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# Producing Battery Grade Lithium Chemicals from Complex Leach Liquors

Grant Harman<sup>1</sup> & Stephen La Brooy<sup>2</sup> June, 2018

<sup>1</sup>Lithium Consultants Australasia, West Perth, Australia

<sup>2</sup>Ausenco, Perth, Australia

# Agenda

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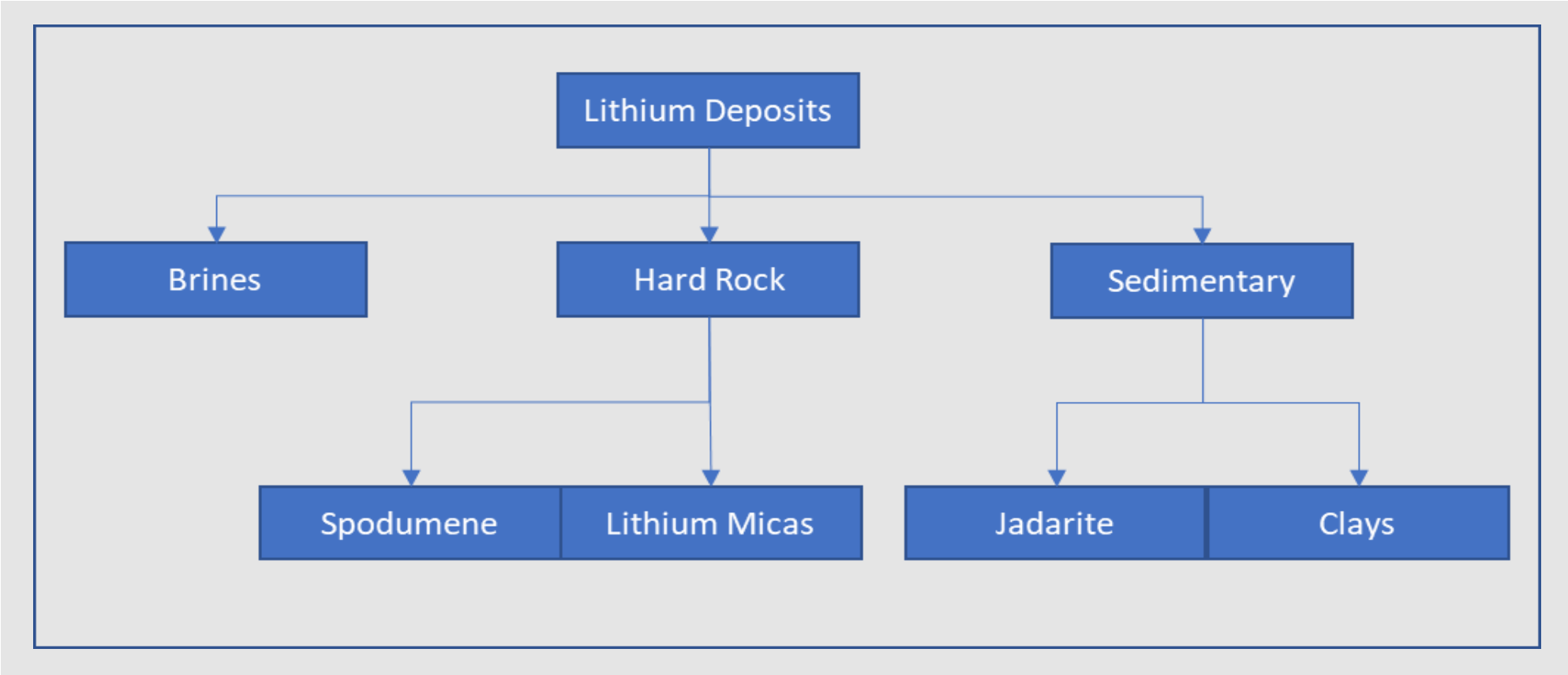
1. Sources for Lithium
2. Limiting Co-Extraction
3. Typical Leach Liquors
4. Battery Grade Impurity Targets
5. Removal Technologies
6. Basis of Choice
7. Conclusions





## Sources for Lithium

# Sources for Lithium



# Sources of Lithium - Notes

- Lithium is currently sourced from either brine or hard rock.
- In the figure the three main options are shown including from sedimentary sources such as clays and jadarite.
- Some lithium is currently sourced from micas but the amount is very small and not significant.

# Feed Minerals

- Feed grades
- Impurities

Mineral	Main Locations	Chemical Formula	Mineral wt% Li <sub>2</sub> O	Con Grade wt% Li <sub>2</sub> O
Spodumene	Australia	Li <sub>2</sub> OAl <sub>2</sub> O <sub>3</sub> (SiO <sub>2</sub> ) <sub>4</sub>	8.0	5-7.5
Petalite	Zimbabwe	Li <sub>2</sub> OAl <sub>2</sub> O <sub>3</sub> (SiO <sub>2</sub> ) <sub>8</sub>	4.9	3-4
Zinnwaldite	Czech Republic	KLiFeAl(AlSi <sub>3</sub> )O(F,OH)	2 - 5	3
Lepidolite	Zimbabwe	K(Li,Al) <sub>3</sub> (Si,Al) <sub>4</sub> O <sub>10</sub> (F,OH) <sub>2</sub>	3.3-7.7	
Hectorite	Mexico, USA	Na <sub>0.3</sub> (Mg,Li) <sub>3</sub> Si <sub>4</sub> O <sub>10</sub> (OH) <sub>2</sub>	1.3	0.6-1.3
Jadarite	Serbia	LiNaSiB <sub>3</sub> O <sub>7</sub> (OH)	7.3	
Amblygonite	Canada	LiAlPO <sub>4</sub> (F,OH)	10.1	
Eucryptite	Zimbabwe	Li <sub>2</sub> OAl <sub>2</sub> O <sub>3</sub> (SiO <sub>2</sub> ) <sub>2</sub>	11.8	
Zabuyelite	China	Li <sub>2</sub> CO <sub>3</sub>	40.4	

# Feed Minerals - Notes

- The table shows the nine lithium minerals which are thought to be commercial.
- Currently spodumene is the dominant mineral source which, until recently, contributed 30% of all the lithium sources.
- Eucryptite, spodumene and petalite are all the same, differing only in the number of silica oxides.
- There is only one zinnwaldite and one jadarite project being progressed by EMH and Rio Tinto respectively.
- There are two advanced clay projects with the Bacanora Minerals, Sonoro project in Mexico being the most promising.
- Most of the secondary lithium minerals have a larger amount of elements in the mineral which are co-leached in varying degrees depending on the roasting/ leaching technology.

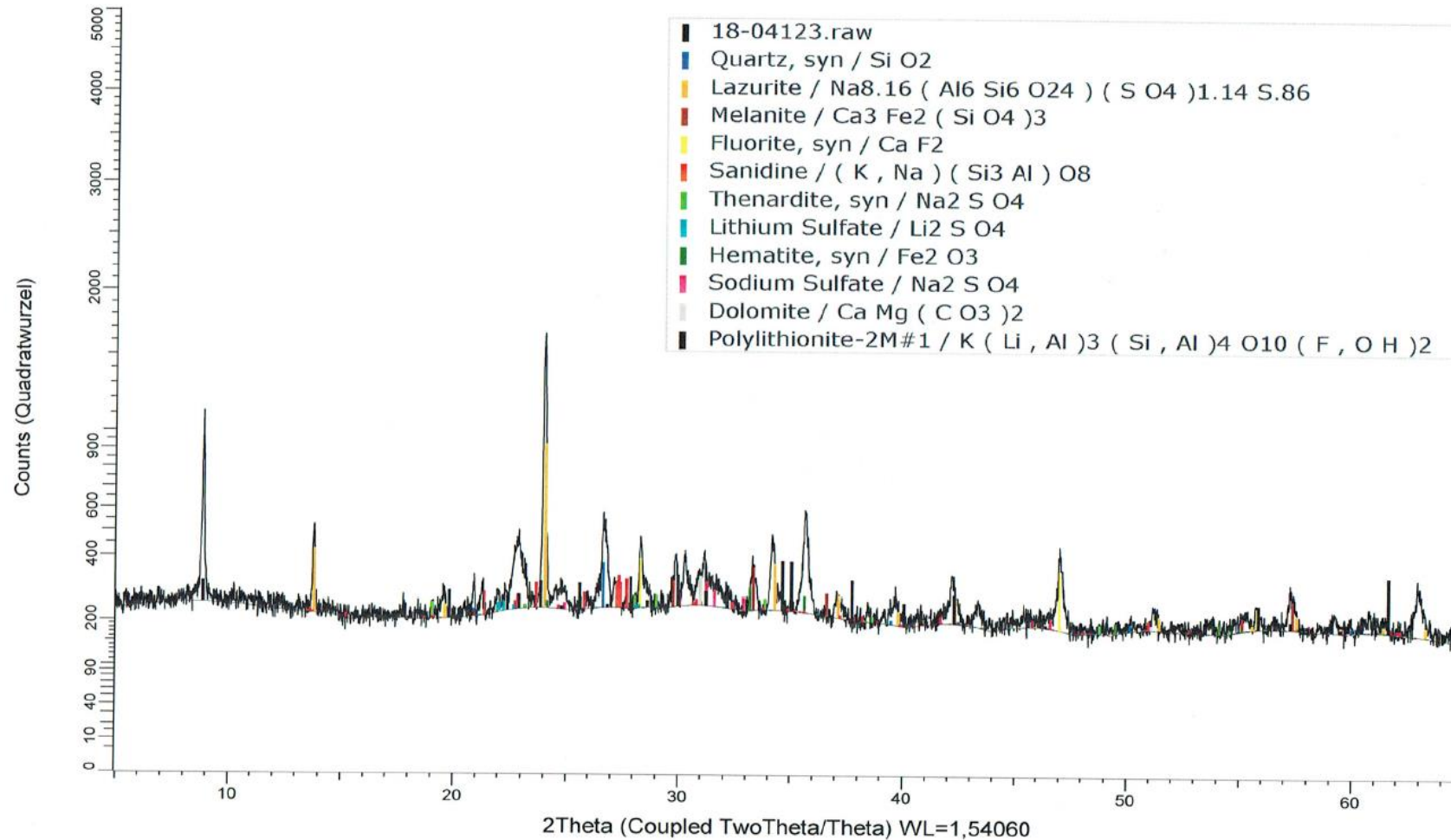
Ausenco



Limiting Co-Extraction



# XRD of a Alkali Salt Roast of a Lithium Mica



# Limiting Co-Extraction - Notes

- The most obvious way to simplify the cleaning of the leach solution is to limit the amount of the impurities being co-extracted with the lithium.
- Alternatively to prevent impurities being introduced in reagents or make-up water.
- The XRD shows the following points of interest:
  - Not all of the polyolithionite is converted
  - The temperature of the roast is too low and the dolomite is not adequately reacted
  - The iron is trapped as melanite and hematite
  - The free silica is trapped as melanite, lazurite and sanidine
  - The fluoride is trapped as  $\text{CaF}_2$

# Changing Roast Conditions to Limit Impurities

	Units	P	Ti	Zn	Nb	Ta	Cs	Sr	F	Cl
Roasted Ore Leach Liquor	mg/L	0.9	<0.1	<0.1	<0.1	<0.1	0.6	1.2	140	2.8
Acid Wash of residue	mg/L	0.3	<0.1	7	<0.1	0.19	0.27	1.3	2,040	136

The roasting and leaching conditions can result in a major impact on the elements extracted.

In the table above the secondary lithium mineral was roasted with alkali salts followed by an acid wash.

The alkali roast limited the amount of impurities that were leached but an acid leach at ambient temperature of the residue with 5 wt% H<sub>2</sub>SO<sub>4</sub> had a profound impact on the elements co-extracted.



## Typical Leach Liquor from Lithium Minerals

# Leach Liquors

	Units	Typical Spodumene	Petalite	Gypsum-lime Roast Leach McDermitt B Clay	175°C 920 g/L H <sub>2</sub> SO <sub>4</sub> lepidolite leach	Typical Zinnwaldite CaSO <sub>4</sub> -CaCO <sub>3</sub> roast leach
<b>Li</b>	g/L	<b>9.6</b>	<b>5.7</b>	<b>2.9</b>	<b>5.1</b>	<b>2</b>
<b>K</b>	g/L	<b>0.2</b>	<b>0.45</b>	<b>13</b>		<b>5.5</b>
<b>Na</b>	g/L	<b>1.28</b>	<b>1.42</b>	<b>3.1</b>		<b>0.2</b>
<b>Rb</b>	mg/L	-				<b>325</b>
<b>Ca</b>	mg/L	<b>100</b>	<b>145</b>	<b>540</b>		<b>180</b>
<b>Mg</b>	mg/L	<b>30</b>	<b>12</b>	<b>30</b>		<b>20</b>
<b>Al</b>	mg/L	<b>1,300</b>	<b>10</b>	-	<b>3,100</b>	<b>131</b>
<b>Fe</b>	mg/L	<b>650</b>	<b>38</b>	-	<b>80</b>	<b>&lt;100</b>
<b>Mn</b>	mg/L	<b>40</b>		-	<b>170</b>	<b>&lt;100</b>
<b>Si</b>	mg/L	<b>40</b>	<b>33</b>	-		<b>50</b>
<b>pH</b>		<b>1.6</b>	<b>0.95</b>	<b>Neut-alkaline</b>		<b>~10</b>

Based on limited information in public domain

# Typical Impurities in a Lithium Leach Liquor

1 <b>H</b> Hydrogen 1.0079																	2 <b>He</b> Helium 4.0026				
3 <b>Li</b> Lithium 6.941	4 <b>Be</b> Beryllium 9.0122															5 <b>B</b> Boron 10.81	6 <b>C</b> Carbon 12.011	7 <b>N</b> Nitrogen 14.007	8 <b>O</b> Oxygen 15.999	9 <b>F</b> Fluorine 18.998	10 <b>Ne</b> Neon 20.179
11 <b>Na</b> Sodium 22.990	12 <b>Mg</b> Magnesium 24.305															13 <b>Al</b> Aluminum 26.982	14 <b>Si</b> Silicon 28.086	15 <b>P</b> Phosphorus 30.974	16 <b>S</b> Sulfur 32.06	17 <b>Cl</b> Chlorine 35.453	18 <b>Ar</b> Argon 39.948
19 <b>K</b> Potassium 39.098	20 <b>Ca</b> Calcium 40.08	21 <b>Sc</b> Scandium 44.956	22 <b>Ti</b> Titanium 47.90	23 <b>V</b> Vanadium 50.941	24 <b>Cr</b> Chromium 51.996	25 <b>Mn</b> Manganese 54.938	26 <b>Fe</b> Iron 55.847	27 <b>Co</b> Cobalt 58.933	28 <b>Ni</b> Nickel 58.71	29 <b>Cu</b> Copper 63.546	30 <b>Zn</b> Zinc 65.38	31 <b>Ga</b> Gallium 69.72	32 <b>Ge</b> Germanium 72.59	33 <b>As</b> Arsenic 74.922	34 <b>Se</b> Selenium 78.96	35 <b>Br</b> Bromine 79.904	36 <b>Kr</b> Krypton 83.80				
37 <b>Rb</b> Rubidium 85.468	38 <b>Sr</b> Strontium 87.62	39 <b>Y</b> Yttrium 88.906	40 <b>Zr</b> Zirconium 91.22	41 <b>Nb</b> Niobium 92.906	42 <b>Mo</b> Molybdenum 95.94	43 <b>Tc</b> Technetium (98)	44 <b>Ru</b> Ruthenium 101.07	45 <b>Rh</b> Rhodium 102.91	46 <b>Pd</b> Palladium 106.4	47 <b>Ag</b> Silver 107.87	48 <b>Cd</b> Cadmium 112.41	49 <b>In</b> Indium 114.82	50 <b>Sn</b> Tin 118.69	51 <b>Sb</b> Antimony 121.75	52 <b>Te</b> Tellurium 127.60	53 <b>I</b> Iodine 126.90	54 <b>Xe</b> Xenon 131.30				
55 <b>Cs</b> Cesium 132.91	56 <b>Ba</b> Barium 137.33	57 <b>*La</b> Lanthanum 138.91	72 <b>Hf</b> Hafnium 178.49	73 <b>Ta</b> Tantalum 180.95	74 <b>W</b> Tungsten 183.85	75 <b>Re</b> Rhenium 186.21	76 <b>Os</b> Osmium 190.2	77 <b>Ir</b> Iridium 192.22	78 <b>Pt</b> Platinum 195.09	79 <b>Au</b> Gold 196.97	80 <b>Hg</b> Mercury 200.59	81 <b>Tl</b> Thallium 204.37	82 <b>Pb</b> Lead 207.2	83 <b>Bi</b> Bismuth 208.98	84 <b>Po</b> Polonium (209)	85 <b>At</b> Astatine (210)	86 <b>Rn</b> Radon (222)				
87 <b>Fr</b> Francium (223)	88 <b>Ra</b> Radium (226)	89 <b>†Ac</b> Actinium (227)	104 <b>Rf</b> Rutherfordium (267)	105 <b>Db</b> Dubnium (268)	106 <b>Sg</b> Seaborgium (271)	107 <b>Bh</b> Bohrium (272)	108 <b>Hs</b> Hassium (270)	109 <b>Mt</b> Meitnerium (276)	110 <b>Ds</b> Darmstadtium (281)	111 <b>Rg</b> Roentgenium (280)	112 <b>Cn</b> Copernicium (285)	113 <b>Nh</b> Nihonium (284)	114 <b>Fl</b> Flerovium (289)	115 <b>Mc</b> Moscovium (288)	116 <b>Lv</b> Livermorium (293)	117 <b>Ts</b> Tennessine (294)	118 <b>Og</b> Oganesson (294)				

What are the Target Maximum Impurity Levels for Battery Grade

# Target Maximum Impurity Levels

- The Chinese specification for battery grade lithium carbonate is shown in the table alongside.
- The specification for fluoride has been assumed based on EV specifications.
- Estimated target impurity levels calculated on the assumption that impurities concentrate up in the solids roughly 20 times.

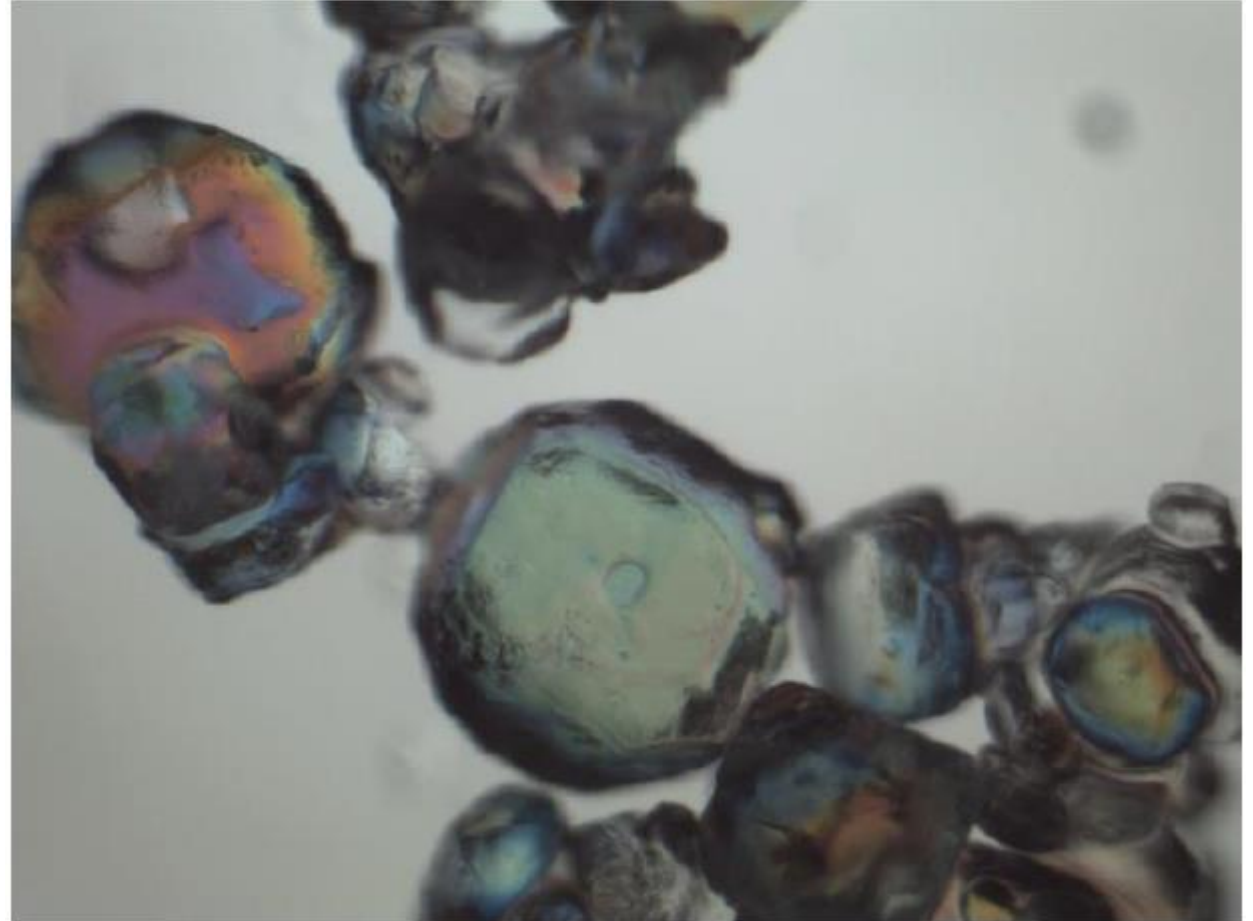
Chemical Properties	Chinese Battery Grade YS/T582- (2013)	Estimate Target Impurity Level
	ppm	ppm
Ca [wt%]	50	2.5
Zn [wt%]	3	0.15
Mg [wt%]	80	4
Fe [wt%]	10	0.5
Ni [wt%]	10	0.5
Al [wt%]	10	0.5
Mn [wt%]	3	0.15
Pb [wt%]	3	0.15
Cu [wt%]	3	0.15
Si [wt%]	30	1.5
Cl [wt%]	30	1.5
F [wt%]	50	2.5



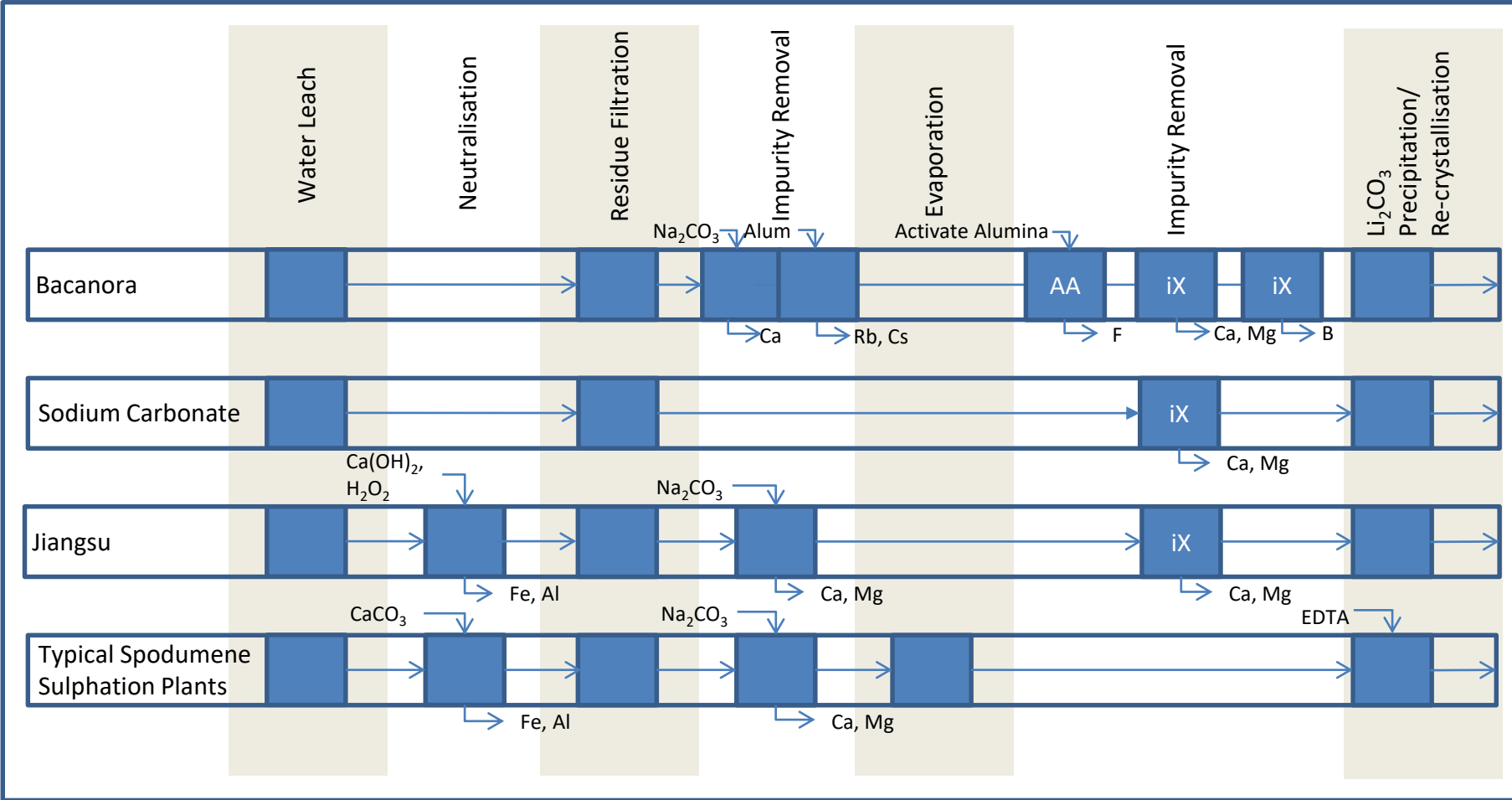
## Impurity Removal Technologies Overview

# Impurity Removal Technologies

- Chemical Precipitation
- Crystallisation
- Adsorption
- Ion exchange
- Solvent Extraction



# Comparison of Impurity Removal Techniques

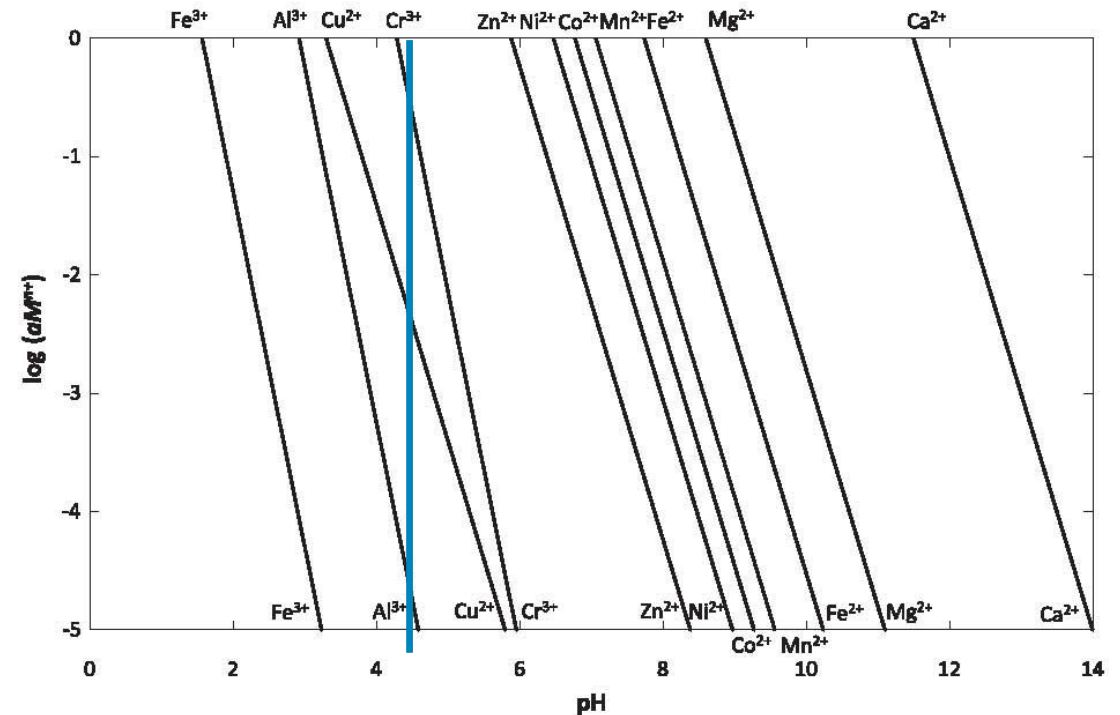




## Impurity Removal Chemical Precipitation

# Chemical Precipitation – Fe & Al

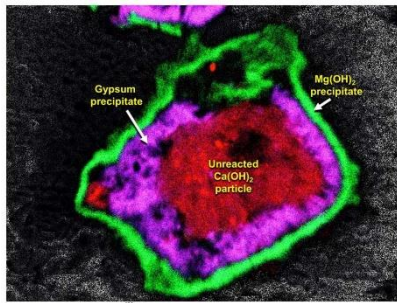
- Hydroxide Precipitation
- Ferric iron & Aluminium
  - pH 4.5-5
  - limestone (or lime)
- Other reactions
  - Some calcium precipitates as gypsum
  - Some fluoride precipitates as  $\text{CaF}_2$  /  $\text{AlF}_3$  down to ~20 mg/L F



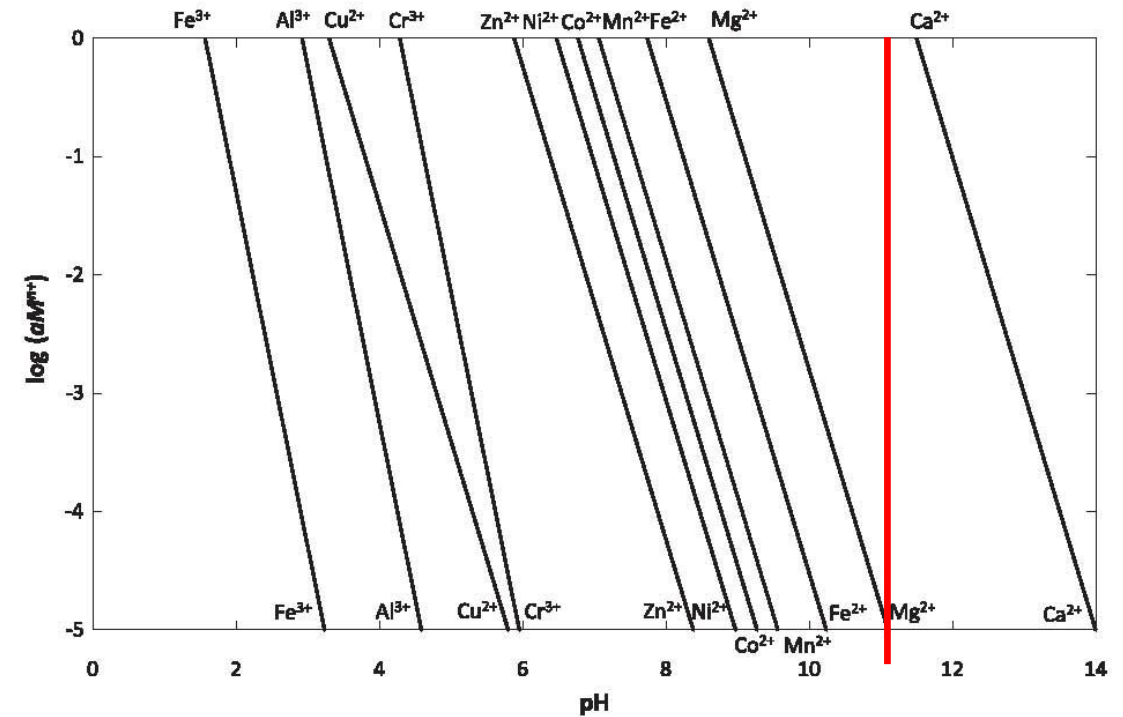
pH effect on hydroxide precipitation

# Chemical Precipitation – Mn & Mg

- Hydroxide Precipitation
- Manganese & Magnesium
  - pH 11
  - Lime, caustic or LiOH



100 μm  
After Ineich et al. 2017



pH effect on hydroxide precipitation

# Chemical Precipitation - Ca

- Precipitation as calcium carbonate with soda ash
- Filtration
- Residual calcium around  $<40$  mg/L



# Chemical Precipitation of Calcium - Notes

- The addition of sodium carbonate is normally done based on stoichiometry with the amount typically in the region of 110% of 10% excess.
- Anecdotally, in the laboratory the amount of sodium carbonate that can be added can be far higher without any adverse effects of co-precipitation of other elements.
- However, in one Chinese plant there is reported precipitation of lithium with the calcium on the surfaces of the tank walls and the piping, and this scale was extremely hard and difficult to remove.
- Depending on the composition of the liquor the temperature and amount of sodium carbonate added might need to be adjusted to minimise or prevent scale formation.
- In order to prevent calcium precipitation in the evaporator downstream, adjusting the pH may reduce scaling of the evaporator.

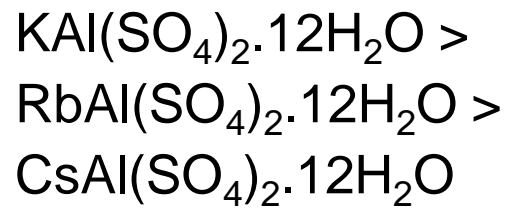




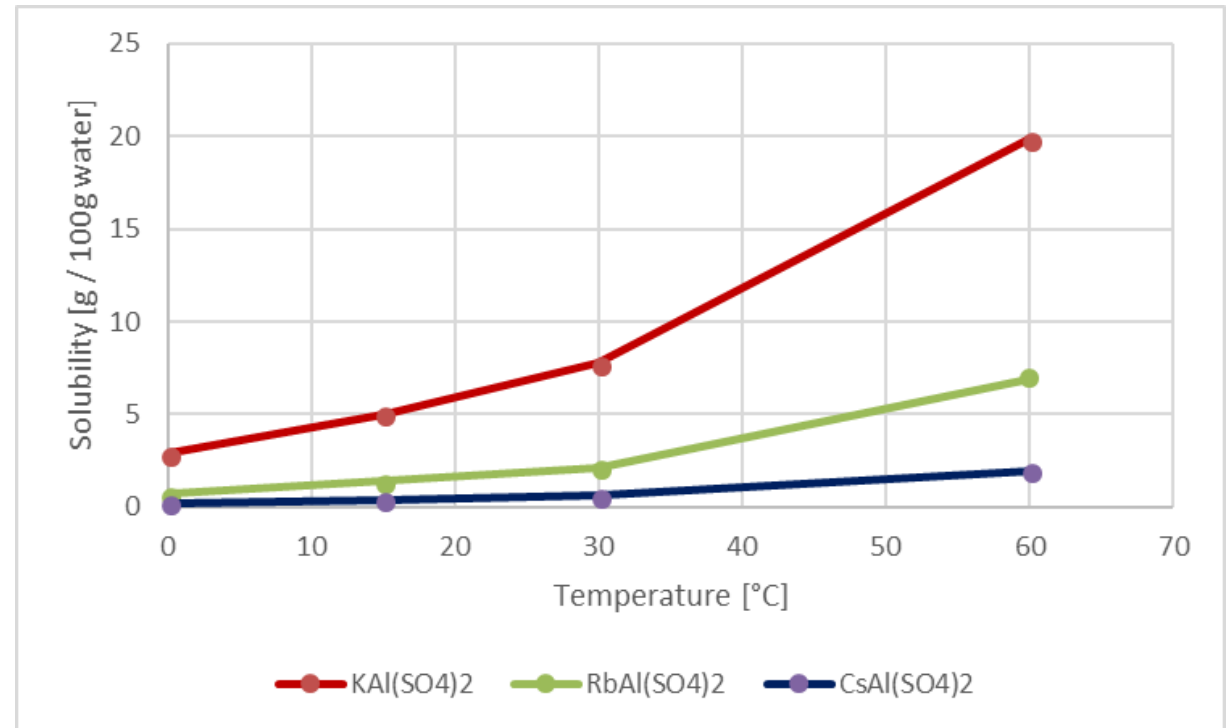
## Impurity Removal Crystallisation

# Crystallisation – Rb & Cs

- Caesium & Rubidium
  - Add acid to ~pH 3
  - Add excess aluminium sulfate
  - Cool to crystallise mixed alums
  - Mixed alum solubility



- Filter / centrifuge
- Add caustic to raise pH



Data from Hart, W.A., Beumel, F & Whaley, T.P., (2013) *The chemistry of lithium, sodium, potassium, rubidium, cesium & francium* (Pergamon Texts in Inorganic Chemistry)

# Crystallisation of Rb & Cs - Notes

- Typically the amount of Rb removed is ~ 50% and 95% for Cs.
- Typically the amount of potassium removed depends on the temperature and is partially removed by cooling to commercially acceptable temperatures.
- The solubility of sodium is far higher and essentially no sodium is removed.
- Lithium appears to act dissimilarly to the other Group 1 analogues.
- Typically an great excess of alum is added and needs to be removed by the addition of sodium hydroxide. The Rb and Cs alums must be filtered before the addition of the sodium hydroxide as the group 1 alums will partially re-dissolve.

# Crystallisation – B, Na, F

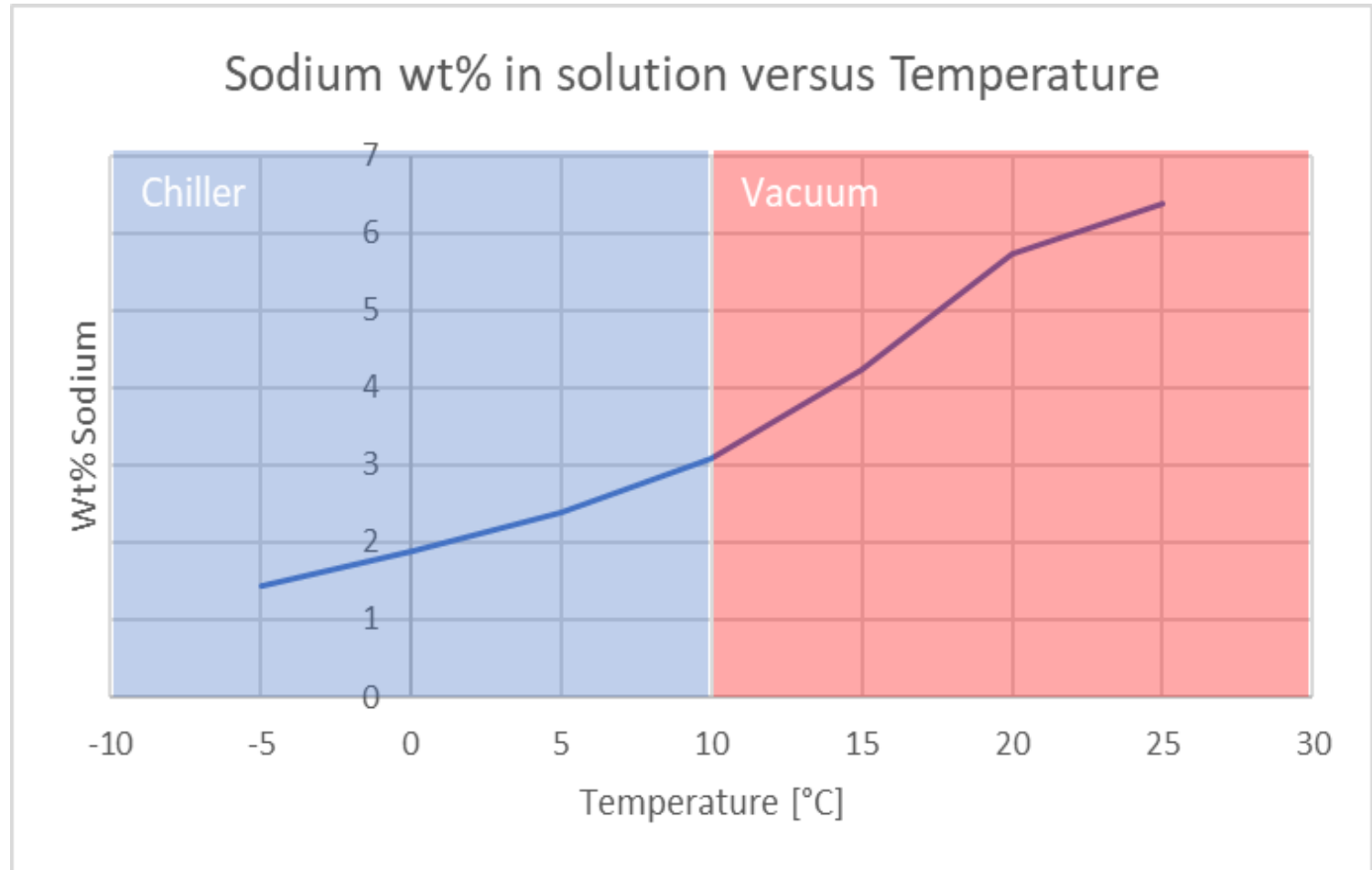
At higher concentrations

- Boron
  - boric acid ( $\text{H}_3\text{BO}_3$  - for jaderite feed)
- Sodium Sulfate bleed
  - Glauber's salt ( $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ )
- Fluoride
  - Khadamite ( $\text{Al}(\text{SO}_4)\text{F} \cdot 5\text{H}_2\text{O}$  – (L-Max process)



# Sodium Sulphate Removal by Cooling Crystallisation

- Cooling down to 10°C possible with vacuum flashing
- Cooling below 10°C requires a chiller





## Impurity Removal Adsorption & Ion Exchange

# Adsorption - F

- Polishing fluoride removal
  - Alum impregnated activated alumina
$$\text{S--OH} + \text{H}^+ = \text{S--OH}_2^+$$
$$\text{S--OH}_2^+ + \text{F}^- = \text{S--F} + \text{H}_2\text{O}.$$
- Residual fluoride concentration <1 mg/L



# Removal of Fluoride - Notes

- Fluoride has been successfully removed using lime and alum but not down to the levels required to produce battery grade lithium carbonate.
- Large excess of alum has been shown to be required and the pH needs to be adjusted to around 3.
- The voluminous precipitate tends to remove up to 10% of the lithium. Washing of the precipitate is not practical as a fair amount of the fluoride is solubilised in the process which defeats the purpose of the removal step.
- Ion exchange not thought to be practical due to the large amount of waste liquor created.
- Similarly attempts to regenerate the activated alumina have not been very successful for the same reason as for ion exchange – large amounts of waste liquor.



# Polishing Ion Exchange – Ca, Mg, Al, B

- Resin columns in lead / lag configuration
- Aminophosphonic cation resin in monovalent cation form:
  - Calcium –  $\text{Ca}^{2+}$
  - Magnesium –  $\text{Mg}^{2+}$
  - Aluminium –  $\text{Al}^{3+}$
- Chelating anion resin with N-methyl glucamine groups:
  - Boron –  $\text{BO}_4^-$



# Basis of Choice

- Efficacy
  - Partial removal to control build up
  - More complete removal for polishing final solutions
- Lithium Losses
  - Co-precipitation
  - Entrained solution in residues
  - Process bleeds
  - By-products
- Opex
  - Cheapest not necessarily most cost effective





## Conclusions

# Conclusions

- Try not to get impurities into solution in the first place
- Understand the impurities that need to be removed
- Evaluate available clean up processes
  - Efficacy
  - Lithium Losses
  - Inherent Opex
  - Ease of integration into flowsheet
  - Additional Opex from integration into flowsheet
  - Final product quality
  - Overall lithium losses



# Thank you.

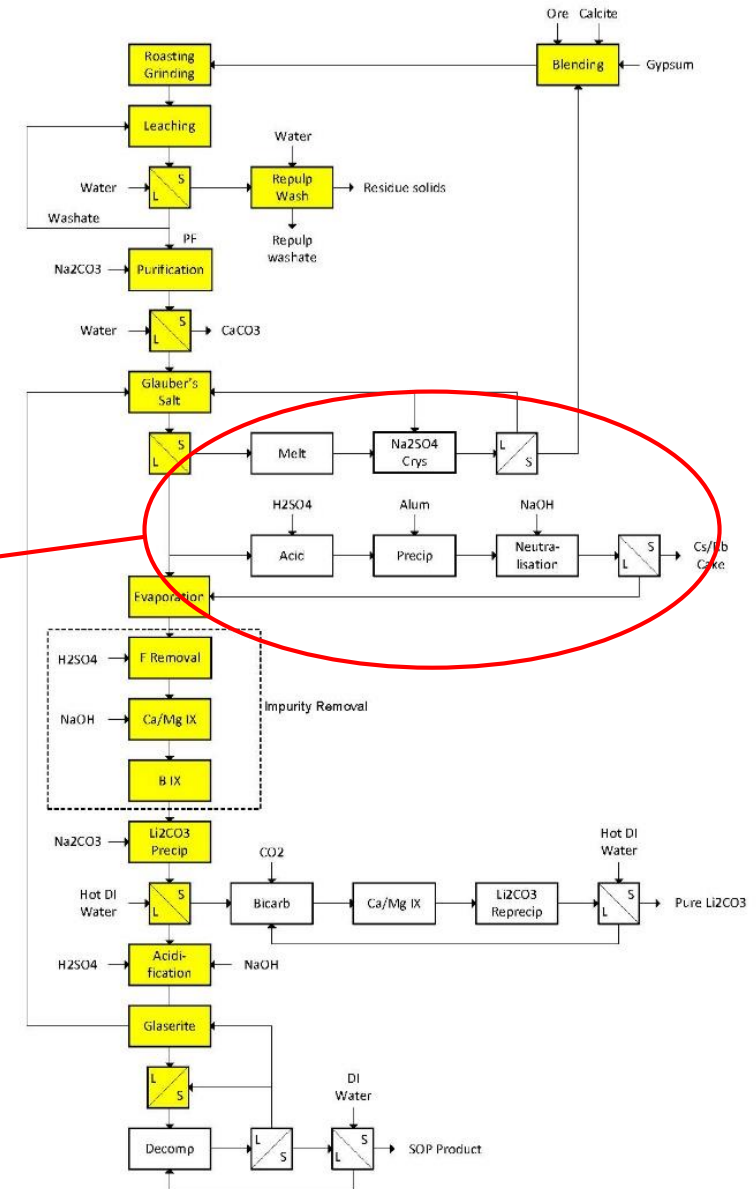
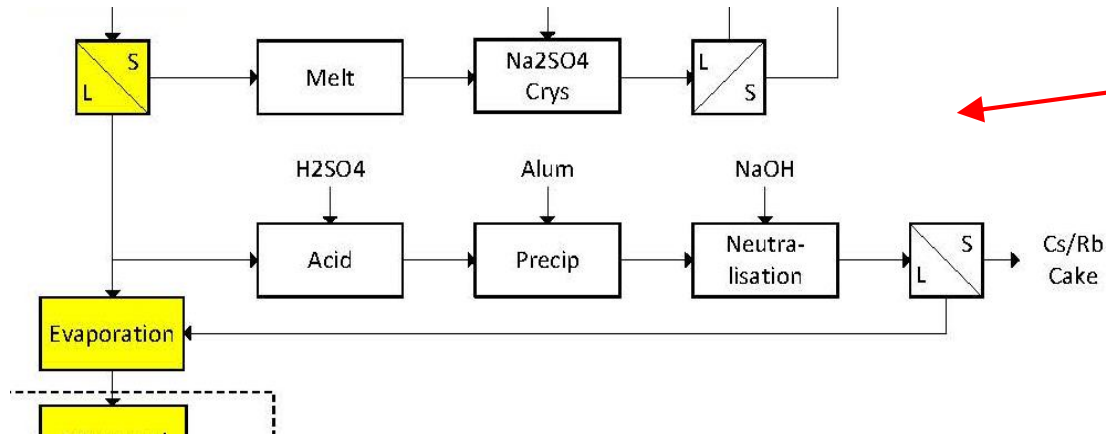
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# Case Study – Cs & Rb

## Caesium / Rubidium Removal by crystallisation of double alum



# Case Study – F, Ca, Mg & B

- Fluoride – activated alumina
- Calcium / Magnesium – aminophosphonic cation resin
- Boron – chelating n-methyl glucamine anion resin

