Lithium Solvent Extraction (LiSX™) Process Evaluation using Tenova Pulsed Columns (TPC)

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Conventional lithium recovery relies almost solely on solar evaporation technology. As lithium prices have exploded in the last couple of years and as this old technology suffers from several drawbacks, the search for a new technology is on. Solvent extraction (SX) bears high promise to be a superior alternative.

Although SX is widely used in mineral processing, SX for lithium was not available until recently. This new process was evaluated in recent years over lab scale tests and its applicability was demonstrated. However, a larger scale evaluation has to be performed if this technology is to be adopted as the chosen alternative for lithium recovery.

It was therefore, the objective of this work, to evaluate the performance of the lithium solvent extraction (LiSX™) process on a larger scale, using Tenova Pulsed Columns (TPC) with a cross section diameter of 40 mm and 100 mm. The results showed that although high pH is required to facilitate the extraction stage, complete lithium recovery is achievable even for neutral raffinate pH. Scrubbing indicated that practically all alkali metal impurity is removed from the loaded solvent, and the striping stage demonstrated the ability of the process to produce saturate lithium salt solution. Overall the LiSX™ process demonstrated its ability to extract, purify and saturate lithium, showing its attractiveness as the new generation lithium recovery process.

1. Introduction

Electric cars are expected to become ever more popular in the coming years [1]. As the key component in its battery is lithium, lithium production is gaining ever increasing interest. Old-school production is based on a series of evaporation ponds with residence time of roughly 18 month [2]. In addition to that, low lithium recovery is but another drawback that this conventional technology has [3].

These drawbacks have initiated a worldwide search for an alternative technology. Although solvent extraction is commonly used in hydrometallurgical processes, it was not considered as an alternative until recently. This new emerging solvent extraction process for the recovery of lithium, LiSX™, was tested on a laboratory scale [4]. The results of the laboratory scale showed that the proprietary Tenova Advanced Technologies (TAT) solvent has a maximum loading capacity of 1.75 g/L lithium (0.25 M). It was also indicated that, the process should be executed in aqueous continuity and that practically 100% of the lithium is recovered when extraction is carried out at pH=12. Stripping was indicated to remove all lithium from the loaded solvent (LS) even at pH=7.

Although promising, these test results required to be validated on a larger scale testing if this technology is to be implemented on a commercial scale. It is therefore the objective of this paper to further the evaluation of this process, and to elucidate the performance of the LiSX™ using small scale industrial equipment – Tenova Pulsed Columns (TPC), in the production of a saturated and pure Li_2SO_4 solution.

2. Experimental

2.1 Reagents

All chemical used in the line of the current work (reagent grade) were used as received. Both aqueous and organic solutions used were synthetically prepared. The aqueous feed solution was synthesized to imitate the expected composition fed to the LiSX™ process when operating with a typical South American lithium solution. As these brines normally contain alkaline earth elements, which are preferably extracted, the synthesized solution was prepared without these elements. In the commercial process this elimination is achieved by an upstream TAT process (LiP™). Feed composition is displayed in Table 1 below.

Table 1 – Aqueous Feed Stream composition

Element	Li	Na	K	B	Cl	S.G.
Units	mg/L	g/L	g/L	mg/L	g/L	
Value	720	115	8.4	500	195	1.235

2.2 Analysis

Analyses of Li, Na, K and B were performed using ICP or Atomic Absorption (AA), while titration was used for Cl^- determination. As a rule, high concentrations of a metal interfere with the determination of other metals that are present in very low concentrations. Therefore, standard solutions were used. These solutions contained a background of the ion present in high concentration in order to determine the ions present in low concentrations. For example, in the case of low lithium concentrations in the presence of high sodium concentrations (mainly for the determination of Li in the aqueous phase) analyses were performed by using standard solutions of Li containing similar Na concentrations to the concentrations in the diluted samples. The lowest concentration of Li that can be determined in this manner is 3 mg/L. In a similar way, low concentrations of other elements were quantified. It should be noted that the analytical accuracy of this method is ±10%. Organic solutions were stripped quantitatively using nitric acid solutions and the resulting aqueous solutions were analyzed. The concentrations in the organic solutions were calculated using the phase ratio in the stripping.

2.3 Hydraulic Test

Hydraulic tests, for all stages of the process, were conducted in counter current using a TPC with 100 mm cross-section diameter – having a total active section height of 7 m (PVDF disk-and-doughnut internals 7 X 90 cm PVDF sections separated by 10 cm glass sections), glass decanters with a diameter of 150 mm (top) and 110 mm (bottom). A mechanical pulsator (piston from PTFE) 120 mm in diameter, pulsating in a frequency of 1 Hz, was used to deliver pulsation to the column. All streams were pumped to the column using VFD controlled FMI (metering) or Peristaltic pumps. Pulsation intensity (PI – the product of the frequency and pulse amplitude) and flux were changed in order to determine the optimal operating parameters. Holdup (the fraction of dispersed phase in the total volume) values were monitored by periodically sampling in order to ascertain the optimal flux and pulsation intensity. For each of the solvent extraction stages (Extraction, Scrubbing and stripping) the test focused on the more challenging side of the column. Hence, for the extraction stage LS was tested with the feed brine (expected conditions at the upper part of the extraction column); for the scrubbing stage LS versus spent scrub solution (expected conditions at the lower part of the scrubbing column) were evaluated and for the stripping stage the purified solvent was tested with the Li_2SO_4 product stream (expected conditions at the lower part of the stripping column).

2.4 Mass Transfer Test

Mass transfer tests, for all stages of the process, were conducted in counter current using a TPC having a 40 mm cross-section diameter – and a total active section height of 7 m (PVDF disk-and-doughnut internals, glass sections), and top and bottom glass decanters having 80 mm in cross-section diameter. A mechanical pulsator (piston of PTFE) with a cross-section diameter of 69 mm, pulsating in a frequency of 1 Hz, was used to deliver pulsation to the column. All streams were pumped to the column using VFD controlled FMI (metering) or Peristaltic pumps. For all tests organic and aqueous samples were periodically collected and analyzed.

For the extraction stage, the lithium feed concentration is 720 mg/L, which sets the extraction organic to aqueous ratio (O:A) at 0.41 (calculated as lithium feed concentration divided by maximum lithium level in the LS). This ratio was maintained throughout the test work. As was previously reported [4] basic pH is required in order to facilitate the extraction process. Therefore, NaOH was added to the feed solution, resulting in feed brine pH of 12.5. In the scrubbing stage 0.73% H_2SO_4 solution was used to scrub the LS. Tests were conducted at O:A=10. While in the stripping stage, the purified solvent (PS) was stripped using a solution containing 61.25 g/L of H_2SO_4 and 246 g/L of Li_2SO_4 at O:A=5.

3. Results and Discussion

3.1 Hydraulic Tests

Extraction hydraulic test were conducted for fluxes raging 10-45 $m^3/m^2/h$. At a flux of 40 $m^3/m^2/h$, or grater, column operation proved to be unstable and flooding was observed regardless of the pulsation intensity (PI) used. The maximal flux which permitted continuous operation without flooding was 35 $m^3/m^2/h$ with a pulsation amplitude of 4mm, which corresponds to column PI=350 mm/min. At these conditions holdup values along the column were between 15-20%.

Scrubbing hydraulics was tested for flux values of 5-20 $m^3/m^2/h$. Flooding was observed at flux of 15 $m^3/m^2/h$ and above at any PI. Maximal flux that enabled continuous operation was 12.5 $m^3/m^2/h$ with an amplitude of 3mm, which corresponds to PI=260 mm/min. At these conditions holdup values along the column were between 25-30%.

Stripping hydraulics was tested for flux values of 5-30 $m^3/m^2/h$. At fluxes above 25 $m^3/m^2/h$, the column was flooded, indicating that the maximal flux that enables continuous operation is 25 $m^3/m^2/h$ with a pulsation amplitude of 3mm, which corresponds to column PI=260 mm/min. At these conditions holdup values along the column were between 25-30%.

3.2 Mass Transfer Tests

Similarly to other metal extraction process, lithium extraction is a chemical process. Thus, solvent deprotonation, achieved by basic pH at the feed brine, facilitates lithium extraction. This process, eliminate proton from the extracting agent and creates an active area on the solvent capable of chemically bonding with the lithium ions from the brine. The extraction profile is display in Table 2 and in Figure 1. As can be seen, near the organic entrance (at the lower section) to the column, the lithium content of the aqueous phase is minimal. In this area the solvent is being loaded with all other impurities, especially sodium. As the solvent flows up the column, lithium replaces those impurities, thus loading the solvent with lithium and removing co-extracted impurities at the same time. The solvent leaving the column is at maximum loading level regarding lithium and minimal loading with regards to other impurities. Those impurities will need, in any case, to be scrubbed out if purified lithium is to be produced.

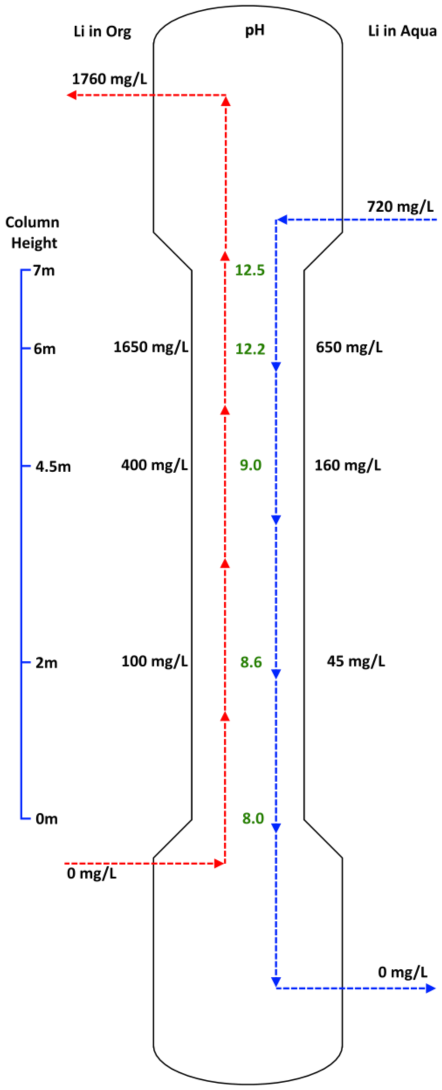

Figure 1 – Extraction Column Profile

Due to the extraction mechanism, a pH profile develops in the column. As protons are released from the organic into the aqueous phase the pH is reduced along the column until the raffinate leaves the column at practically neutral pH. This column pH profile is achieved by an optimal addition of NaOH. Excessive addition would result in higher pH level in the raffinate, whereas the outcome of inadequate addition will be incomplete lithium extraction due to insufficient active extraction sites on the solvent, and subsequently lithium loses to the raffinate.

As lithium concentration in the raffinate is driven below the detection limit, these results indicate that lithium was completely extracted from the feed. Moreover, the lithium purity, from feed brine to loaded solvent, was increase from roughly 0.6% to 92% on metal base, or from ca. 1.4% to 92% on either LiCl or Li_2SO_4 basis, which further highlights the advantages the solvent extraction process bears for lithium production.

Table 2 – Extraction Column Profile

Height	Stream	Li	Na	K	B	Cl	pH
m		mg/L	mg/L	mg/L	mg/L	mg/L	
7	LS	1760	365	23	<3	<3	12.5
	Feed	720	115000	8400	500	195000	
6	Org	1650	455	37	15	<3	12.2
	Aqu	650	110000	8200	490	190000	
4.5	Org	400	2885	45	23	25	9.0
	Aqu	160	108000	8300	510	195000	
2	Org	100	5630	70	64	60	8.6
	Aqu	45	105000	8000	500	195000	
0	BS	<3	<3	<3	<3	<3	8.0
	Raff	<3	109000	8300	500	200000	

The scrubbing process is aimed at removing the co-extracted impurities and producing highly pure lithium solution. This is achieved by partial stripping of the solvent. As the objective is to maximize the impurity levels in the spent scrub solution while minimizing its lithium content the exact acid concentration in the scrub solution is determined to allow pH=12 in the spent scrub. In this pH the lithium levels at the spent scrub solution are assumed to be minimal and as, in the industrial plant, this solution will be fed back to the extraction stage, this level would not increase the caustic demand.

As sodium is the major impurity, acid consumption is based solely on its concentration. In this process, each proton triggers the scrubbing of one sodium ion. pH=12 will be reached if sodium ions are in excess of 0.01 M over H^+ ions, which will induce proton elimination from the water resulting in a solution with OH^- concentration of 0.01 M.

The acid used in this stage will be the same acid used in the stripping stage in order to minimize the final product contamination. Therefore, H_2SO_4 was used as scrubbing acid. As the scrub solution is expected to be weak acidic one a specific gravity of 1 is assumed and O:A=10 is being taken into account in calculating the required acid concentration:

$$[\%H_2SO_4] = \frac{M_{w_{H_2SO_4}} \frac{g}{mol}}{2} \times \left(\frac{[Na_{org}] \frac{g}{l}}{M_{w_{Na}} \frac{g}{mol}} \times O:A - 0.01 \frac{mol}{l} \right) \times 0.1 \frac{l}{100gr}$$

Where $[\%H_2SO_4]$ is the acid concentration in the scrub solution, $M_{w_{H_2SO_4}}$ is the molecular weight of the sulfuric acid, $[Na_{org}]$ is the sodium concentration in the LS, and $M_{w_{Na}}$ is the molecular weight of sodium. Calculating the required acid concentration for this case gives:

$$[\%H_2SO_4] = \frac{98 \frac{g}{mol}}{2} \times \left(\frac{0.365 \frac{g}{l}}{23 \frac{g}{mol}} \times 10 - 0.01 \frac{mol}{l} \right) \times 0.1 \frac{l}{100gr} = 0.73\%$$

The results of the scrubbing test is displayed in Table 3, as can easily been seen all the impurities were successfully scrubbed out of the solvent resulting in PS containing practically only lithium. Additionally, lithium concentration in the spent scrub was indeed minimal. Nevertheless, there will be no lithium losses in the industrial scale, as this solution will be fed back to the extraction stage. The PS purity is adequate to allow for solvent stripping and production of the purified lithium solution.

Table 3 – Scrubbing results

Stream	Li	Na	K	B	Cl	pH
	mg/L	mg/L	mg/L	mg/L	mg/L	
LS	1760	365	23	<3	<3	
PS	1730	<3	<3	<3	<3	
Spent Scrub	250	3850	250	10	15	11.5

Similarly to scrubbing the stripping is a chemical neutralization reaction, where one proton is required to strip one lithium ion. The concentration of the strip solution is then derived from the designed O:A ratio, which is set on 5. This ratio is set in order to facilitate better phase dispersion in the column, and minimize axial mixing that would otherwise (in higher ratios) dominate column operation and may hinder lithium stripping. Thus, the required H_2SO_4 concentration is calculate as the product of O:A and lithium concentration in the PS (taken as 0.25 M), resulting in acid concentration of 1.25 N (0.625 M). In order to limit the demand for process water consumption, in the industrial plant, and to produce 40 g/L lithium solution (Li_2SO_4 solubility limit), part of the product stream is cycled back to the stripping and mixed with 98% H_2SO_4. Therefore the strip solution concentration is 61.25 g/L of H_2SO_4 and 246 g/L of Li_2SO_4. As the stripping process requires only one stage this mixing procedure bares no impact on the overall process.

The results of the stripping stage are shown in Table 4. As can be seen the target lithium concentration was achieved, and the product solution has a neutral pH which indicates complete proton consumption by the solvent from the aqueous solution. Impurity levels are minute and indicate lithium purity of 99.97% on metal base and 99.99% on Li_2SO_4 basis. This purity level significantly exceeds the 99.5% that is considered battery grade, and serves as an additional indication of the ability of the LiSX™ process to become the next generation technology for the production and recovery of lithium.

Table 4 – LiSX™ product composition

Li	Na	K	B	Cl	pH
g/L	mg/L	mg/L	mg/L	mg/L	
39.5	7	5	<3	<3	7.4

4. Conclusion

Lithium recovery via solvent extraction using TPC was evaluated. The solvent was shown to selectively extract the lithium where lithium purity of 0.6 (on metal basis) in the feed brine was elevated to 92% in the loaded solvent, with essentially obtaining 100% lithium recovery. Column pH profile revealed that although the feed brine entering the extraction stage is extremely basic (12.5) raffinate pH is practically neutral.

As some co-extraction takes place, scrubbing of alkali metals and other non-metallic impurities is required. 0.73% H_2SO_4 solution was used to scrub the loaded solvent. Virtually all impurities where scrubbed out were minimal lithium concentration was detected in the spent scrub solution. As this solution will be cycled to the extraction stage these lithium levels will not contribute to any lithium loses. The stripping of the purified solvent has produced saturated (40 g/L) and pure (99.97% on metal base) lithium sulfate solution.

The results presented in this paper indicate that the solvent extraction process outperforms the traditional solar evaporation technology. The current study continues to underline the validity of the LiSX™ process as an attractive alternative to the existing lithium production technology.

References

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