Lithium Processing - Spodumene

APPLICATION PAPER

PIAPSP2LIHEN

Lithium Refining; Hard rock to Lithium Hydroxide

Introduction

The Electrical Vehicle (EV) market is undergoing a revolution that is transforming the transportation landscape using Lithium-Ion battery technology. The demand for lithium ion battery is projected to increase to 4900 Gwh in 2030 as compared to 1500 Gwh in 2024[1]. To meet this challenge, high purity Lithium Hydroxide and Lithium Carbonate are required as essential materials to formulate these batteries.

The primary sources of Lithium are either brine lakes (Salars) or mineral deposits of mostly Spodumene ore. The Spodumene ore contains up to 6 % weight Lithium and is extracted from the ground in conventional mining operations (see Figure 1) that can be either underground pit excavation or surface strip mining depending on the location of the mineral lode.

Figure 1: Spodumene Mining Operations

Mining Applications

Mining operations typically involve the quarrying of the lithium rich ore from the surrounding rock followed by crushing & grinding operations, bulk separation by gravity difference or flotation and transport. Various mechanical operations are involved including crusher machines, mechanical shovels, large capacity haul trucks, transport belts, control systems, rotating equipment, and remote generators. Water treatment and fuel conditioning are also essential to the mining operation. Separation applications in mining are described in Table 1 for hydraulic fluids, lube oil fluids, diesel and process fluids, and water treatment.

Application	Filtration Value	Pall Product
Hydraulic	Prevent malfunction of hydraulic control systems due to contaminant fouling and fluid degradation	Particulate Filtration and Dehydration
Lube Oil	Reduce wear and reduced reliability of rotating parts due to contaminant abrasion and sluid viscosity losses	
Diesel and Process Fluids	Break emulsions and prevent damage to internal combustion engines and contamination of other process fluids	Liquid-Liquid Coalescers and High Flow Particulate Filters
Inlet Water, Recycle Process Water and Discharge (Waste) Water	Provide process water, environmental clean up and remote camp drinking water	MF System and High Flow Particulate Filters

Table 1: Mining Separation Applications

Lithium Refining: Spodumene concentrate to battery grade Lithium Hydroxide Monohydrate (LHM)”

The spodumene concentrate ore is converted into Lithium Hydroxide for use as an essential component to make Lithium-Ion Batteries. The process for making Lithium Hydroxide is illustrated in Figure 2.

The first step is calcination / decrepitation of the spodumene ore performed at a high temperature of 1,100 °C. Here the crystal structure of the spodumene is changed to open the pore structure in the material to a format more easily extracted. To prevent fine particle emissions from the furnace, a hot gas blowback filter system (1) can be installed. The next step involves roasting with sulfuric acid at 250 °C followed by neutralizing and water leaching. The Lithium is now converted into a Lithium Sulfate salt solution and contains other dissolved impurities and tailings. A belt filter is typically used to remove bulk tailing solids followed by a cartridge type filter (2) to catch any remaining fine particulate. Undesirable dissolved contaminants are removed by the use of chemical precipitation. A cartridge filter(3) is used to treat the injected precipitation chemicals to prevent contaminants from entering the Lithium Sulfate stream.

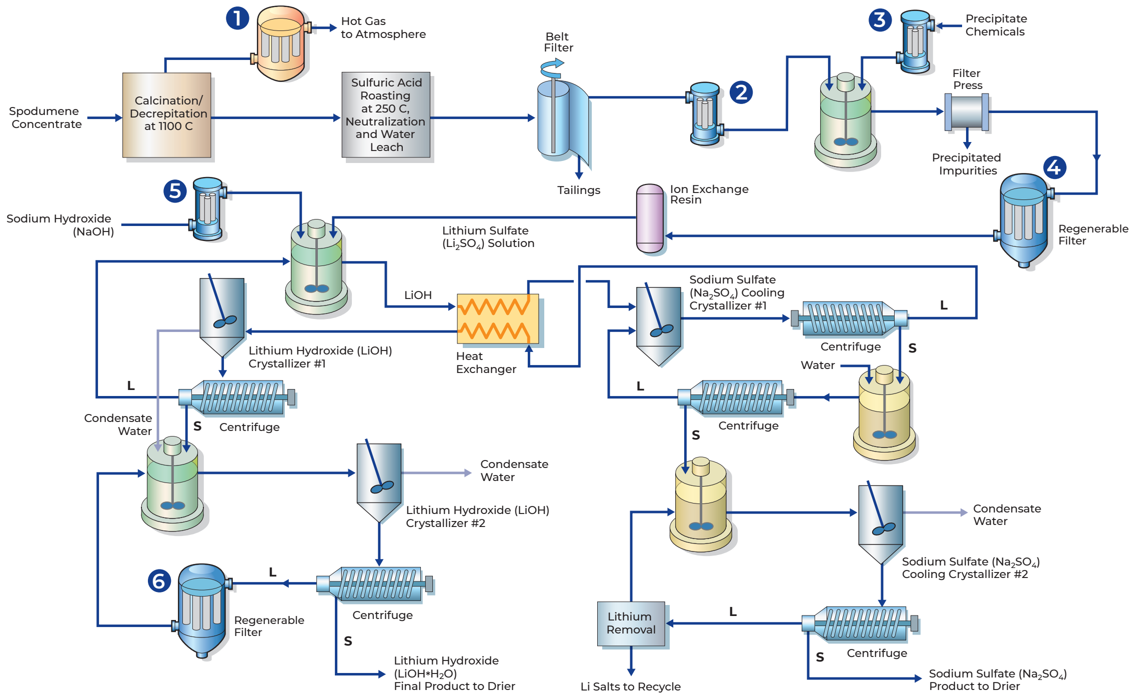
The precipitated contaminants are separated from the Lithium Sulfate stream using a filter press. A regenerable (candle) filter (4) can be installed downstream of the filter press to remove any remaining fine particulate that could adversely affect the ion exchange resin bed used primarily to remove divalent cations such as Ca+ and Mg+. Sodium Hydroxide is filtered by cartridge filters (5) before being mixed with the Lithium Sulfate solution.

This causes a chemical reaction that creates the desired Lithium Hydroxide and a byproduct of Sodium Sulfate. This stream is cooled through a heat exchanger to cause the Sodium Sulfate to crystallize out of solution.

The Sodium Sulfate is separated out of the solution using a centrifuge and is further purified by re-dissolving, re-cooling, re-crystallization and then collected by a second centrifuge to make the final Sodium Sulfate by product for sale.

After the Sodium Sulfate has been removed, the process stream then goes to LiOH crystallizers. The crystallizers also incorporate vacuum dehydration to both concentrate and cool the solution leading to the crystallization of the Lithium Hydroxide product. The Lithium Hydroxide solids are separated out of solution by a centrifuge. The Lithium Hydroxide solids are dissolved in pure condensate water to further purify and then are re-cooled and re-concentrated in a second LHM crystallizer to produce the final Lithium Hydroxide product that is collected in a second centrifuge. A regenerable (candle) filter (6) can be installed to catch any fine Lithium Hydroxide particles that pass through the centrifuge in the mother liquor and during any water washing of the product. The Lithium Hydroxide is then dried and milled to a fine particle distribution and packaged for sale.

The process depicted here is based on conventional operating plants and there are many new methods in development in this emerging industry.



Filter	Filtration Value	Separation Product
1	Remove solid particulate from furnace flue gas to prevent emissions	Gas Blowback Filter
2	Prevent ingression of tailings impurities and carryover sand into system from upstream processess	1 - 5 Micron Filter
3	Prevent ingression of impurities into system from injected precipitation chemicals	1 - 5 Micron Filter
4	Protect Ion Exchange (IX) and crystallizer from carryover solids coming from the filter press	Regenerable Filter
5	Prevent ingression of impurities into system from injected Sodium Hydroxide solution	1 - 5 Micron Filter
6	Recover fine particles of Lithium Hydroxide from mother liquor recycle stream	Regenerable Filter

Figure 2. Lithium Refining Process

Material Purity Specifications

Lithium-Ion batteries have strict purity requirements for the materials used in their manufacture. Impurities can lead to poor charging performance including reduced vehicle range of operation, more frequent need to charge, problems with batteries starting at colder temperature and in some extreme cases to the batteries catching on fire. A major issue with the current Lithium conversion practice is reliable operation in producing the high-quality Lithium products. Battery grade purity specs are provided in Table 2 for Lithium Carbonate. For Lithium Carbonate the minimum purity requirement is 99.5 wt. %.

Battery Grade LioH-H_2O (Lithium Hydroxide Monohydride) Purity Specs

LiOH, wt%	56.5	min
CO_2, wt%	0.35	max
Cl, wt%	0.0020	max
SO_4, wt%	0.010	max
Ca,wppm	15	max
Fe,wppm	5	max
Na, wppm	20	max
Al, wppm	10	max
Cr, wppm	5	max
Cu, wppm	5	max
K, wppm	10	max
Ni, wppm	10	max
Si, wppm	30	max
Zn, wppm	10	max
Heavy metals as Pb	10	max
Acid Insolubles, wt%	0.010	max

Grade	LioH-H_2O	Li_2CO_3
Battery	56.5% LiOH	99.5

Max Theoretical Purity of LiOH in LiOH-H_2O is 57.0 wt%

Table 2: Battery Grade Purity Specifications[2]

Improved filtration and separation can play an important role in improving both the process reliability for producing consistent high purity products and also for improving the product yields, reducing product re-work, and reducing operation costs.

EV Battery Value Chain

The various stages in the Electric Battery (EV) value chain are given in Figure 3. For each segment, filtration and separation play a vital role in meeting process goals for yield, purity, and reliability. For base materials, mining and unique material processing are required for Nickel, Cobalt and Aluminum as well as Lithium as described in this paper. Active materials involve treating of chemicals, specialty chemicals and polymers to make the essential battery components consisting of the separator, electrolyte, and anode/cathode. The battery cells also use chemicals and specialty chemicals that must be at rigorous purity levels for preparing the casing, filling operations, and preparing slurries. The battery pack will have micro-electronics and automotive components and require cleanliness monitoring.

Pall Corporation is your partner for filtration and separation needs and has experience throughout the EV battery value chain. Pall has over 400 qualified Engineers and Scientists that can provide: prototype testing, on site pilot testing, best practice training, process optimization, audits, contaminant analysis, application troubleshooting, validation services, presentations at scientific forums, and journal publications.

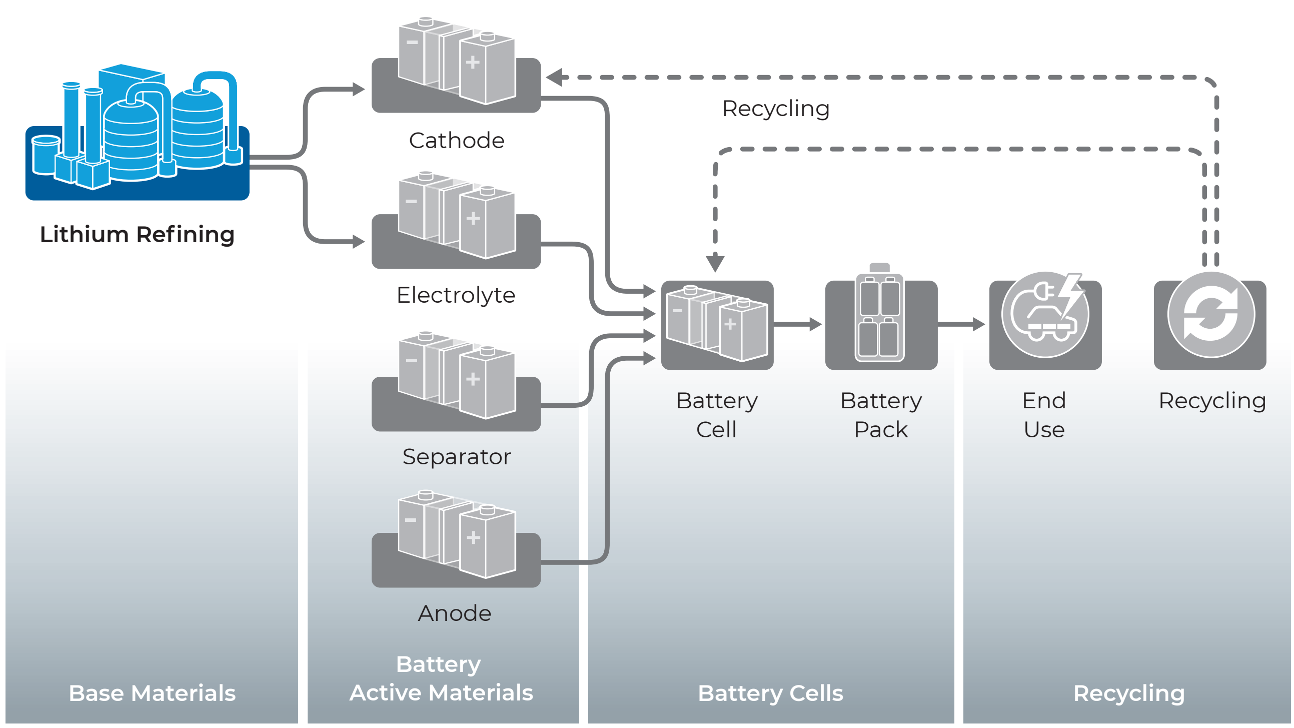


Figure 3: Applications in the EV Battery Value Chain

References

1. *Battery monitor 2023 (Roland Berger & RWTH Aachen university)*
2. *https://livent.com/wp-content/uploads/2018/09/QS-PDS 1021-r3.pdf*

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