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REMOVAL OF MINOR AND TRACE IMPURITIES FROM LITHIUM LEACH LIQUORS

By

¹Stephen La Brooy and ² Grant Harman

¹Ausenco, Australia

²Lithium Consultants Australasia, Australia

Presenter and Corresponding Author

Stephen La Brooy

stephen.labrooy@ausenco.com

ABSTRACT

It is relatively straightforward to extract lithium from minerals and clays. However, the number and amount of impurities that are co-leached can vary significantly. Limiting lithium losses during removal of impurities can pose significant challenges in the production of battery grade lithium chemicals.

Typically leach liquors from lithium mica ores and clays contain higher levels of impurities than from spodumene. Sighter testwork is required to identify the best technology to remove each impurity. This then needs to be followed by locked cycle testwork. It is necessary to simulate as many of the recycle loops as possible to determine the effect of each loop, to understand what level of impurity removal is possible and how impurities will build up in the circuit. In most cases a process bleed is required to limit the build-up to be able to produce battery grade lithium chemicals.

This paper presents the typical impurities found in the extraction of lithium from various ores and reviews some of the issues with removal of minor and trace impurities from leach liquors such as: boron, fluoride, caesium, rubidium and magnesium. Techniques discussed are chemical precipitation, crystallisation, adsorption, selective ion exchange and solvent extraction for the production of battery grade lithium carbonate.

Keywords: lithium carbonate, battery grade, impurities, boron, fluoride caesium, rubidium, magnesium, leach liquor, lithium chemistry, precipitation, crystallisation, adsorption, ion exchange and solvent extraction

INTRODUCTION

Until recently the world's lithium supply was sourced from the salars located in the Golden Triangle in South America and from the Talison Greenbushes mine in Australia. The cost to produce lithium from the salars was, and remains, significantly cheaper than all the hard and sedimentary rock options. As a result of the increasing demand and the limitations of the salars and Talison to supply the growing market, the marginal cost to produce lithium chemicals has increased. This has allowed lower grade secondary lithium mineral resources, such as micas and clays, to be considered.

This paper focusses on the production of lithium chemicals from secondary lithium minerals and compares the challenges with processing spodumene. It is relatively straightforward to extract lithium from micas and clays. However, the range and quantity of impurities that are present in the leach solution can vary significantly, depending on the extraction technology and feed materials. This results in more complex leach liquors than from the standard spodumene sulfation route.

When 'impurity' quantities are high enough and there are markets for them, there is the potential for by-product credits such as by production of potassium salts for fertiliser applications, or possibly boric acid from the processing of brine and jadarite. However, in most cases dealing with impurities just adds to processing costs. In addition lithium losses during removal of impurities can pose significant challenges.

BACKGROUND

Source Materials

Current commercial sources for lithium chemical production are based on brines and spodumene hard rock deposits, as these offer the highest feed grades. Figure 1 summarises current and potential lithium feed sources. There has been considerable activity in development of more spodumene deposits as they are quicker to bring on line than brine deposits (Hard Rock project is typically 5 years versus 7 years for brines⁽¹⁾), combined with availability of commercially proven beneficiation technology to produce saleable concentrates.

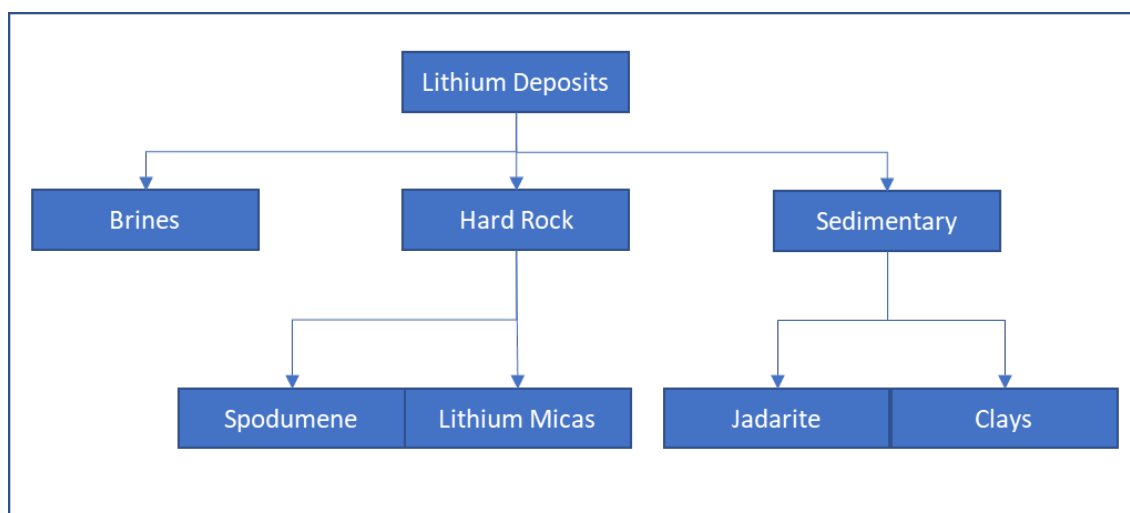


Figure 1: Feed sources for lithium chemical production

Brines

Commercial operations currently recovering lithium from brines with 250-1,800 ppm Li⁽²⁾ are mainly located in South America (Chile, Argentina and Bolivia) along with limited production in USA and China. Solar evaporation increases the feed lithium concentration to at least 6 g/L, accompanied by high concentrations of potassium, sodium, sulfate and boron. (Unless otherwise stated all lithium concentrations in this paper are expressed as lithium not Li₂O.) While the operating cost of solar evaporation is low, it takes around two years of evaporation to concentrate up the feed brine to a level suitable for further processing. The evaporation is dependent on sunny days and low rainfall.

Spodumene

Pure spodumene $\text{Li}_2\text{OAl}_2\text{O}_3(\text{SiO}_2)_4$ has a lithium content of 3.7 wt% (8% Li_2O). Mines usually target a concentrate grade around 6 wt% Li_2O , with concentrates traded ranging from 5-7.5 wt% Li_2O . Petalite $\text{Li}_2\text{OAl}_2\text{O}_3(\text{SiO}_2)_8$ has a lithium content of 4.88 wt% Li_2O and can generate concentrates with 3.5-4.5 wt% Li_2O ⁽³⁾. Most lithium chemical production plants are limited by calciner capacity; hence their output depends on the lithium grade of the concentrate, which also affects transport costs. Impurities in the spodumene can add to the processing cost.

Table 1 summarises the common lithium containing minerals along with mineral and concentrate lithium grades.

Table 1: Common Lithium Containing Minerals and their Properties

Mineral	Main Locations	Chemical Formula	Mineral wt% Li_2O	Con Grade wt% Li_2O
Spodumene	Australia	$\text{Li}_2\text{OAl}_2\text{O}_3(\text{SiO}_2)_4$	8.0	5-7.5
Petalite	Zimbabwe	$\text{Li}_2\text{OAl}_2\text{O}_3(\text{SiO}_2)_8$	4.9	3-4
Zinnwaldite	Czech Republic	$\text{KLiFeAl}(\text{AlSi}_3)\text{O}(\text{F},\text{OH})$	2 - 5	3
Lepidolite	Zimbabwe	$\text{K}(\text{Li},\text{Al})_3(\text{Si},\text{Al})_4\text{O}_{10}(\text{F},\text{OH})_2$	3.3-7.7	
Hectorite	Mexico, USA	$\text{Na}_{0.3}(\text{Mg},\text{Li})_3\text{Si}_4\text{O}_{10}(\text{OH})_2$	1.2	0.6-1.3
Jadarite	Serbia	$\text{LiNaSiB}_3\text{O}_7(\text{OH})$	7.3	
Amblygonite	Canada	$\text{LiAlPO}_4(\text{F},\text{OH})$	10.1	
Eucryptite	Zimbabwe	$\text{Li}_2\text{OAl}_2\text{O}_3(\text{SiO}_2)_2$	11.8	
Zabuyelite	China	Li_2CO_3	40.4	

Lithium Micas

Potential mica sources of lithium include: lepidolite and zinnwaldite. While there may be some potential for upgrade of ores by flotation and other physical processes, lithium mica concentrate feed grades are lower than for spodumene concentrates. Lepidolite $\text{K}(\text{Li},\text{Al})_3(\text{Si},\text{Al})_4\text{O}_{10}(\text{F},\text{OH})_2$ has a variable lithium content 3.3-7.7 wt% Li_2O ⁽³⁾⁽⁴⁾. Zinnwaldite $\text{KLiFeAl}(\text{AlSi}_3)\text{O}(\text{F},\text{OH})$ is essentially a high iron form of lepidolite generating concentrates containing 2-5 wt% Li_2O ⁽³⁾. The mineral is named after the locality Zinnwald, Erzgebirge, Sachsen. Zinnwaldite is a phyllosilicate with properties similar to that of biotite, while it resembles lepidolite in its chemical aspects with high Si/Al ratio, high Li content and replacement of OH by F. Zinnwaldite can be considered to be part of a solid solution series of the ferrous lithium micas. The main criteria being:

- if the Li occupies fewer than 0.25 octahedral sites the mineral is termed a siderophyllites;
- if the Li occupies between 0.25 and 0.75 sites the mineral is termed a protolithionites;
- if the Li occupies between 0.75 and 1.25 sites minerals are defined as zinnwaldites; and
- if the Li occupies more than 1.25 sites minerals are considered as lepidolites.

The series is characterized by the progressive replacement of Li^+ by Fe^{2+} , with an average replacement ratio of 2.0 Li^+ for 1.5 Fe^{2+} . Siderophyllites and protolithionites can contain significant amounts of Fe^{3+} , zinnwaldites have some Fe^{2+} , while Fe^{2+} is low in all the lepidolites. Processing lepidolite type material generates some potassium sulfate by-product credits, along with additional costs for fluoride removal.

Clays

Clays such as hectorite $\text{Na}_{0.33}(\text{Mg}, \text{Li})_3\text{Si}_4\text{O}_{10}(\text{OH},\text{F})_2$ are an even lower grade source of lithium with grades around 0.3-0.6% Li (0.65-1.38% Li_2O)⁽⁵⁾⁽⁶⁾. Hence transport costs mean on-site processing is likely to be the only option and even then processing costs are likely to be more expensive than for the higher grade spodumene or even mica concentrates.

LITHIUM EXTRACTION TECHNIQUES

Prior to the increase in demand during the Second World War lithium chemicals were manufactured from micas such as lepidolite by calcining with neutral alkali metal salts such as potassium sulfate, followed by water leaching. The increase in demand provided the impetus for processes to treat the more challenging spodumene concentrates that only gave about 70% lithium extraction after calcining with neutral alkali metal salts⁽⁷⁾.

Spodumene concentrates are currently mainly processed by acid roasting - calcining at around 1,000°C to convert α -spodumene to β -spodumene, followed by roasting at around 250°C and water leaching, based on the process first described in the US Patent by Ellestad and Leute⁽⁸⁾. In the absence of conversion of α -spodumene to β -spodumene, it is highly resistant to acid attack unless fluoride is present to solubilise the silicate matrix. Alkaline roasting of spodumene with lime and calcium carbonate, followed by leaching with calcium chloride solution to produce lithium chloride was investigated by the US Bureau of Mines⁽⁷⁾, while White and McVay⁽⁹⁾ investigated calcination with limestone as alternative pre-treatments. The Lime-spodumene reaction was used by both Foote Mineral Company at Simbright, Virginia, and American Lithium Chemicals at San Antonio, Texas, in the 1950's to produce the hydroxide⁽¹⁰⁾.

In the late 1980s the US Bureau of Mines investigated extraction of lithium from Nevada clays in case future lithium demand for battery applications required additional feed sources to satisfy the demand. They looked at 11 process options and concluded that the limestone-gypsum roast process was the most attractive option, but was uneconomic at 1988 lithium carbonate prices⁽⁵⁾. More recently this approach has been further developed⁽¹¹⁾ for lepidolite type materials. There have been attempts to reduce reagent cost by replacing some of the gypsum with sodium and/or potassium sulfate as these are available from process by-products. Micas and clays can also be acid treated after fine grinding (mechanical activation), eg P₈₀ 75 μ m as in the Lepidico process⁽¹²⁾.

In 1994 Talison built a plant to treat calcined spodumene concentrate by the soda ash autoclave process, but it was put on care and maintenance in 1997. The soda ash autoclave process is currently being considered by Klieber Oy⁽¹³⁾ and is considered to be a simpler process that produces a purer leach solution requiring less clean up.

INDICATIVE LEACH LIQUOR CONCENTRATIONS

The gypsum-limestone roast approach⁽⁵⁾ was developed for clays and micas to minimise the divalent metal content of the leach liquor by producing a neutral to alkaline leach liquor. On the other hand acid dissolution processes especially with fluorides present, bring almost everything into solution, resulting in higher concentrations of aluminium, magnesium, iron and calcium. Catovic⁽¹⁶⁾ flags K, Na, Cs, Rb, Si, Al & Fe 'metal' impurities in leach liquor, in addition to sulfate and fluoride anions from the lixiviant. Table 2 summarises indicative leach liquor concentrations based on public domain information and experience.

Table 2: Indicative Leach Liquor Concentrations

	Units	Typical Spodumene	Petalite ⁽¹⁴⁾	Gypsum-lime roast leach McDermitt B ⁽⁵⁾	175°C 920 g/L H ₂ SO ₄ lepidolite leach ⁽¹⁵⁾	Typical Zinnwaldite CaSO ₄ -CaCO ₃ roast leach
Li	g/L	9.6	5.7	2.9	5.1	2
K	g/L	0.2	0.45	13		5.5
Na	g/L	1.28	1.42	3.1		0.2
Rb	g/L	-				0.325
Ca	g/L	0.1	0.145	0.540		0.18
Mg	g/L	0.03	0.012	0.030		0.02
Al	g/L	1.3	0.010	-	3.1	0.131
Fe	g/L	0.65	0.038	-	0.080	<0.1
Mn	g/L	0.04		-	0.170	<0.1
Si	g/L	0.04	0.033	-		0.05
pH		1.6	0.95	Neut-alkaline		~10

Alkali roasting tries to minimise solution purification costs, while the acid leach approach may offer the possibility of saleable by-products from some of the co-extracted elements. In addition to impurity removal costs, lithium losses during impurity removal need to be considered. Addition of sodium and/or potassium sulfates to the gypsum-limestone roast approach lowers the leach pH and increases the leach liquor concentrations of species such as magnesium.

TESTWORK REQUIREMENTS

Sighter Tests

The first step in understanding what impurities are significant is to carry out sighter testwork to identify suitable conditions to optimise lithium extraction into the leach liquor and develop some understanding of how impurity concentrations vary with lithium extraction. For micas and clays a starting point for the gypsum-limestone roast approach can be the conditions identified by the US Bureau of Mines⁽⁵⁾. However, optimisation of lithium recovery will require the sighter testwork program to identify the most suitable additives and roast conditions for the particular feed material. Provided the leach solutions are analysed for the full range of species of flagged in Table 2 plus fluoride and boron, this testwork program will also provide information on the species of concern and their likely concentration ranges in the initial leach liquor.

Once the basic leach feed pre-treatment steps and impurities of concern have been identified the second phase of the sighter testwork program can commence. This would look at the required purification process and determine how they need to be configured to achieve the required purity in the pregnant liquor feed to final lithium carbonate precipitation (or lithium hydroxide crystallisation). The choice of purification technologies and their order needs to take into account that some are only applicable to certain sections of the flowsheet (e.g. selectivity of ion exchange can be affected by total ionic strength). In addition, lithium losses can be significantly influenced by chemicals used for precipitation (e.g. lime for divalent metal precipitation) and the concentration of other species, eg fluoride⁽¹⁶⁾.

Locked Cycle

While the sighter batch tests can provide an indication of the impurities of concern and how they might be dealt with, it is necessary to move on to locked cycle testing of as much of the flowsheet as possible, to allow determination of impurity build up, bleed requirements, as well as lithium losses during recycle loops and from bleed streams. The key outcomes required from the locked cycle tests are:

- confirm the impact of recycle streams and the impact that impurities have on the process and their buildup,
- determine effect of impurities on product and by-product quality,
- confirm amounts of reagents required, and
- estimate overall lithium recovery and confirm that excessive amounts are not being lost in residues and bleed streams.

TYPICAL MINOR IMPURITIES

For the purposes of this paper, trace elements are considered to have a concentration in the liquor of <0.01% and minor components are considered to have a concentration between 0.1% and 0.01%⁽¹⁷⁾. In general, as shown in Table 2, Na, K and Al would be considered as major impurities and the removal of these are not covered in this paper. Their removal will be covered in the companion presentation to be presented at AusIMM International Lithium Conference to be held in June 2018.

The detailed split between major and minor impurities will depend to some extent on the extraction route. Hence boron is a major impurity in brine systems but a minor impurity for most other options. Also some of the clean-up techniques may add species such as aluminium added as alum in rubidium removal or used for activation of alumina, that then need to be removed later in the flowsheet.

Boron

Boron is a significant component in brines but for lithium recovery from micas and clays boron is a minor impurity. Its removal may well be able to wait until solution clean up before primary lithium carbonate precipitation, after major sodium (and potassium) reduction to reduce the overall solution TDS. The main reason for its removal is that it builds up in the circuit and does not naturally co-precipitate or crystallise out with any other species.

Caesium and Rubidium

Caesium and rubidium are in Group 1 of the periodic table below lithium, sodium and potassium. All the members of Group 1 form similar analogues with lithium normally being the only exception. This difference allows the other Group 1 elements to be removed from solutions by the addition of alum and lime. Figure 2 (after⁽¹⁸⁾) shows relative Group 1 mixed alum solubilities.

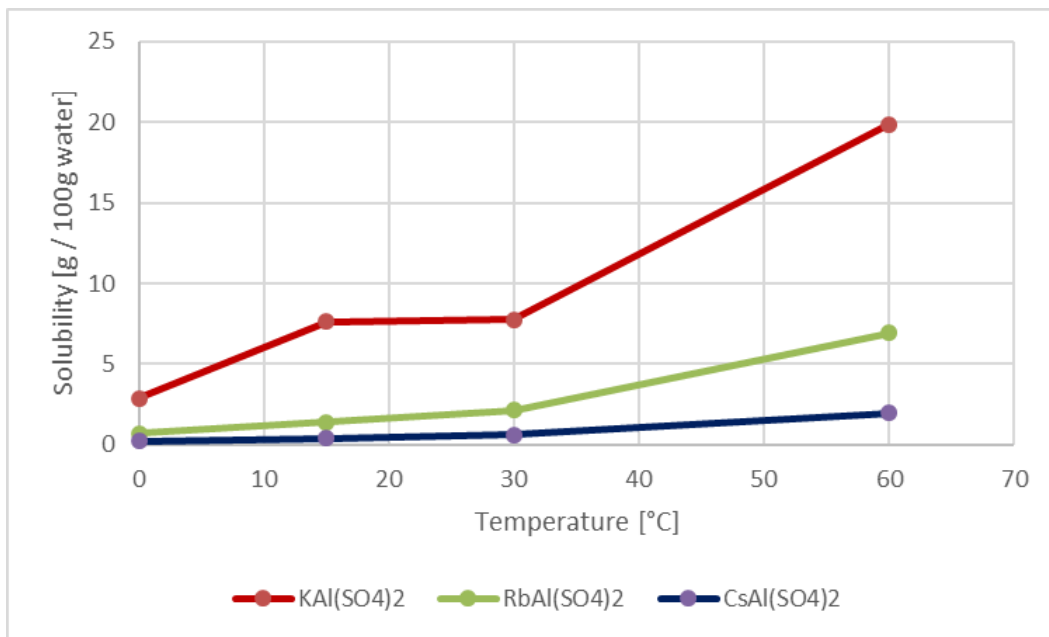


Figure 2: Relative solubility of Group 1 Alums (after⁽¹⁸⁾). Sodium has not been displayed for clarity as the solubility is significantly higher than the other analogues.

In leach liquor from clay processing the caesium tenor can be as high as 1 g/L and rubidium roughly half this value. In a mica leach the rubidium level can roughly be the same as for clays but typically the caesium tenor is far lower than rubidium. In these cases the impact of recycling streams with high caesium and rubidium results in the lithium tenor being similar to caesium and rubidium.

Calcium

Calcium extraction from the ore is usually low and calcium would be considered a minor impurity. However, calcium is added to the roast as a reagent and or as a neutralising agent after a spodumene leach and as a result levels can be in the region of 500 – 800 mg/L.

Fluoride

A number of the secondary lithium minerals shown in Table 1 contain fluoride. In the extraction of the lithium some of the fluoride is co-extracted. Lithium extraction technologies which dissolve more mineral dissolve more of the fluoride, for example the L-Max process⁽¹²⁾.

By adjusting the roasting conditions through adding the right reagents and the right mix, it is possible to limit the co-extraction of fluoride to give leach liquor concentrations below 100 mg/L. For example, calcium in the roast can form calcium fluoride. Hence calcium addition in the form of limestone or lime can mop up fluoride as well as free silica and iron.

Magnesium

In general the concentration of magnesium in spodumene acid roasts and secondary lithium mineral gypsum roast leach solutions is low and below 10 mg/L. However, acid digestion of secondary lithium minerals can result in magnesium tenors similar to that of the lithium.

With the gypsum-limestone roast approach for lithium extraction from micas and clays most of the magnesium is fixed during calcination, so that the magnesium is not a major leach liquor impurity as in acid digestion processes. However, substitution of some of the gypsum with potassium sulfate to improve lithium extraction reduces the leach liquor pH and can increase the magnesium concentration in the leach liquor.

Silica

Disruption of alumina-silicate minerals to release lithium may be expected to also bring some silica into solution, especially with acid leaching in the presence of fluoride. In the lime(stone)-gypsum roast pre-treatment process, one of the functions of the lime is to react with free silica to lock it up as calcium silicate, so dissolved silica levels in the leach solution are low. Under these conditions the low/trace levels of silica may be adequately removed by adsorption during removal of other impurities.

MAXIMUM TARGET IMPURITY TENORS IN FEED LIQUOR TO LITHIUM CARBONATE PRECIPITATION

The maximum target tenors of impurities in the feed to lithium carbonate precipitation are set by the specification of the lithium carbonate solid product. In general, the concentration of an impurity in the lithium carbonate solid is between 15 – 20 times higher than the tenor of the impurity in the liquor. For this reason, the typical target values for the design of the plant are set as shown in Table 3.

Impurity	Maximum Target Value (mg/L)
Ca	<5
Mg	<1
Mn	<1
Al	<1
Fe	<1
F	<1
Si	<1

Table 3 : Maximum Target Impurity Tenors in Feed Liquor to Lithium Carbonate Precipitation

In all secondary lithium mineral plants the quality of the lithium carbonate from precipitation will not meet battery grade and secondary purification of the lithium carbonate is required. This is currently always done by bicarbonation. The lithium carbonate is redissolved by bubbling carbon dioxide through the liquor to form lithium bicarbonate. After filtration the solution is then heated to around 95°C to re-precipitate the lithium carbonate.

A common mistake is to think that bicarbonation will purify the lithium carbonate and get rid of all the unwanted impurities. The problem is that while in theory this is correct, in order to do this the size of the bleed from the liquor which is recycled can be excessive. For a complete discussion of the effect of impurities on battery grade and battery manufacture and performance see⁽¹⁹⁾.

IMPURITY REMOVAL TECHNOLOGIES

Figure 3 shows typical unit operations used in various approaches to lithium extraction.

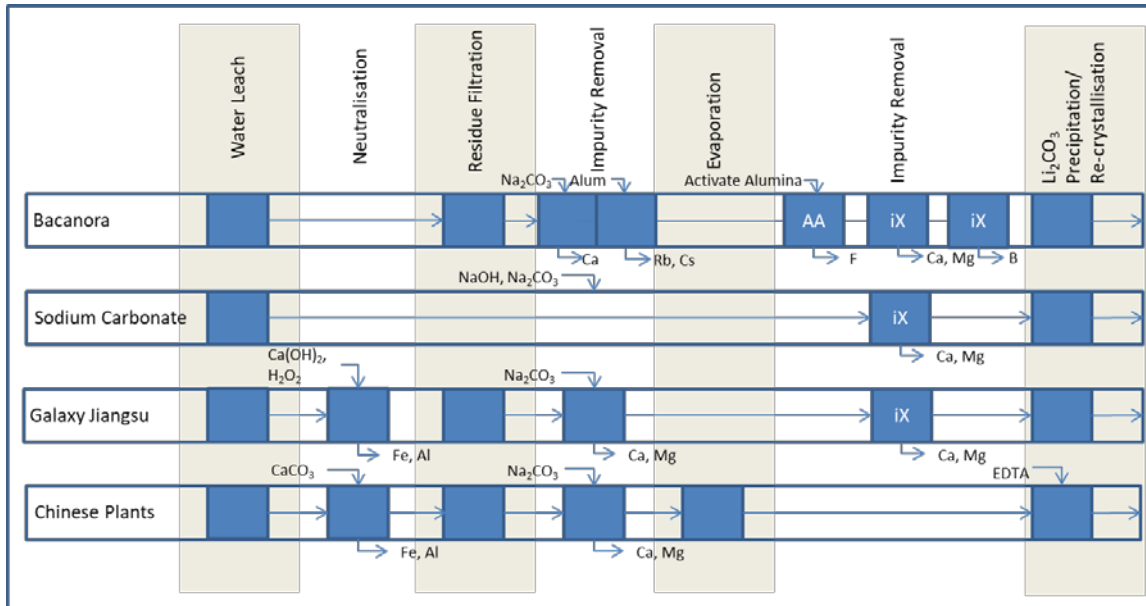


Figure 3: Summary of Unit Operations in Selected Lithium Extraction Technologies

Chemical Precipitation

The most important technology for the removal of bulk impurities in lithium flowsheets is chemical precipitation. Metal cations can be removed by precipitation as hydroxides or carbonates. Using this approach iron, aluminium, magnesium, manganese and calcium can be almost totally removed from the solution. Figure 4 (after⁽²⁰⁾) illustrates the relationship between metal hydroxide precipitation and pH.

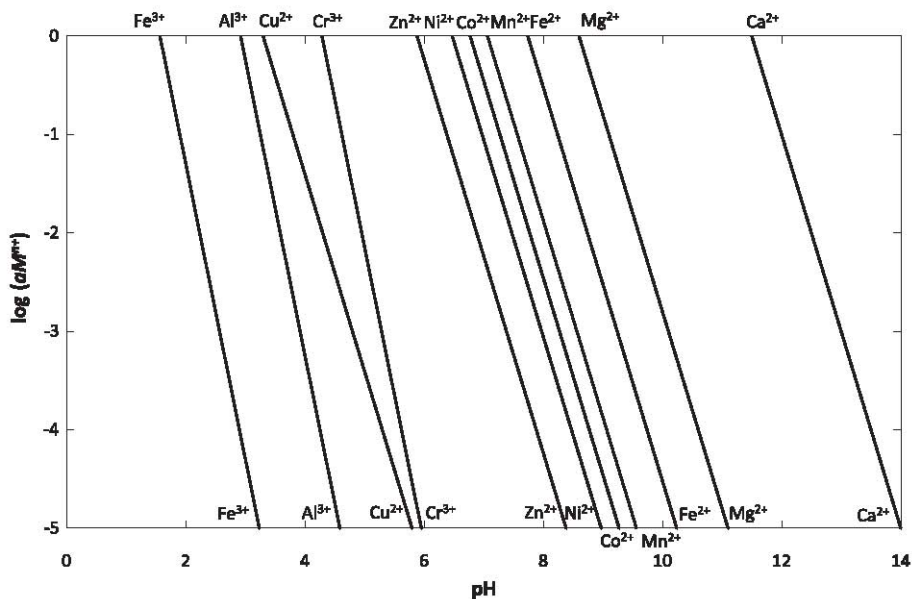


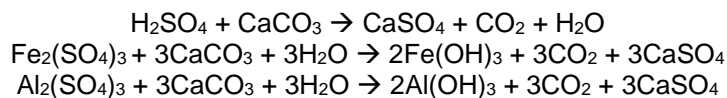
Figure 4: Effect of pH on the Solubility of Metal Hydroxides (after⁽²⁰⁾)

Iron and Aluminium Removal

In a typical sulfation roast of calcined spodumene the leach slurry has a very low pH as is shown in Table 2. The leach slurry is neutralised using limestone or lime to a pH of between 6 and 7 which results in all the iron(III) and aluminium being precipitated.

A key consideration in the choice of the best neutralising reagent is the combination of cost, impurities in the reagent and the impact on the filterability of the residue. In general, the use of limestone results in the formation of gypsum (CaSO_4) which coats onto the limestone and typically reduces the

utilisation to around 50%. The gypsum coated limestone particles assist in the filtration of the residue. The limited limestone utilisation is due to the practical fineness of the available limestone and the gypsum coatings of the surface, which essentially prevent further reaction. The chemical reactions are:



If lime is used the reagent utilisation is greater, with fine gypsum formed in the solution, that is no help in the filtration of the aluminium and iron hydroxides which are notoriously difficult to filter.

Manganese and Magnesium Removal

The removal of manganese and magnesium is typically done after the neutralisation in a conventional sulfation plant. The pH is raised by addition of lime or sodium hydroxide to between 10 and 12. As shown in Figure 4 this result in almost all the magnesium and manganese precipitating out of solution, as hydroxides, along with most of the other metal impurities.

Calcium Removal

Most of the residual calcium following initial precipitation as gypsum during iron and aluminium removal is removed as calcium carbonate by addition of soda ash (Na_2CO_3) to reduce the calcium concentration to around 50 mg/L (as in the lime softening process).

Normally the stoichiometric amount of soda ash is added but a larger amount can be added without adverse effect. Some of the soda ash will react with the lithium but operationally there should be very little and since the amount of calcium being removed is small, the lithium entrained with the residue is likely to be far more significant.

Fluoride Removal

For high fluoride concentrations following acid leaching, fluoride can be precipitated as calcium and aluminium fluorides by addition of limestone / lime in a two stage process. The pH is initially raised to pH to 3.5-4 with limestone or lime. It is then raised to pH 10.5-11 with lime once most of the aluminium and fluoride has precipitated⁽¹⁶⁾. The use of calcium fluoride precipitation as a pre-treatment is recommended by Tramfloc (2012) ahead of adsorption on activated alumina for feed fluoride concentrations above 15-20 mg/L.

Alternatively, alum can be used to remove fluoride. However, testwork has shown that the amounts of lime and/or alum that are required to be added is excessive, not only from a reagent cost perspective but also the amount of waste residue that has to be disposed of. The other major consideration is the amount of lithium entrained with the residue. Anecdotally this is in the region of 10 – 20% of the lithium in the feed. In theory this could be recovered by washing of the residue, however this would create a lithium fluoride stream that would require further processing. Basically alum addition has been found to not offer an acceptable solution.

Crystallisation

Crystallisation can be applied by evaporation and/or cooling a solution so that the solution concentration of a salt exceeds its solubility at that temperature. It is more suited to species present at high concentrations, as significant concentrations of the target salt usually remain in solution after the crystallisation process, due to inherent solubility. Hence it is more suited to control of major species such as potassium and sodium salts. The advantage of crystallisation over chemical precipitation is that the products are usually more easily separated from the solution and may offer a way to generate materials that can sold as by-products such as potassium salts for fertiliser applications.

Boron

The common technologies for the removal of bulk boron from liquor are crystallisation and solvent extraction. Ion exchange is typically used to remove the remaining trace amounts. In crystallisation the boron is crystallised out as boric acid which typically involves cooling to in the region of 38°C and filtering the slurry to collect the boric acid crystals.

Sodium Sulfate

Sodium sulfate is typically present in concentrations well above trace levels. It can be removed as:

- anhydrous sodium sulfate in an evaporative crystalliser operating above 75°C
- Glauber's salt (Na₂SO₄.10H₂O) by cooling the liquor.

Fluoride

Johnson et al.⁽¹²⁾ have proposed recovery of fluoride by crystallisation as khadamite (Al(SO₄)F.5H₂O) to produce a mixed aluminium fluoride sulfate salt that can be further processed to generate by-products. This technology is suited for high levels of fluoride.

Rubidium & Caesium

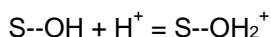
Crystallisation can also make use of mixed alum salts to recover species such as caesium and rubidium, after addition of the appropriate excess of aluminium sulfate to generate the mixed alum. An example would be deliberate addition of aluminium (sulfate) to be able to extract caesium as caesium alum, CsAl(SO₄)₂.12H₂O, followed by the more soluble rubidium as rubidium alum, RbAl(SO₄)₂.12H₂O and potassium alum as proposed by Jandova et al.⁽²¹⁾ and Johnson et al.⁽¹²⁾.

This is more applicable to treatment of a bleed stream due to the need for well over stoichiometric quantities of aluminium, with potassium alum also crystallising out at the same time, before caesium and rubidium extraction can be completed. Liquors containing up to 5 g/L caesium have been treated successfully using crystallisation to remove most of the caesium along with around 50% of the rubidium. This is adequate to prevent the levels building up too high in the circuit.

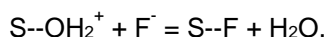
Adsorption

Trace / minor levels of fluoride can be effectively removed by adsorption onto activated alumina. The alumina needs to be activated by treatment with acid or aluminium sulfate solution to enhance the fluoride adsorption efficacy and capacity. The fluoride can be stripped from the alumina by acid and/or alkali treatment followed by rinsing. However, the volumes of strip solution generated in the process may well be similar to that of the solution treated, so that the process water balance might not be amenable to reuse of the alumina.

Alum impregnated activated alumina⁽²²⁾⁽²³⁾ is effective for fluoride removal over a broad range of concentrations and able to achieve up to 99% fluoride removal with effluent fluoride concentrations below 1 mg/L. The maximum fluoride removal capacity of the activated alumina occurs around pH 6.5, with a significant reduction in capacity as the pH rises, falling to around 20% extraction by pH 10. Tripathy et al.⁽²²⁾ proposed that the initial acidic activation of the alumina resulted in protonation of the oxide surface:



that could then adsorb the negative fluoride ions:



They also suggest that precipitation on the alumina surface may be involved. Tramfloc⁽²³⁾ warn that presence of bicarbonate can cause a significant reduction in the fluoride adsorption capacity, with much less effect from sulfate and chloride ions. Hence activated alumina adsorption is suitable for treatment of the pregnant solution before primary lithium carbonate precipitation, but is probably not suitable for polishing the bicarbonate solution ahead of final lithium carbonate precipitation. Tramfloc⁽²³⁾ do not provide any pH data for their solutions, but the reported reduction in capacity seems to be greater than what might be expected by the rise in pH from spiking the solutions with sodium bicarbonate.

Selective Ion Exchange

Ion exchange is well suited for stripping low concentration species from solutions. Within lithium chemical production it can be considered for final polishing for removal of low concentrations of boron, calcium and magnesium. However, it is necessary to consider what else is in solution, in the choice of the ion exchanger and the chemical form that it is used in. It is also necessary to consider the

overall solution ionic strength (total dissolved salts – TDS,) as selectivity can be drowned out by high background ionic strength. Hence ion exchange resins are more applicable for polishing the bicarbonation solution ahead of precipitation of high purity lithium carbonate, than for a high TDS leach liquor ahead of primary lithium carbonate precipitation. It is also necessary to consider the solution pH to ensure that the target species is in the correct ionic form, (eg $B(OH)_4^-$ anion at pH >9) as well as the initial form of the resin to ensure selectivity.

Solvent Extraction

Choice of the appropriate extractant or combination of extractants can often offer the highest selectivity and is appropriate over a wider concentration range than for selective ion exchange or adsorption. Hence it is the standard route for boron removal at the g/L concentration range for lithium extraction liquors sourced from brines. However while selectivity can be high the process might need to be repeated a number of times. Hence typically three or four stages in series are required for boron removal to get the boron concentration down.

Solvent extraction has also been proposed as an option to recover lithium from brines to produce a purified stream for lithium recovery⁽²⁴⁾.

DISCUSSION

Basis of Choice

Efficacy

The first factor to consider in the choice of an impurity removal process is the efficacy on the particular solution. Processes such as crystallisation can be selective but are likely to leave a significant concentration of the species in solution due to the high solubility of many of the species under consideration. Hence, they are applicable to providing a process bleed, but not for polishing a final pregnant liquor. Other processes such as selective ion exchange work well on low to moderate ionic strength solutions, but can be ineffective in the presence of high concentrations of competing ions of the same charge. Hence ion exchange for calcium removal is less effective on the high TDS liquor ahead of primary lithium carbonate precipitation, but more applicable to polishing removal of calcium from the solution in bicarbonation, when there are only trace levels of divalent cations and lower levels of potassium and sodium in solution. Adsorption onto activated alumina is less affected by ionic strength than ion exchange, but is susceptible to interference by bicarbonate ions, so can be used before primary lithium carbonate precipitation, but may be less suited to polishing the bicarbonation solution. Hence, efficacy for a particular solution can drive the choice of option and where it fits into the flowsheet.

Lithium Losses

Kings Mountain plant is reported to have achieved a lithium leach extraction of 93% and an overall lithium recovery in the plant of 88%. Current secondary lithium mineral plants are typically designing to achieve an overall lithium recovery >80%. In all plants the major point of lithium loss in the flowsheet is the wet residue which typically disposed of in a Tailings Storage Facility (TSF). The other points where lithium can be lost are:

- entrained with other residues
- by-products, and
- process bleeds.

Lithium losses can be reduced by washing solids and reducing the amounts of impurities that are added with the reagents. It is easy to see that an unplanned lithium loss of 10% in impurity removal, or as a result of increased moisture in a residue can have a dramatic effect on the plant economics.

Opex

As noted earlier the cheapest reagent is not necessarily the most cost effective if it results in higher lithium losses. Order/combo of process stages also needs to be considered to minimise the number of times that the pH needs to be adjusted up or down. Each change brings added reagent

demand to get back to the required conditions to complete the process, as well as increasing the salt load that has to be managed to maintain the water balance. It is fairly obvious that expensive ion exchange resins for selective removal will need to be regenerated, but it is not as clear cut for the use of activated alumina for fluoride adsorption, where cost savings from reuse are less clear and the reuse option may be ruled out by the process water balance.

Case Study

Figure 5 shows the flowsheet developed for the Bacanora lithium project⁽²⁵⁾ that will serve to demonstrate how the different aspects discussed above have been brought together for removal of the minor and trace impurities in the process liquor stream.

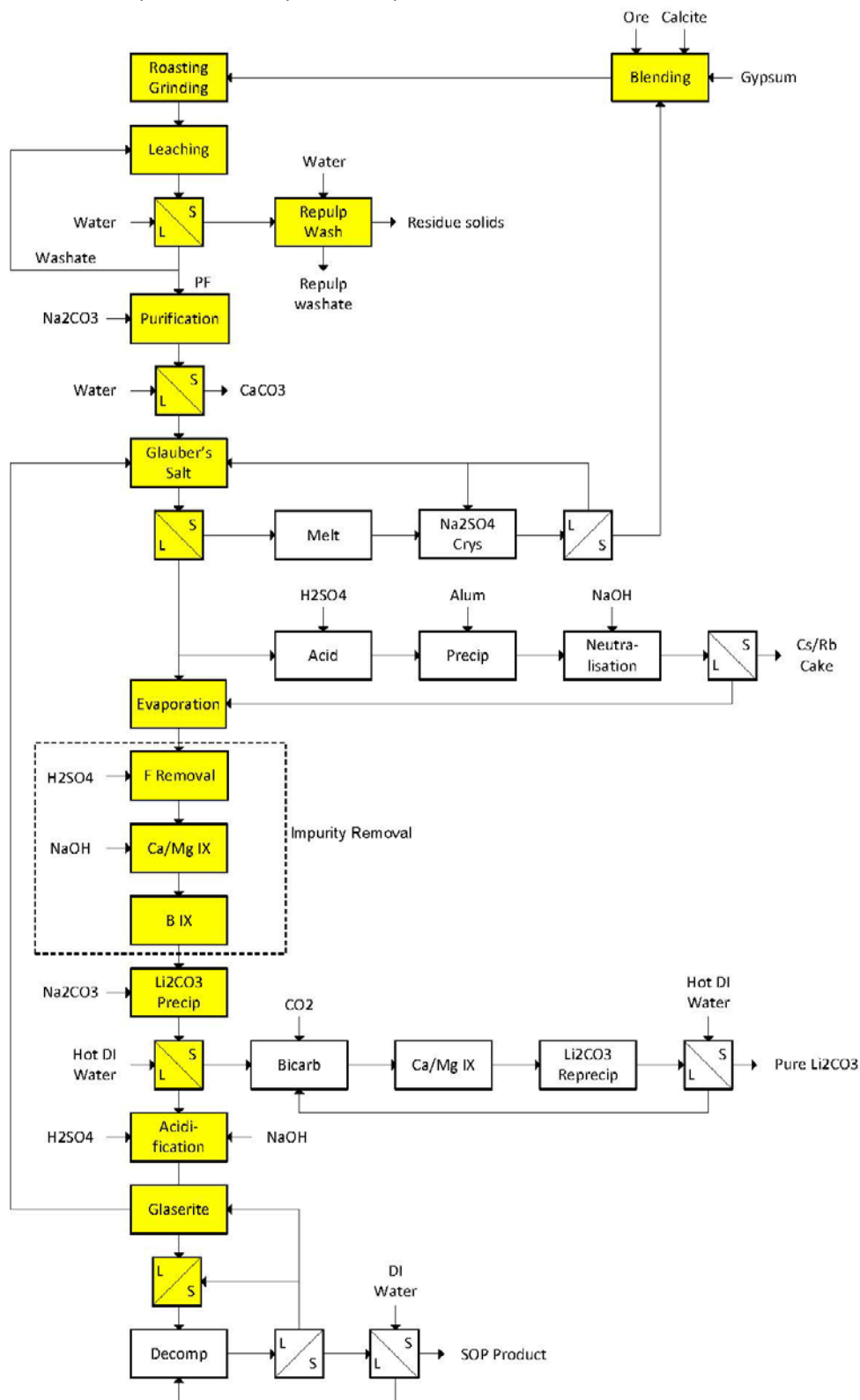


Figure 5 : Sonora lithium carbonate production flowsheet (after⁽²⁵⁾)

Caesium / Rubidium Bleed

Caesium and rubidium are the first of the minor/trace impurities to be dealt with following Glauber's salt crystallisation. Mixed alum crystallisation is used to control the caesium and rubidium concentrations in the in the recycled process liquor. It is carried out on a split stream to reduce reagent requirements as it needs to be preceded by acidification and followed by neutralisation to minimise scale formation, when the bleed stream is sent to evaporation to concentrate up the lithium. In addition, excess aluminium sulfate addition is required to favour crystallisation, so it needs to be early enough in the flowsheet so that the excess aluminium can itself be dealt with.

Fluoride Removal

Fluoride is removed by adsorption onto alumina that has been activated by the use of aluminium sulfate. Hence residual aluminium sulfate in the recycled stream from caesium and rubidium control is not a problem as it can help activation of the alumina and enhance fluoride removal. Sulfuric acid is added as required to maintain the solution pH around pH 6 to maximise the loading capacity of the activated alumina.

Calcium / Magnesium Removal

The flowsheet includes an ion exchange stage for removal of residual levels of polyvalent cations such as calcium, magnesium and aluminium. Aminophosphonic cation exchange resins (such as Puromet™ S9500) in a monovalent cation form are normally able to provide excellent polishing for removal of polyvalent ions in water treatment applications. The resin also provides a trap for any aluminium that might leak through from the fluoride adsorption step. Selectivity for polyvalent cations is higher at higher pH, so caustic is added to raise the solution pH ahead of resin contact. However, as noted earlier the high concentrations of potassium and lithium in the liquor limit the efficacy of the resin, so that a further ion exchange stage is included in this flowsheet. Prior to use the resin needs to be conditioned with lithium hydroxide, to avoid addition of other contaminants. After use the resin is regenerated with sulfuric acid.

Ion exchange is used for a further calcium / magnesium removal stage on the lower ionic strength bicarbonation liquor ahead of final lithium carbonate precipitation.

Boron

A chelating anion exchange resin with N-methyl glucamine functional groups (such as UltraClean™ UCW1080 from Purolite) has good selectivity for boron (in the form of borate, $B(OH)_4^-$ at pH >9). Hence the raised solution pH for the calcium / magnesium removal stage does not need further pH adjustment ahead of boron removal. After use the boron is stripped from the resin with sulfuric acid and the resin then regenerated with hydroxide.

CONCLUSIONS

The design of an impurity removal flowsheet starts with an understanding of the impurities of concern and their likely concentrations in the initial leach liquor from sighter batch testwork. The required removal efficiencies for each component can then be assessed, based on what can be tolerated in the final pregnant solution for lithium salt production.

Available clean-up process options can then be assessed for their suitability either singly or in combination to achieve the required impurity removal. They also need to be evaluated in the light of their operating conditions and potential lithium losses, to see how they might be inserted into the flowsheet to work together, to minimise pre and post treatment steps such as pH control and minimise lithium losses. The main issues to understand are solution contamination through added chemicals, operating removal efficacy and lithium losses on actual process solutions. Potential solution contamination issues will drive where a particular impurity removal process fits within the flowsheet to minimise the effect on the process. The ability to reduce lithium losses across a removal process, if certain solution components are minimised, will also drive the order in which removal processes need to be carried out to minimise losses.

Locked cycle testwork of the combined flowsheet can then be carried out to test the effect of the recycle loops and determine overall lithium recovery to product.

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