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LITHIUM ION SIEVE TECHNOLOGY FOR RECOVERY OF LITHIUM FROM BRINE

By

Mike Dry

Arithmetek Inc., Canada

Presenter and Corresponding Author

Mike Dry

mike.dry@arithmetek.com

ABSTRACT

Conventional technology for the production of lithium carbonate from salar brine is based on solar evaporation and is economically limited to brines in which the ratio of divalent cations such as calcium and magnesium to lithium is such that the cost of the reagents (lime, sodium hydroxide, sodium carbonate) required to precipitate the divalent cations ahead of the precipitation of lithium carbonate is not prohibitive. The Smackover formation in the southern United States constitutes a large reserve of lithium, but the high ratio of calcium to lithium in this brine renders conventional technology based on solar evaporation uneconomic.

This paper presents a novel circuit based on lithium ion sieve chemistry, that can extract lithium from brine in the presence of large amounts of calcium and does not require prior concentration of the brine. The circuit has been developed through laboratory-batch and continuous mini-pilot testing, to a demonstration plant in Arkansas that was commissioned early in 2020.

This paper outlines the basic chemistry and preliminary economics of the circuit for an oilfield brine. It also presents a comparison of the novel circuit against conventional solar evaporation technology for extracting lithium carbonate from a conventional salar brine.

Keyword: Lithium, high-Ca brine, lithium ion sieve.

INTRODUCTION

The coming EV (electric vehicle) revolution will require substantial increases in production of the metals used for making the requisite batteries. Another presentation at this conference⁽¹⁾ outlines the amounts of nickel, cobalt and lithium called for by two scenarios published by the International Energy Agency⁽²⁾. The lower of these, called the “New Policies Scenario”, predicts 130 million EVs on our roads by 2030. The higher scenario, called the “EV30@30 Scenario”, predicts 250 million EV’s by 2030. Table 1 is an extract from that presentation listing the amounts of lithium required for various Li ion batteries, assuming a single battery to have a capacity of 100 kWh (for a range roughly equivalent to that of the cars most of us drive at present).

Table 1 – Lithium requirements per 100 kWh battery

Type	Li, kg
LFP	7.8
NCA	11.2
NMC 1:1:1	13.9
NMC 6:2:2	12.6
NMC 8:1:1	11.1

Current known global reserves of lithium are 80 million tonnes. In 2018 and 2019, respectively, the annual production of lithium was 95 and 77 thousand tonnes per year⁽³⁾. Multiplying the amounts of lithium per individual battery (Table 1) by 130 or 250 million gives the amounts of lithium that would be required for the various battery types in the two IEA scenarios. Table 2 lists these numbers as Mt (million tonnes) and as percentages of reserves and percentages of the global 2019 production.

Table 2 – Lithium demand for EV batteries

Type	Li required, Mt		% of known reserves		% of 2019 production	
	Low	High	Low	High	Low	High
LFP	1.0	2.0	1.3	2.4	132	250
NCA	1.5	2.8	1.8	3.5	189	353
NMC 1:1:1	1.8	3.5	2.3	4.3	235	451
NMC 6:2:2	1.6	3.2	2.0	3.9	193	409
NMC 8:1:1	1.4	2.8	1.8	3.5	187	360

According to these numbers, the world has the lithium called for by these two scenarios and much more, but the amounts required entail between approximately doubling and quadrupling the current global production. This would require many, many new lithium production operations to come on-stream. A recent World Bank presentation⁽⁴⁾ goes even further, predicting that by 2050 the demand for lithium could be almost 10 times the current global production.

CONVENTIONAL BRINE PROCESSING

Lithium bearing brines exist as three categories, geothermal, salar and oilfield brines⁽⁵⁾. At present, only salar brines are exploited commercially. Table 3 lists the levels of some elements in these brines.

Table 3 – Lithium bearing brine compositions, ppm

Assay	Geothermal brine	Salar brine	Oilfield brine
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

Conventionally, solar evaporation is used to concentrate the lithium and crystallise out sodium and potassium chloride. Where necessary, the brine is limed (either before or at some suitable point in the solar evaporation

sequence) to remove magnesium and sometimes also sulphate, thereby avoiding lithium loss due to the precipitation of lithium-bearing double salts. The concentrated brine ex solar evaporation is purified to remove boron (solvent extraction and/or ion exchange), residual magnesium and calcium (precipitation via the addition of sodium hydroxide/carbonate, and sometimes also ion exchange) before lithium carbonate is precipitated by the addition of more sodium carbonate. To achieve the purity requirements for battery grade product, the precipitated lithium carbonate can be redissolved in carbon dioxide and water at low temperature and moderately elevated pressure⁽⁶⁾, the resulting bicarbonate solution being filtered and purified further if required. Releasing the pressure and heating the purified solution of lithium bicarbonate releases carbon dioxide (that can be recycled) and precipitates purified lithium carbonate.

In the conventional processing of any given lithium brine, the total amount of sodium required (as carbonate and/or hydroxide) per unit of lithium produced is set by the ratio of divalent cations (mainly magnesium and calcium) to lithium in the feed brine. If that ratio is too high, the cost of the sodium reagents needed to remove the divalent cations outweighs the value of the lithium carbonate produced and conventional processing of that brine is not economically viable. Table 4 lists some cost calculations⁽⁷⁾ for conventional brine processing that clearly show why the only brine currently processed commercially is salar brine (the current selling price for lithium carbonate is somewhere between \$10 and \$15 per kilogram).

Table 4 – Partial reagent costs for conventional brine processing

Reagent	\$/t	Requirement, kg/kg Li ₂ CO ₃			Reagent cost, \$/kg Li ₂ CO ₃		
		Geothermal	Salar	Oilfield	Geothermal	Salar	Oilfield
CaO	150	9	1.1	5.3	1.4	0.2	0.8
NaOH	560	0.1	0.02	0.1	0.1	0	0.2
Na ₂ CO ₃	370	69.5	1.8	61.2	25.7	0.7	22.6
		Sub-total			27.1	0.8	23.5

Along with new operations, one way in which the extra lithium required for EV batteries might be sourced would be via expansion of the current conventional brine (and, of course, hard rock) operations. In the case of salar-based operations, the production capacity of any given operation depends on the hydrogeology of the salar; simply increasing the rate of brine extraction can have adverse effects on adjacent sources of fresh water, for example, and opposition to solar evaporation operations is beginning to emerge⁽⁸⁾. New solar evaporation and hard rock operations are, of course, part of the solution.

LITHIUM ION SIEVES

One example of oilfield brines is the Smackover brine in Arkansas, USA, that is currently being exploited by Lanxess for the extraction of bromine. Recovery of lithium from this brine would be attractive because this is a resource already being exploited; lithium recovery would be an add-on and require no new “mining” or “tailings disposal” because these already exist from the bromine operation. Table 5 lists a partial analysis of Smackover brine⁽⁵⁾.

Table 5 – Smackover brine

Element	ppm
Mg	2677 - 2946
Ca	31243 - 35930
Na	59357-69660
K	1783 - 2453
Li	129 - 196

In Smackover brine (and oilfield brines in general) the ratio of calcium and magnesium to lithium is way too high for conventional processing. Economic recovery of lithium from these brines requires technology that can selectively extract lithium in the presence of high levels of calcium. One potentially suitable approach, being developed by Standard Lithium of Vancouver, Canada⁽⁹⁾, entails the application of a class of compounds called lithium ion sieves^(10,11,12). These are crystalline materials containing H⁺ ions in locations too small to allow exchange with any other cations except Li⁺. These materials have been found to extract lithium very selectively from solutions containing vastly more other cations such as sodium, potassium, magnesium and calcium.

ENABLING TECHNOLOGY

One material that has been found to have the properties needed for lithium ion sieves is H_2TiO_3 , meta-titanic acid^(10,11,12). When placed into a neutral lithium bearing brine, it exchanges a proton for a lithium ion according to the following equilibrium reaction (bold denotes the solid phase):

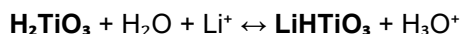


Table 6 shows some data⁽¹³⁾ for contacting H_2TiO_3 with Smackover brine. The sorbent (H_2TiO_3) was contacted with a sample of the feed brine, then the loaded sorbent was recovered from the brine, washed with water and contacted with dilute hydrochloric acid, converting the loaded sorbent ($\text{LiHTiO}_3/\text{H}_2\text{TiO}_3$) back to H_2TiO_3 and releasing Li^+ . This load/strip sequence reduced the molar ratio of calcium and magnesium to lithium by two orders of magnitude. By way of comparison, the values for salar brine in Table 3 give molar ratios of Ca to Li of between 0.01 and 7 and molar ratios of Mg to Li of between 0.2 and 0.5. The strip solution, therefore, would be an economically viable feed for producing lithium carbonate if the cost of the load/strip sequence is low enough.

Table 6 – Li extraction from Smackover brine⁽¹³⁾

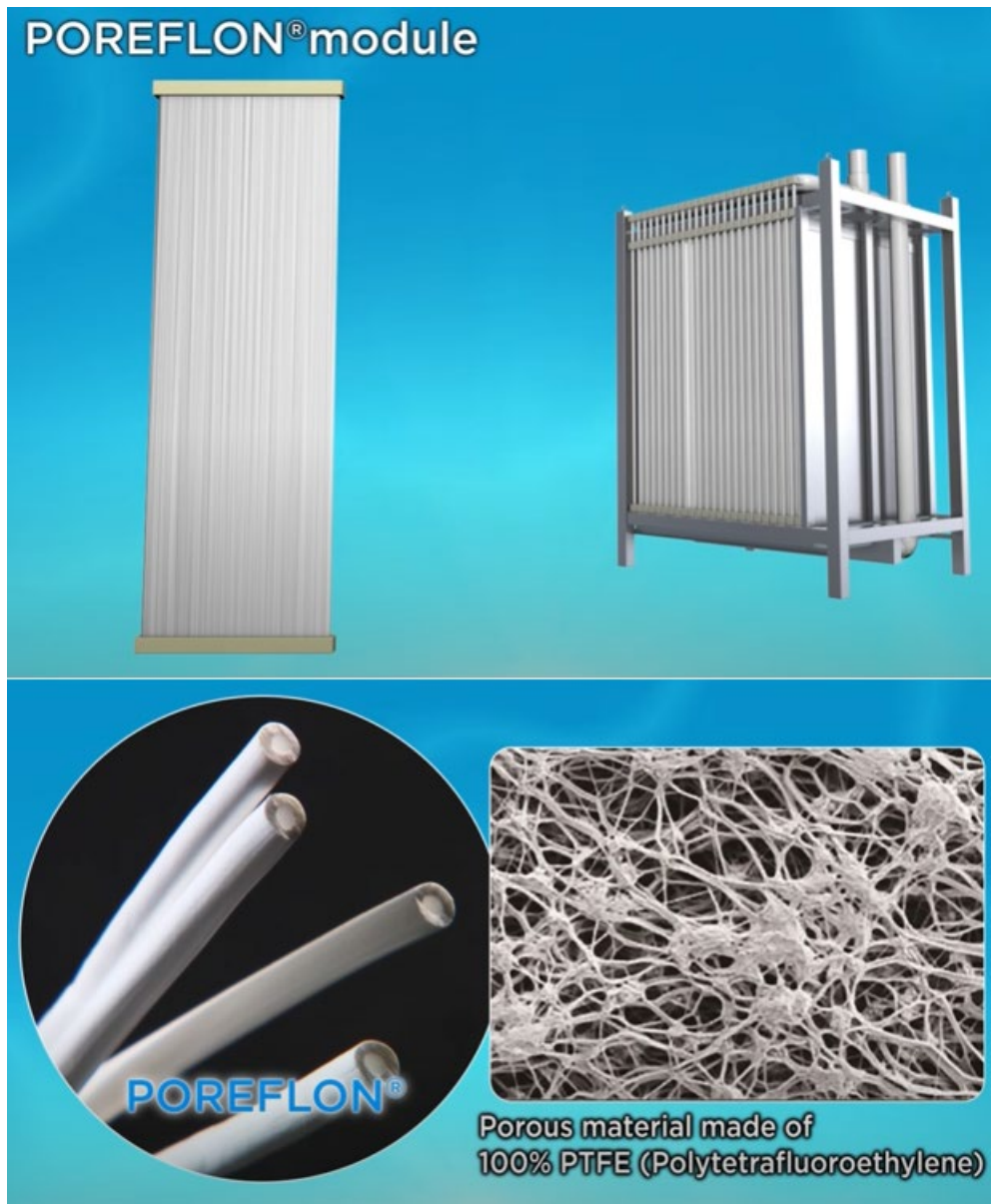
Solution	Measured concentration, mg/L			Mole ratio	
	Li	Ca	Mg	Ca:Li	Mg:Li
Feed brine	244	22000	2170	15.6	2.5
Strip solution	4300	1400	76	0.1	0.01
Barren brine	61				
Extraction	75%	0.3%	0.1%		
Selectivity	-	277	503		

The adsorption of lithium into meta-titanic acid is a solid-state diffusion process, therefore achieving good kinetics requires short distances through which the Li^+ must diffuse. That requires small particle size, for a sufficiently large surface to volume ratio. Figure 1 shows the particle size distribution of the material used to generate the data in Table 6⁽¹³⁾.



Figure 1 - H_2TiO_3 particle size distribution⁽¹¹⁾

One challenge in using a solid of this size distribution to recover lithium from a brine is re-capturing the solids efficiently. The equipment used in ion exchange (packed or fluidised beds) cannot be used with solids of the size range shown in Figure 1. A suitable technology comes from the waste-water industry; microfiltration using hollow fibre membranes⁽¹⁴⁾, such as the unit shown in Figure 2. This system is made up of small-diameter tubing of porous PTFE in modules that are air-agitated to prevent solids accumulation on the outside of the tubing. The pore size of the material is $0.45\ \mu\text{m}$ or less. Reasonable slurry density (of the fine $\text{H}_2\text{TiO}_3/\text{LiHTiO}_3$) and liquid flux through the membrane material have been achieved with air agitation preventing solids accumulation from blocking the tubing and no solids passing through the tubing⁽¹³⁾.



<https://www.youtube.com/watch?v=PsH-snVKGw4>

Figure 2 – Hollow fibre filtration membrane

CIRCUIT AND PRELIMINARY ECONOMICS

The technology described above is being developed by Standard Lithium⁽¹⁵⁾, a company based in Vancouver, Canada. The name chosen for the technology is LiSTR. Process modelling was used to help develop a circuit exploiting the technology and to evaluate its economics. The process model was divided into two circuits, first the LiSTR technology extracting lithium from Smackover brine after the extraction of bromine (Table 5) into a purified solution containing lithium chloride, then conventional technology for producing refined lithium carbonate from the solution ex the first plant. The LiSTR circuit is illustrated in Figure 3⁽¹⁵⁾. The loading and stripping reactors utilise the hollow fibre membranes shown in Figure 2. The two wash sections are counter-current decantation trains. The solid black lines denote the flows of H_2TiO_3 and $LiHTiO_3$. The thicker solid blue lines denote the brine flows. The solid thinner blue lines show the lithium flows after stripping. The dashed blue lines denote utility and reagent flows.

Acidic brine from the bromine extraction process is neutralised (sodium hydroxide or ammonia) and filtered, then contacted counter-currently with recycled H_2TiO_3 in two loading reactors. The resulting $LiHTiO_3$ is washed with water to displace entrained brine, then stripped with dilute hydrochloric acid to recover the lithium and regenerate H_2TiO_3 . The regenerated H_2TiO_3 is washed with water and recycled to the loading reactors. The lithium removed from the $LiHTiO_3$ exits the stripping reactor in a dilute chloride solution at about pH 2. This solution contains mainly lithium chloride and some entrained other ions, the amount depending on the efficiency of the counter-current decantation train ahead of the strip stage. This solution is neutralised and

further purified using ion exchange to remove the residual divalent cations. The purified solution is concentrated using reverse osmosis. Lithium carbonate is recovered from the concentrated and purified solution.

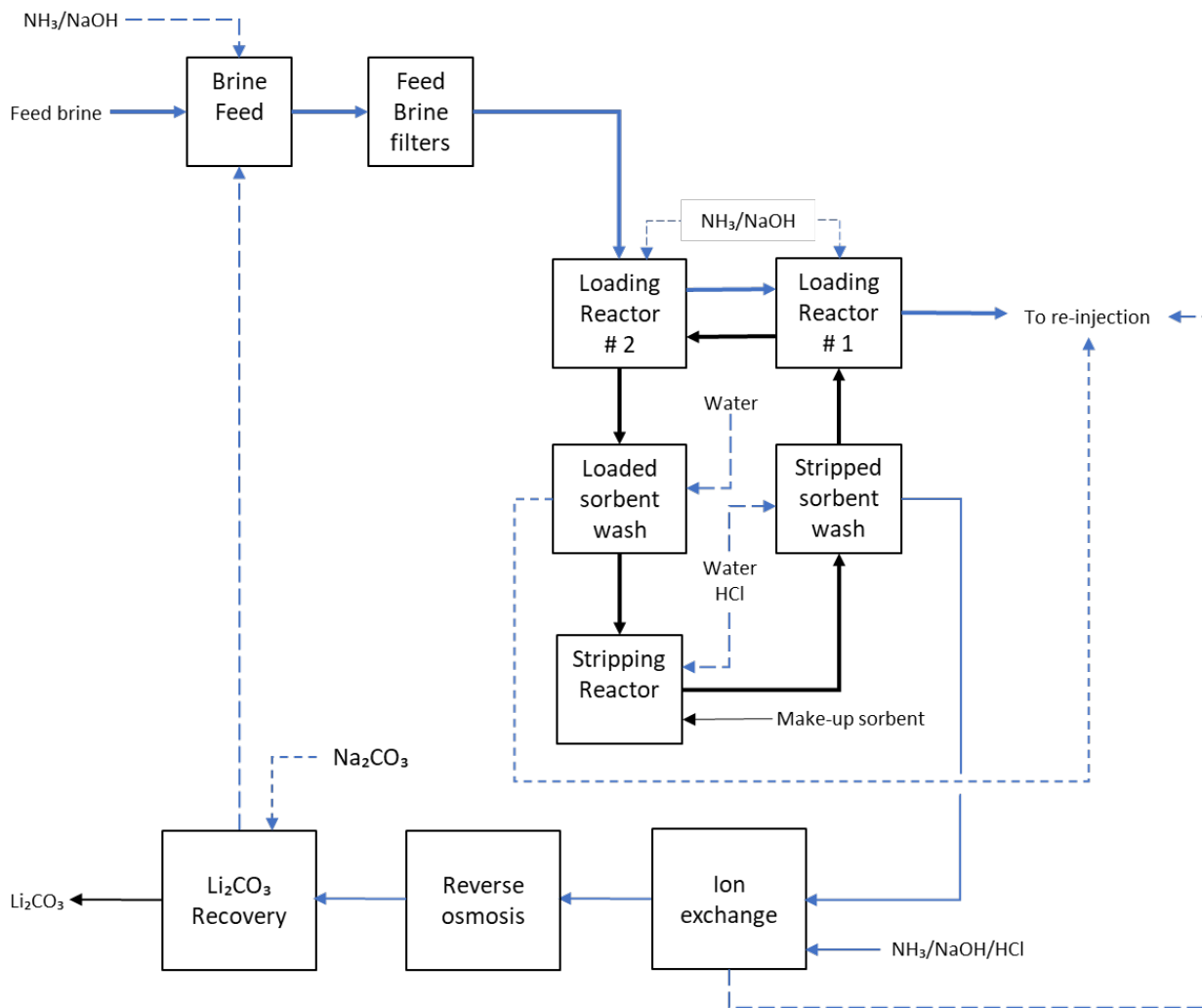


Figure 3 – LiSTR circuit⁽¹⁵⁾

A preliminary economic assessment of the circuit⁽¹⁶⁾ gave the results shown in Table 7. The operating cost, at \$90 million per year, translates to \$4306 per tonne of lithium carbonate. From these numbers, and with the current lithium price, the technology would seem to be economically viable. The LiSTR circuit is presently being demonstrated in a pilot plant at the Lanxess facility in Arkansas⁽¹⁴⁾.

Table 7 – Economics (US\$)

Production	20,900 t/y
Plant Operation	25 years
Total Capital Cost	\$437 million
Variable operating Cost	\$3 107/t Li ₂ CO ₃
Fixed operating cost	\$1 199/t Li ₂ CO ₃
Average Selling Price	\$13 550/t Li ₂ CO ₃
Annual Revenue	\$283 million/y
Internal Rate of Return (IRR) Pre-Tax	42%
Internal Rate of Return (IRR) Post-Tax	36%

COMPARISON WITH CONVENTIONAL TECHNOLOGY

The numbers in Table 7 predict that the LiSTR technology can economically extract lithium from the Smackover brine leaving the Lanxess bromine extraction process. The numbers in Table 4 indicate that conventional technology (via solar evaporation) most certainly cannot economically extract lithium from Smackover brine. This leads to a question – how might the LiSTR process compare to conventional technology for brines of the type presently processed via solar evaporation? To examine this question, a hypothetical salar brine was defined, as listed in Table 8. These numbers are the averages of the ranges listed in Table 3 for salar brine.

Table 8 – Hypothetical brine, ppm

Mg	4826
Ca	415
Na	487500
K	24900
Li	1960

Two process models were built, one assuming conventional solar evaporation or LiSTR technology to process the brine. Both circuits were assumed to produce refined lithium carbonate via precipitation from lithium chloride with sodium carbonate, then re-dissolution of the crude lithium carbonate in water and carbon dioxide followed by re-precipitation of refined lithium carbonate.

Conventional Circuit

The front end of the conventional circuit is illustrated in Figure 4. Brine from the wellfield is limed, the resulting mixture of gypsum and magnesium hydroxide is settled out and the remaining brine is concentrated by solar evaporation. The solar evaporation is modelled as two steps, first crystallizing out sodium chloride and then crystallising out potassium chloride. (The two pond icons shown, of course, each represent several actual solar ponds.)

Hydrochloric acid is added to the evaporated brine to lower the pH and the acidified briner is warmed by heat exchange with steam, then passed through solvent extraction to remove the bulk of the boron. The boron-loaded organic phase is stripped with aqueous sodium hydroxide and the resulting strip solution is disposed of in a waste pond.

The boron-depleted brine is then dosed with sodium carbonate to precipitate the bulk of the remaining calcium and magnesium, the precipitate being settled and filtered. The filter cake is washed with water and disposed of. The filtrate is passed through two ion exchange steps, first to remove residual calcium and magnesium, then to remove residual boron. In these ion exchange steps, the loaded resin is stripped with dilute hydrochloric acid and regenerated with dilute sodium hydroxide. The spent reagents are disposed of in the waste pond.

The back end of the conventional circuit is illustrated in Figure 5. The purified brine is concentrated further by evaporation against condensing steam, with some of the remaining sodium chloride crystallizing and being removed. The concentrated brine is dosed with sodium carbonate, precipitating lithium carbonate that is recovered by thickening. Part of the thickener underflow is recycled to the precipitation step as seed and the balance is filtered. The filter cake is washed with water and the filtrate is recycled to the Ca/Mg precipitation step in the front end of the circuit to bleed out any impurities (Ca, Mg, B).

The washed filter cake is mixed with water and carbon dioxide at ambient temperature and somewhat elevated pressure (about 3 bar). The carbon dioxide reacts with the carbonate, forming bicarbonate and thereby re-dissolving the lithium. The addition of CO₂ is manipulated to re-dissolve the lithium carbonate while leaving impurities such as calcium carbonate undissolved. The bicarbonate solution is filtered and the solid impurities are discarded. The filtrate is heated and depressurised, causing the aqueous bicarbonate to revert to carbonate and carbon dioxide, re-precipitating purified lithium carbonate that is recovered, washed with water in a centrifuge, then dried. The primary centrate is recycled to the redissolution step. The wash centrate and fresh water are used to dissolve solid sodium carbonate to make up the near-saturated solution of sodium carbonate that is used to precipitate lithium carbonate from the solution ex evaporation.

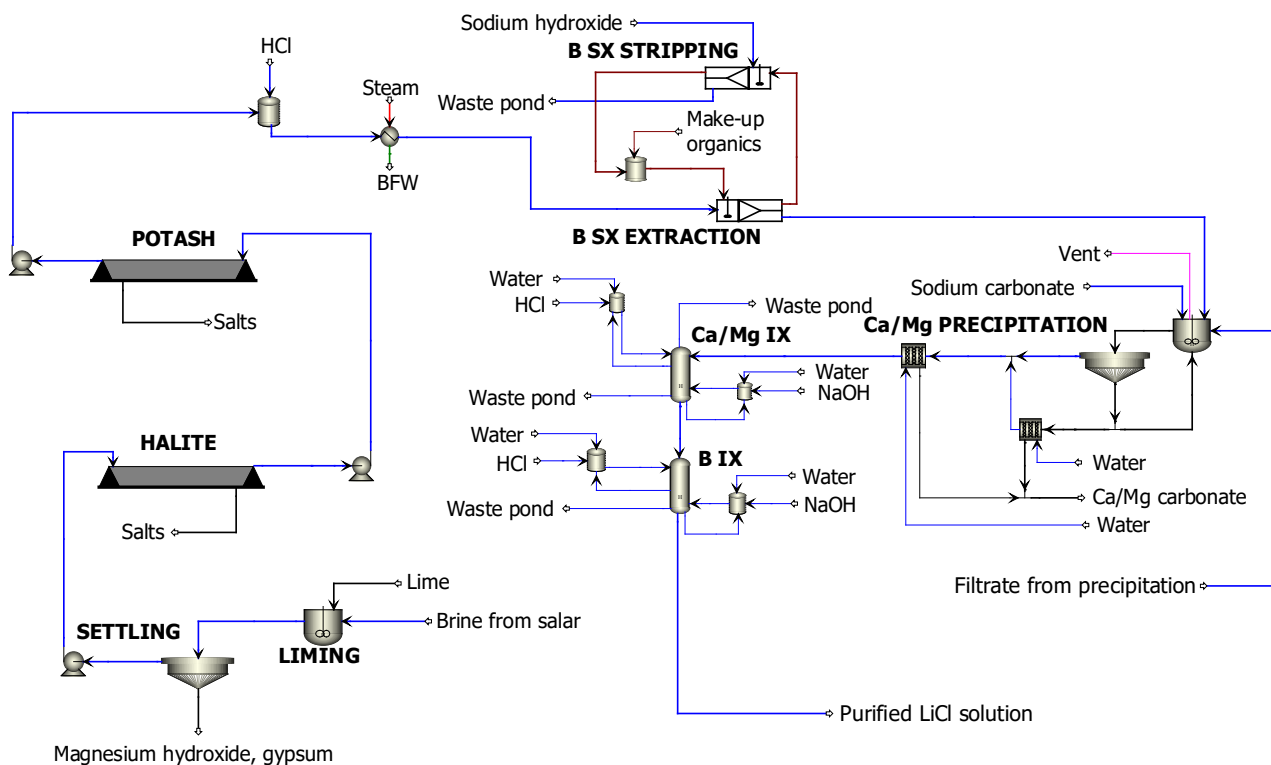


Figure 4 – Conventional circuit processing salar brine

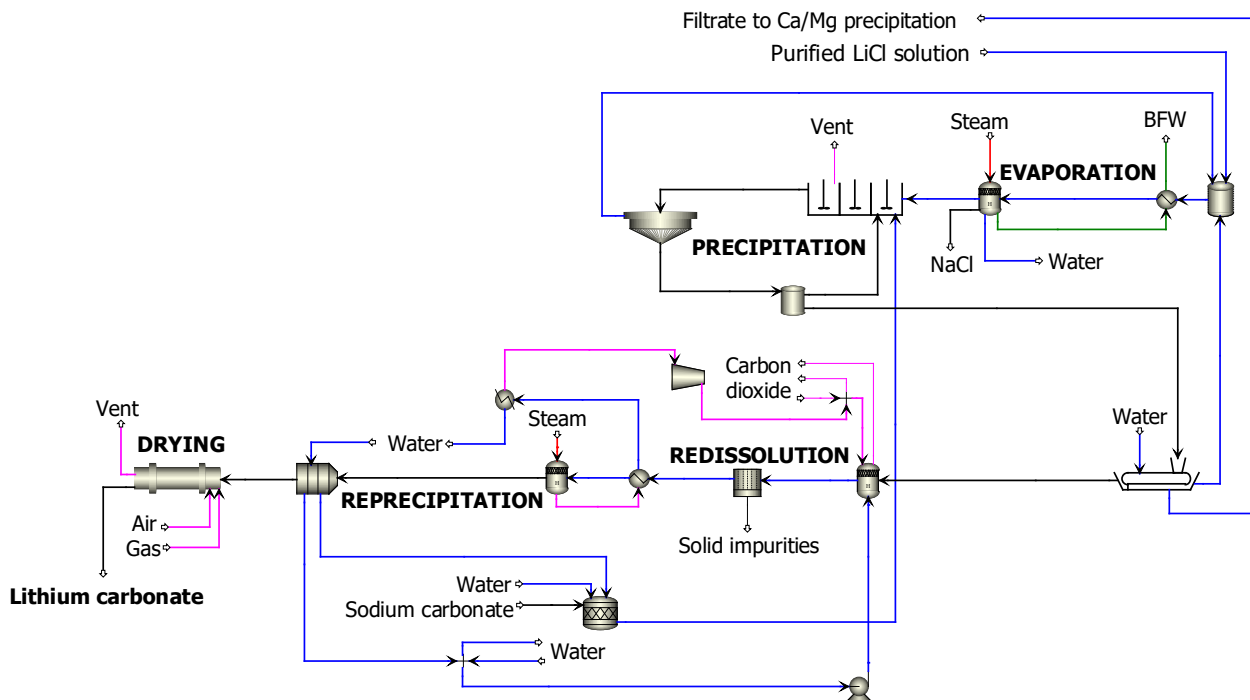


Figure 5 – Precipitation and refining of lithium carbonate

LISTR Circuit

Incoming brine is mixed with recycled solution from the ion exchange purification stage and filtrate from the first precipitation of lithium carbonate, then passed through two counter-current stages of loading, where the lithium is absorbed into the lattice of the H_2TiO_3 sorbent, releasing protons. The loading reactors are held close to neutral (pH 7) by the addition of ammonium hydroxide. The reactors use the hollow fibre membrane system illustrated in Figure 2 to separate the solid sorbent and the (partly or fully) depleted brine.

The resulting loaded sorbent (a mixture of H_2TiO_3 and $LiHTiO_3$) is washed with water in a five-stage counter-current decantation train, then stripped a recirculating solution of lithium chloride (from the first thickener in the

subsequent counter-current decantation train) that is held at about pH 2 by addition of concentrated hydrochloric acid into the circulating solution. This configuration avoids local low pH spots in the stripping reactor and thereby minimises dissolution of the H_2TiO_3 sorbent. The regenerated H_2TiO_3 is washed with water in a second five-stage counter-current decantation train, then recycled to the loading reactors.

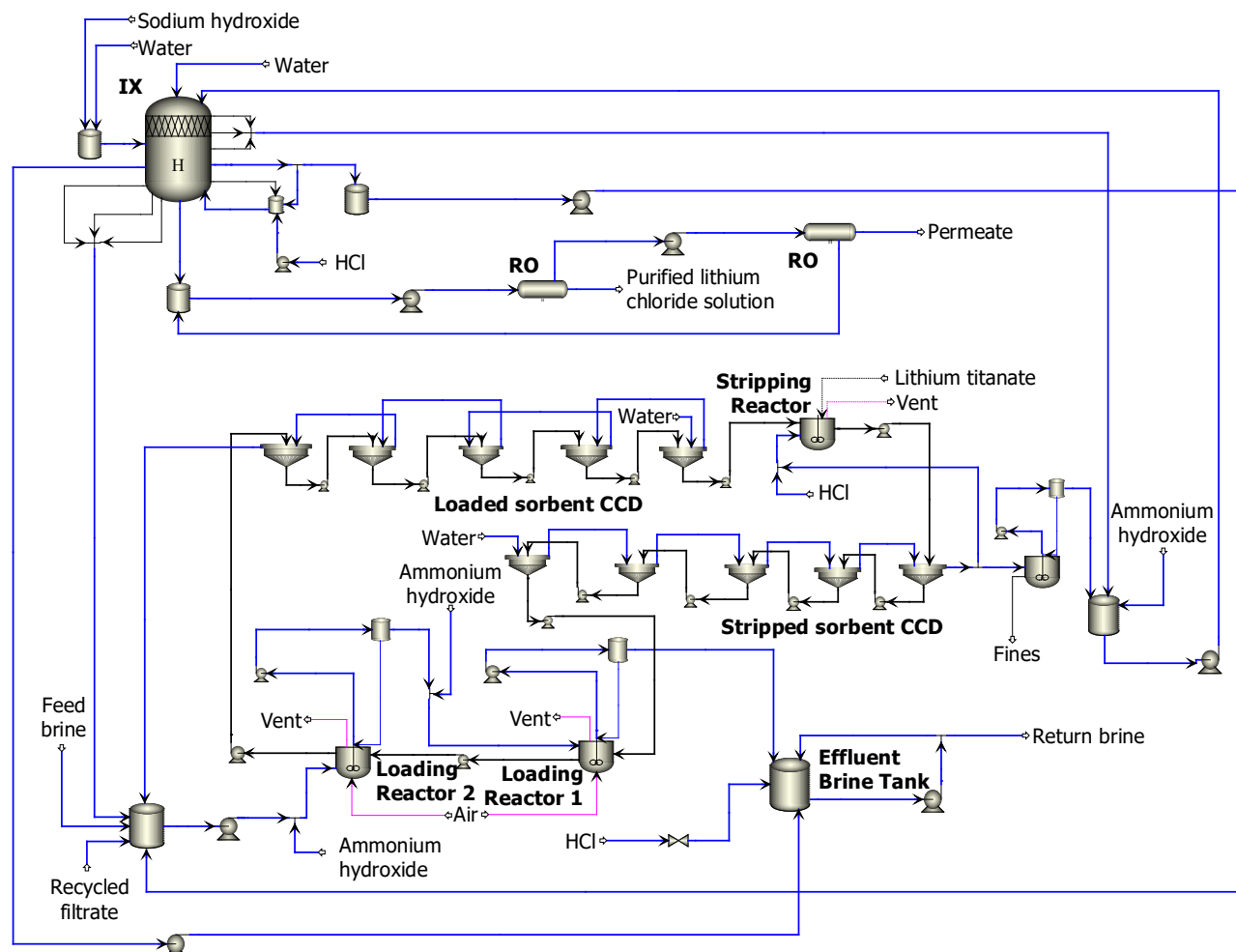


Figure 6 – LiSTR circuit

A bleed from the circulating strip solution is filtered (using the same system as the loading reactors) to capture and remove any ultra-fine solids, these being replaced by fresh sorbent added to the stripping reactor. The pH of the resulting solids-free solution is raised and ion exchange is used to remove residual divalent cations (mainly Ca^{2+}). The resin is stripped with hydrochloric acid and regenerated with sodium hydroxide. The spent strip acid is recycled to the feed tank ahead of the ion exchange section. The spent regenerant is recycled to the feed tank ahead of the loading reactors. The purified $LiCl$ eluate is concentrated further in two stages of reverse osmosis.

The resulting purified and concentrated solution of lithium chloride goes to a lithium carbonate plant, which is identical to the back end of the conventional circuit (Figure 5). While it could, the LiSTR circuit modelled does not have a boron removal step, so any boron not washed out in the counter-current decantation train ahead of the stripping section in the LiSTR circuit follows the lithium through the ion exchange and onwards. To avoid accumulation boron in the lithium precipitation and crystallization loops, the filtrate from the precipitation of lithium carbonate is recycled to the feed tank upstream of the loading reactors, where the bulk of the boron is rejected to the barren brine and the lithium is re-captured.

Comparison

The process models were used to calculate the quantities of reagents and utilities required per tonne of the final lithium carbonate product. The resulting numbers were combined with estimates of the various unit costs to calculate variable operating costs for the extraction of battery grade lithium carbonate from the generic salar and oilfield brines. The results are listed in Table 9. The costs for brine pumping and solar pond harvesting come from technical reports published by Standard Lithium⁽¹⁶⁾ and Lithium Americas⁽¹⁷⁾, and were assumed to be the same for this exercise.

A notable difference between the solar evaporation route and the LiSTR route is that LiSTR does not require solar evaporation of the brine. This eliminates the cost associated with pond maintenance, salt harvesting and tailings (salts) storage. (By eliminating the salt tailings; it also avoids actual or potential adverse effects on adjacent fresh water aquifers because the barren brine would be returned to the lithium-bearing aquifer, hence not drawing down its volume.)

The difference in variable cost for producing refined lithium carbonate from the purified lithium chloride brine is, as would be expected, similar for the two circuits because they both use the same unit operations for this part of the process. The only significant difference is the amount of steam required, because the conventional and LiSTR circuits produce the purified LiCl brine at different concentrations (17 g/L and 12 g/L, respectively), therefore the LiSTR circuit has to evaporate more water per unit of lithium. In this exercise the evaporation was assumed to be a single-effect operation; there would certainly be worthwhile savings (which would further advantage the LiSTR circuit) to be had from multiple-effect evaporation.

Table 9 – Variable costs, Conventional and LiSTR circuits, per tonne Li₂CO₃ from salar brine

Reagent/Utility	Consumption per tonne Li ₂ CO ₃		Variable cost, \$/tonne Li ₂ CO ₃	
	Conventional	LiSTR	Conventional	LiSTR
Extraction and purification of lithium chloride				
Ammonia (\$435/t)	-	231 kg	-	100
Lime (\$60/t CaO)	3 604 kg	-	216	-
32% HCl (\$155/t)	4 655 kg	3 379 kg	712	530
50% NaOH (\$345/t)	3 258 kg	5 kg	1 124	2
100% Na ₂ CO ₃ (\$300/t)	22 kg	-	6	-
Make-up Li ₂ TiO ₃ (\$8000/t)	-	9 kg	-	73
Porous membrane replacement	-	(Proprietary)	-	20
Steam (\$20/t)	491 kg	-	10	-
Electricity (\$0.1/kWh)	48 kWh	1 867 kWh	5	111
Fresh water (\$2 per m ³)	20	52	40	83
Sub-total reagent/utility			2 119	919
Brine pumping and solar pond harvesting			333	14
Precipitation and refining of lithium carbonate				
Na ₂ CO ₃ (\$300/t)	2 238 kg	2 252 kg	671	676
Make-up CO ₂ (\$50/t)	41 kg	49	2	2
Steam to evaporation (\$20/t)	21 123 kg	48 782 kg	420	976
Steam to re-precipitation (\$20/t)	5 526 kg	2 895 kg	111	58
Electricity (\$0.1/kWh)	52 kWh	9 kWh	3	0
Fresh water (\$1.61 per m ³)	0 m ³	0	0	0
Sub-total reagent/utility cost per tonne Li ₂ CO ₃			1 207	1 712
Combined reagent/utility cost per tonne Li ₂ CO ₃			3 659	2 645

The major difference in reagent costs between the two circuits arises from the differences in the amounts of hydrochloric acid and sodium hydroxide consumed, which is mainly due to the solvent extraction of boron in the conventional circuit. This is unnecessary in the LiSTR circuit because that circuit selectively extracts lithium and leaves boron in the barren brine (other than the minor entrainment not washed out by the counter-current decantation train between the loading and stripping sections).

In the solar evaporation route, while some boron is removed with the other salts in the solar evaporation sequence, not removing the remaining boron ahead of the precipitation of lithium carbonate would leave it in the solution from which lithium carbonate is precipitated. Were the removal of boron by solvent extraction and ion exchange to be removed from the conventional circuit, while the precipitation of lithium carbonate might not, on its own, give excessive boron in the precipitate, recycling the filtrate would cause an accumulation of boron with no exit other than into the lithium carbonate, making it impossible to meet the product specification for boron. Solvent extraction of boron requires the brine to be acidified to pH 4-5, where the boron is present as boric acid (H₃BO₃) that the extractant takes into the organic phase while not co-extracting lithium⁽¹⁸⁾. Stripping is done by contacting the loaded organic solution with a base (NaOH in this case), which converts

the boric acid to borate ($B(OH)_4^-$) that is released from the organic phase. More sodium hydroxide is required to raise the pH of the raffinate for subsequent precipitation of magnesium and calcium.

In the LiSTR circuit, the loading chemistry is selective against boron. The only boron following the lithium to the precipitation and refining steps is the minor amount not washed out in the counter-current decantation train between the loading and stripping sections, and that is bled back to the loading stage where it exits with the barren brine.

CONCLUSION

Lithium ion sieve technology appears to be a good solution to the previously unmet challenge of extracting lithium from high-calcium oilfield brines. This technology also appears to offer appreciably lower variable costs, compared to the conventional solar evaporation route.

In addition to unlocking substantial resources of previously inaccessible lithium, this technology does not require pre-concentration of the brine (such as evaporation), and its application enables the barren brine to be returned to the brine source after processing, thereby eliminating the deposition of vast amounts of waste sodium/potassium chloride (as in the conventional solar evaporation route) and also not jeopardising adjacent aquifers of fresh water via the permanent extraction of brine, the accompanying loss of huge amounts of water to evaporation and reduction in volume of the brine in the salar.

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