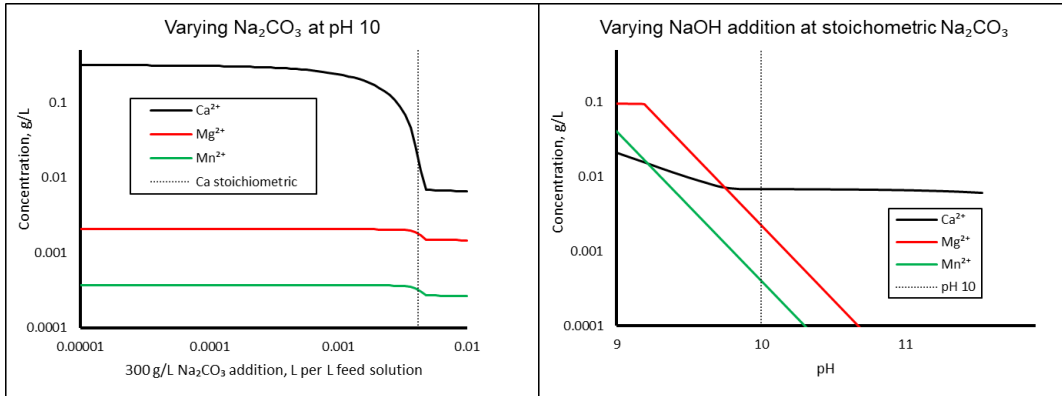


Figure 5 – Ca and Mg removal using NaOH and Na₂CO₃

The chemistry model also predicts that lithium carbonate can be precipitated at pH 10 and higher, if the amount of sodium carbonate added exceeds the stoichiometric amount for calcium. Figure 6 shows the predicted effect of the amount of sodium carbonate added at pH 10 on the amounts of solids precipitated. The feed solution is the solution from spodumene after oxidation with air and neutralization with lime. Loss of lithium carbonate to the precipitate begins just beyond the amount of sodium carbonate theoretically required to precipitate the calcium and manganese as carbonates. The chemistry model predicts that only calcium is precipitated as a carbonate, until lithium carbonate begins to precipitate. Mg²⁺ and Mn²⁺ are predicted to precipitate as hydroxides.

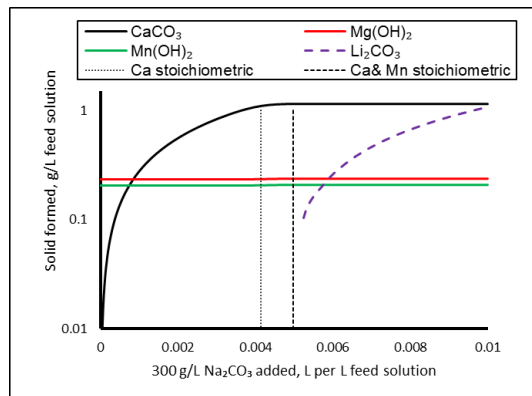


Figure 6 - Effect of Na₂CO₃ addition at pH 10

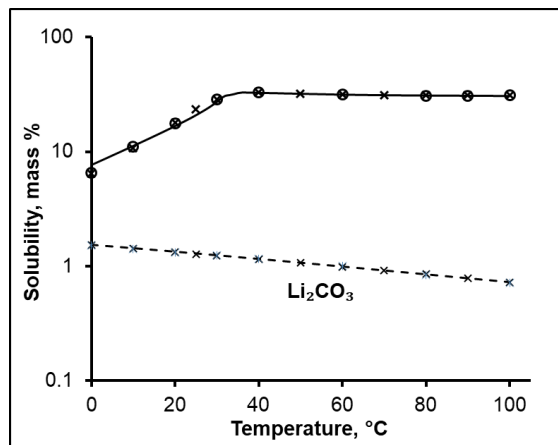


Figure 7 – Solubility of sodium and lithium carbonate in water

The conventional way of recovering lithium from a purified solution is via the precipitation of lithium carbonate, by addition of sodium carbonate. Figure 7 shows the solubility in water of lithium and sodium carbonate. Note that the solubilities are plotted on a logarithmic scale. Reasonably high recoveries of lithium are achievable from solutions containing sufficiently high concentrations of lithium. Figure 8 shows the results predicted via chemistry modelling for the precipitation of lithium carbonate from the solution produced from spodumene (Table 5), after purification. In this example, the model predicts the recovery of lithium carbonate to be over 80 percent, and the final purity to be about 98 percent, at 20 percent excess sodium carbonate. The curve showing purity in the left-hand graph of Figure 8 shows an initially low purity because the preceding purification steps do not remove absolutely all of the divalent ions; the residual divalent cations in the solution precipitate ahead of the lithium, then get diluted as the bulk of the lithium precipitates. This could be exploited by doing a two-step precipitation; the first small portion of the lithium carbonate, with most of the impurities, could be removed and recycled, leaving the bulk of the precipitate as a more purified lithium carbonate product. Alternatively, of course, ion exchange could be used as a polishing step just ahead of the precipitation of lithium carbonate.

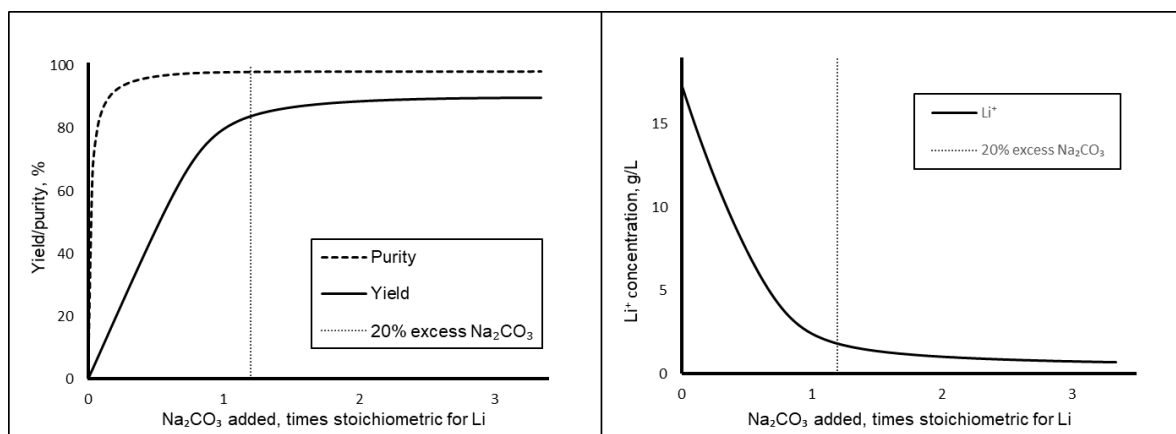


Figure 8 – Precipitation of lithium carbonate at 75°C, spodumene source

The curve in the right-hand graph in Figure 8 shows the remaining concentration of lithium as the precipitation proceeds. At 20 percent excess sodium carbonate the residual dissolved lithium is about 1.8 g/L.

The solution derived from clay (Table 5) has a lithium concentration of only 1 g/L, therefore that solution (after purification) would not be a good feed for the precipitation of lithium carbonate without significant concentration. Figure 9 shows the model prediction for evaporating this solution, after oxidation with air and neutralization with lime.

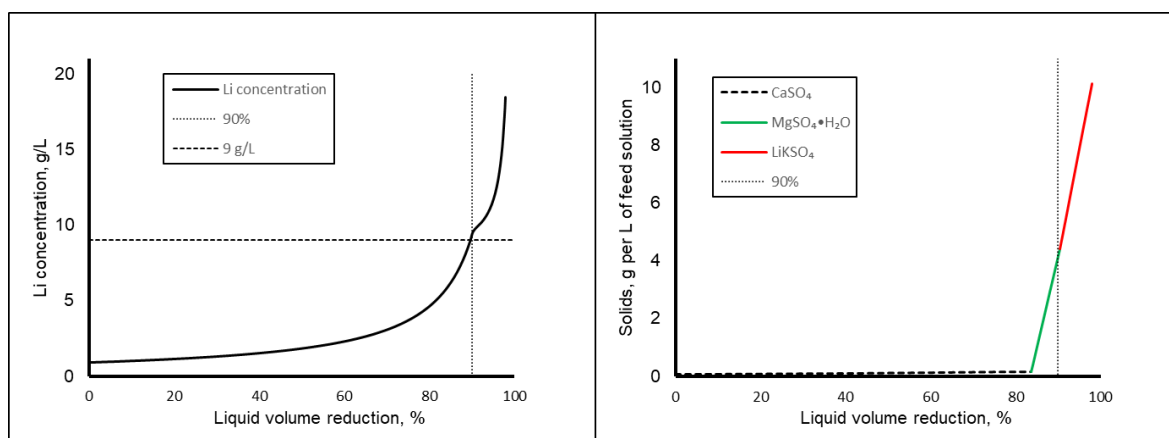


Figure 9 – Evaporation of oxidised/neutralised solution from clay

The evaporation causes the precipitation of a small amount of anhydrite until 84 percent volume reduction, kieserite between 84 and 91 percent and then the double salt LiKSO₄ from there onwards (in this example, of course; other solutions would give different numbers). The inflection point in the

curve in the left-hand graph corresponds to the point at which the double salt first appears. To avoid loss of lithium to the precipitated salt, the extent of evaporation should be limited to just before LiKSO_4 begins to precipitate, giving this example a maximum lithium concentration of about 9 g/L.

Figure 10 shows the model predictions for precipitating lithium carbonate from the evaporated and purified solution coming from clay. Because this solution cannot be concentrated to the same lithium level as the solution from spodumene, the recovery of lithium to lithium carbonate is appreciably lower, not quite reaching 50 percent at 200 percent excess sodium carbonate. As for the lithium carbonate from spodumene, the purity starts low and rises to almost 100 percent Li_2CO_3 because the residual divalent cations precipitate ahead of the lithium, then are diluted into the bulk of the precipitate.

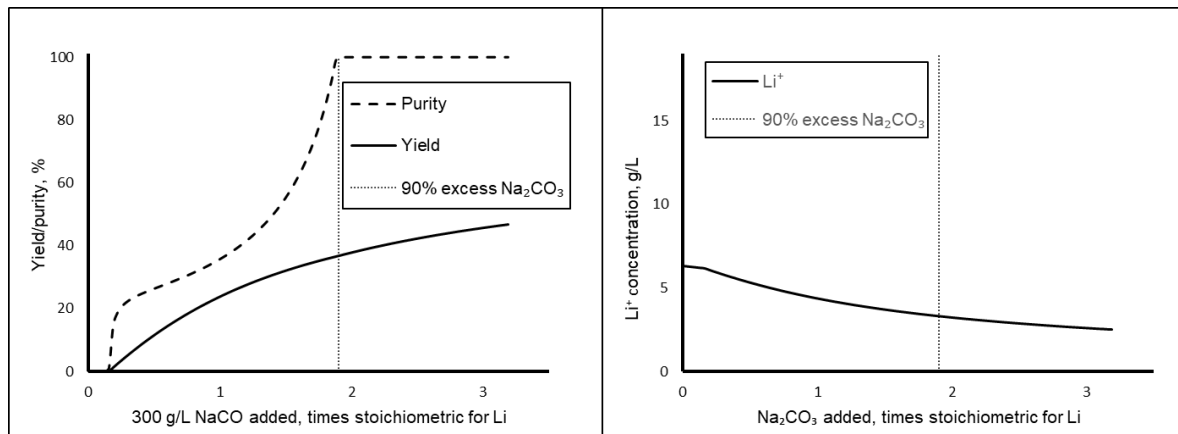


Figure 10 - Precipitation of lithium carbonate at 75°C, clay source

CHLORIDE SYSTEMS IN LITHIUM CHEMISTRY

Conventional extraction of lithium from salar brines begins with a solar evaporation sequence in which the brine is concentrated substantially. As the evaporation proceeds, various salts crystallize out. Garrett⁽³⁾ gives this sequence:

- Halite (NaCl);
- Halite and sylvite (KCl) as a mixture of NaCl and KCl called sylvinite;
- Halite, sylvite and potassium lithium sulphate (KLiSO_4);
- Halite, kainite ($\text{KCl}\cdot\text{MgSO}_4\cdot 2\frac{3}{4}\text{H}_2\text{O}$) and lithium sulphate ($\text{Li}_2\text{SO}_4\cdot\text{H}_2\text{O}$);
- Halite, carnallite ($\text{KCl}\cdot\text{MgCl}_2\cdot 6\text{H}_2\text{O}$) and lithium sulphate;
- Bischoffite ($\text{MgCl}_2\cdot 6\text{H}_2\text{O}$);
- Bischoffite and lithium carnallite ($\text{LiCl}\cdot\text{MgCl}_2\cdot 7\text{H}_2\text{O}$).

Many brines contain potassium at levels that justify the production of potash (KCl) in addition to the lithium. Potash is recovered from the salts harvested from the evaporation of the brine, and when this is to be done, it becomes important to design the evaporation sequence such that the recovery of potash is facilitated, i.e. the evaporation is made to first crystallize out sodium chloride to just short of where potassium chloride begins to crystallize. In addition to the problem of maximising a separation in the crystallization of sodium and potassium chlorides, lithium-bearing brines can also carry calcium, magnesium and boron. Magnesium and sulphate can precipitate as lithium-bearing salts, for which reason lime is sometimes added to the brine to remove magnesium as magnesium hydroxide and sulphate as calcium sulphate, thereby reducing losses of lithium. Another element that can crystallize out is boron. Boron is an undesirable impurity in lithium carbonate and lithium hydroxide and is usually removed from the concentrated brine by solvent extraction after the solar evaporation sequence, thus any boron precipitation in the evaporation sequence reduces the load on the subsequent boron removal step.

Determining the extent of evaporation that maximises the separation of NaCl and KCl along with determining the extent of boron crystallization experimentally is possible, of course, and ultimately essential, but solar evaporation is a slow process and good experimental work may not be practical in the early stages of a new project. Examination of the relevant chemistry ahead of experimental work, using the appropriate tools, is an excellent way to save appreciable time and money in developing any given circuit for recovering lithium (and KCl, if appropriate) from a new brine. Modelling liming a salar brine with a composition at the mid-points of the assays shown for the salar brine in Table 2, with 0.2 g/L of Mg^{2+} added, gives the results shown in Figure 11.

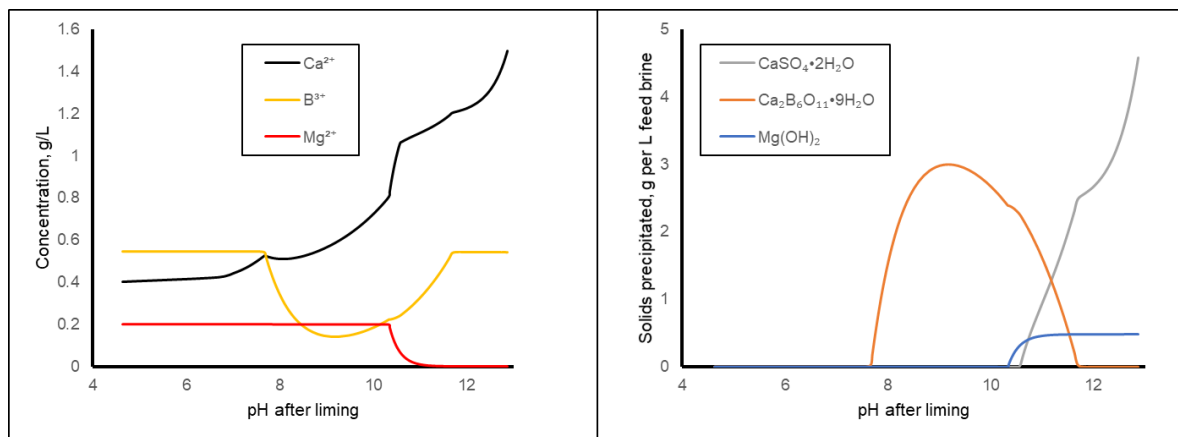


Figure 11 – Liming a salar brine

Raising the pH with lime to a little over 10 causes magnesium to precipitate as $Mg(OH)_2$. By about pH 11 practically all of the magnesium is removed from the liquid phase. Interestingly, the OLI software used in this exercise predicts that boron is also precipitated, as $Ca_2B_6O_{11} \cdot 9H_2O$, and that a maximum in the precipitation of boron occurs close to pH 9. A two-stage liming sequence at pH 9 and pH 11, with intermediate removal of the precipitate, would reduce the load on the downstream solvent extraction of boron and also remove magnesium from the brine. For a single-stage liming step at pH 11, the chemistry model predicts that the boron would precipitate and then much of it would re-dissolve.

Figure 12 shows the results of modelling the solar evaporation of the limed brine in two stages, the first (top two graphs) terminating just before the onset of KCl crystallization and the second (bottom two graphs) terminating just before the onset of crystallization of $Li_2B_4O_7 \cdot 3H_2O$, at which point the concentration of lithium in the remaining brine is about 12 g/L.

Figure 13 shows the predicted results for purifying the brine after removal of the remaining boron, by adding NaOH to raise the pH to just over 10 and Na_2CO_3 to precipitate the remaining calcium as calcium carbonate. The amount of sodium carbonate that can be added at this point is limited by the onset of precipitation of lithium carbonate.

Figure 14 shows the model predictions for precipitating lithium carbonate from the purified brine by adding sodium carbonate. In this case (chloride system) it would seem that the levels of divalent cations remaining in the purified brine are appreciably lower than in the sulphate brines, hence the much steeper initial slope of the purity curve in the left-hand graph of Figure 14. The residual dissolved lithium is similar to the residual in the sulphate systems, at about 1.6 g/L.

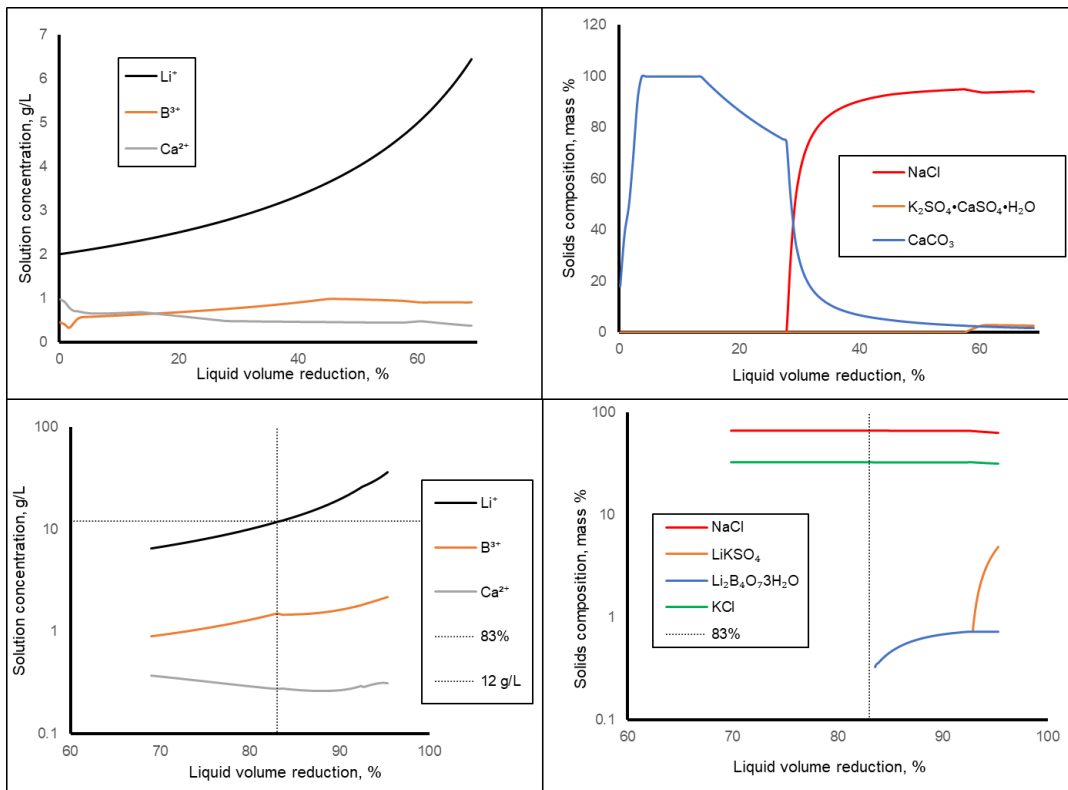


Figure 12 – Solar evaporation of limed brine

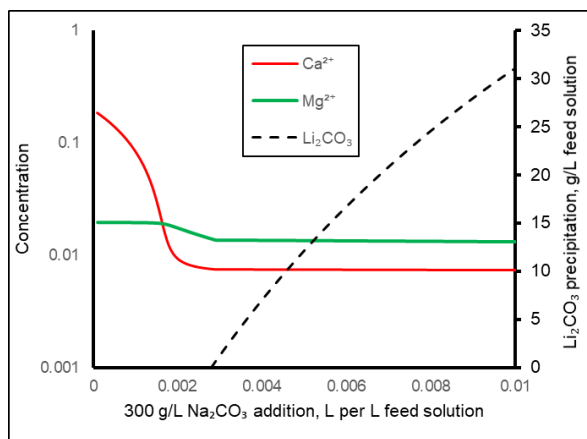


Figure 13 – Purification of brine after solar evaporation

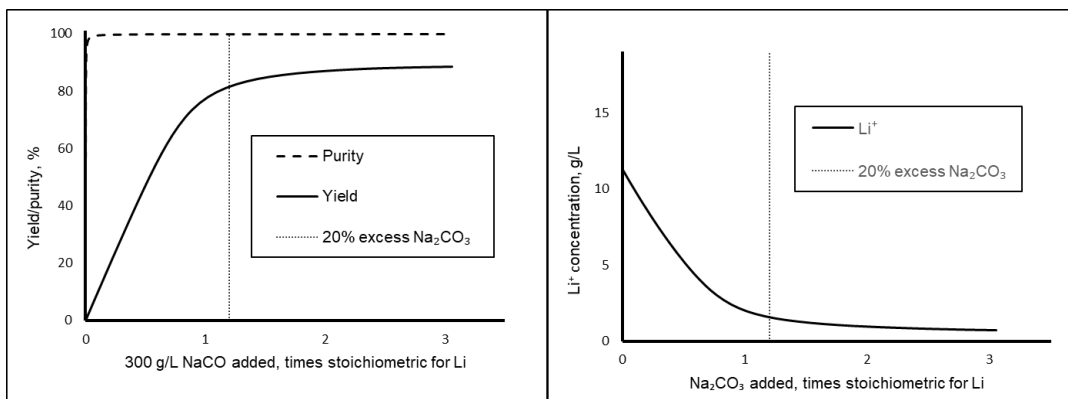


Figure 14 – Precipitation of Li_2CO_3 from purified brine

SCALING AND CORROSION

The solar evaporation of lithium brines involves evaporation ponds of large area, sized for particular extents of evaporation in each pond, with the brine being pumped from one pond to another. Since the ponds are designed to evaporate water and crystallize salt, the solution leaving a pond is saturated in the salt crystallized in that pond, and possibly even slightly super-saturated. This leads to a tendency for crystallization to continue in the solution leaving the pond, which then causes the crystallizing salt to form scale in the piping and pumps moving the solution onwards. The standard way of preventing this is to dilute the brine with water, just enough to make it very slightly under-saturated, thereby eliminating crystallization in the piping and pumps. However, the addition of water partially undoes the evaporation; any water added has to be evaporated in the subsequent pond. Because the volumes of brine involved are large, this can also constitute an appreciable consumption of fresh water, often in arid regions where fresh water is not abundantly available. Therefore, the addition of water is a delicate balance, too little being ineffective and too much being expensive.

Optimal design of this aspect of solar evaporation requires the ability to accurately predict the onset of scaling, in order to add just enough and not too much water. Figure 15 shows the scaling tendency predicted using the OLI software, for brine leaving after the solar evaporation stage in which KCl is crystallized. A scaling tendency of unity means just saturated. In this example, pumping the brine without scaling issues would require dilution with 18 liters of fresh water per cubic meter of brine to be pumped.

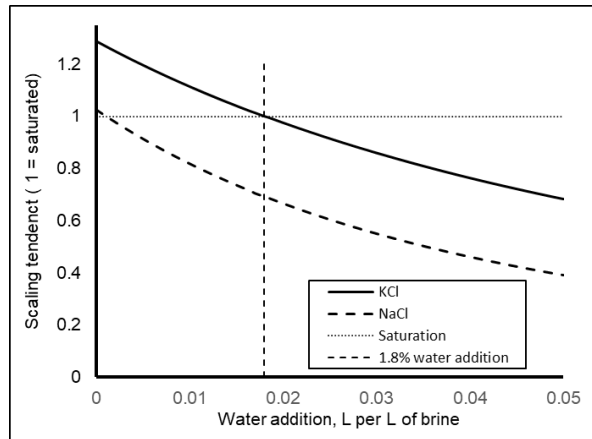


Figure 15 – Scaling tendency versus water addition

Aerated chloride solutions are corrosive to some materials of construction and this needs to be taken into account in the design process. The OLI software used in this exercise has a large database^(18,19,20) on corrosion, covering steel and many alloys, and software correlations for predicting rates of corrosion in solutions at different conditions of temperature, pressure, pH, etc. Figure 16 shows computed general corrosion rates of corrosion for carbon steel and for a duplex stainless steel in chloride brine (about 80 percent evaporation, exiting the evaporation step in which KCl is crystallized), between 5°C and 25°C under aerated conditions at pH 4 (left-hand graph) and at pH 2 (right-hand graph). Note that the vertical axes in Figure 16 are logarithmic. For carbon steel, the rate of corrosion in the brine increases by about an order of magnitude at pH 2, compared to in the brine at pH 4. The pH does not affect corrosion of the duplex stainless steel anywhere near as much as it affects the corrosion of carbon steel.

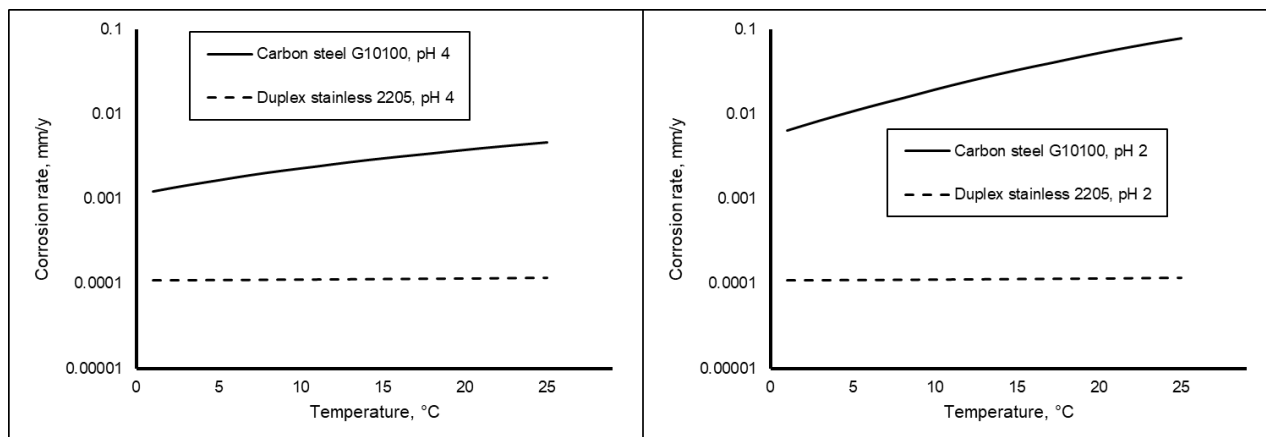


Figure 16 – Corrosion in evaporated brine

CONCLUSION

The production of lithium carbonate and lithium hydroxide suitable for use in the manufacture of lithium-ion batteries depends on the aqueous chemistry of the relevant systems. To design the processing circuits effectively, it is necessary to develop and exploit a thorough understanding of the aqueous chemistry.

The examples presented in this paper demonstrate how high-quality computer software can be used to generate the required understanding and to search for the optimal process conditions.

The approach presented here is in no way meant to replace experimental work. This approach is, however, excellent for investigating the aqueous chemistry and developing sound understanding that leads to more efficient and effective experimental work.

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