

Lithium Brine to Lithium Carbonate / Lithium Hydroxide Process Separation Solutions

Introduction

The Electrical Vehicle (EV) market is undergoing a revolution that is transforming the transportation landscape using Lithium-Ion battery technology. The demand for electrical vehicles is projected to increase over five times the 2022 production values by 2030. 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 that can be either underground pit excavation or surface strip mining depending on the location of the mineral lode.

Brine Applications

Brine is pumped from Salars into surface ponds for evaporation (Figure 1). Initial brine contains Lithium Chloride ranging from 200 to 1,400 ppm. Impurities include Mg, K, SO₄, Ca and others precipitate out of solution before Lithium Chloride. A series of ponds may be used and chemicals to adjust pH and precipitate out impurities.

When the brine is concentrated to 6% Lithium, it is pumped into a processing plant and converted to lithium carbonate or lithium hydroxide

More than half of the lithium consumed today comes from brines that are located in South America in the Lithium triangle made up of the countries Argentina, Bolivia, and Chile. Other notable brine reserves exist in China and the Western USA.

Extraction of Lithium from brines is a less expensive method compared to processing Spodumene or other ores due to the requirements for mining, grinding, high energy costs to heat and calcinate and the use of sulfuric acid for leaching. However, it does require regional desert like conditions to allow for extended evaporation and takes a much longer period to be processed from raw brine to final product.

Besides the use of primary evaporation ponds, an adsorbent bed can be used to remove Lithium by Direct Lithium Extraction (DLE). A major drawback of this method is the need for fresh water to elute the Lithium off of the adsorbent bed after it has been collected from the brine. The feasibility of using an adsorbent bed can also be affected by the ratio of contaminants in the brine such as high levels of Magnesium compared to Lithium and how selective the adsorbent material is to Lithium.



Figure 1. Lithium Brine Salar Operations

Lithium Processing – Evaporation Ponds

While most brine processing converts the Lithium brine into Lithium Carbonate, it is also possible to go to Lithium Hydroxide using different chemicals to crystallize out the final products. The process for making Lithium Carbonate is illustrated in Figure 2.

The first step is pumping the brine (200 -1,400 ppm Li) up from underground lakes called Salars. The raw brine is filtered at location (1) with 20-40 micron filter cartridges to remove silt and undissolved salts before it goes to evaporation ponds. The evaporation process will usually consist of a series of ponds that allow contaminants (Calcium, Magnesium, Potassium, Sulfate, and others) to precipitate out and leave behind Lithium Chloride in solution as it become more concentrated. Ultimately when the brine reaches 6 % Lithium concentration, it is pumped into a processing plant and is filtered at location (2) with 10 micron filter cartridges to avoid contaminating the plant.

Chemicals are then added to further precipitate out contaminants that are then separated from the brine stream at location (3) typically through use of either a filter press or a centrifuge type separator. An improved method for this separation step has been developed using automated regenerable cartridge filtration. Following this step, any remaining fine contaminants are separated at location (4), using filter cartridges rated at 1-5 micron to protect the Ion-Exchange resin bed from

fouling. The Ion-Exchange resin bed is primarily used to remove divalent dissolved contaminants remaining such as Ca^{2+} and Mg^{2+} .

Downstream of the Ion-Exchange resin bed, any carryover fragments of resin bed or undissolved salts in the brine are separated at location (5) using a 1 micron filter cartridge to protect the crystallizer and any adverse effect on final product purity.

Sodium Carbonate is added to convert the Lithium brine to the desired Lithium Carbonate product which is separated from the liquid stream using a crystallizer. The solid Lithium Carbonate product is collected typically using either a centrifuge or filter press at location (6).

A belt press filter is then used to further separate out and process the Lithium Carbonate particles through a rinse stage using deionized water. An improved method has been developed using automated regenerable cartridge filtration that can replace the centrifuge, filter press and belt filter. A filter cartridge rated at 10 micron is used at location (7) to protect the Reverse Osmosis Membrane System from fouling prematurely.

To achieve battery grade final Lithium products, multiple crystallization, re-dissolution and rinsing stages are often required that are not shown in this flow schematic for simplicity. Also, the process depicted is based on conventional operating plants and there are many new methods in development in this emerging industry.

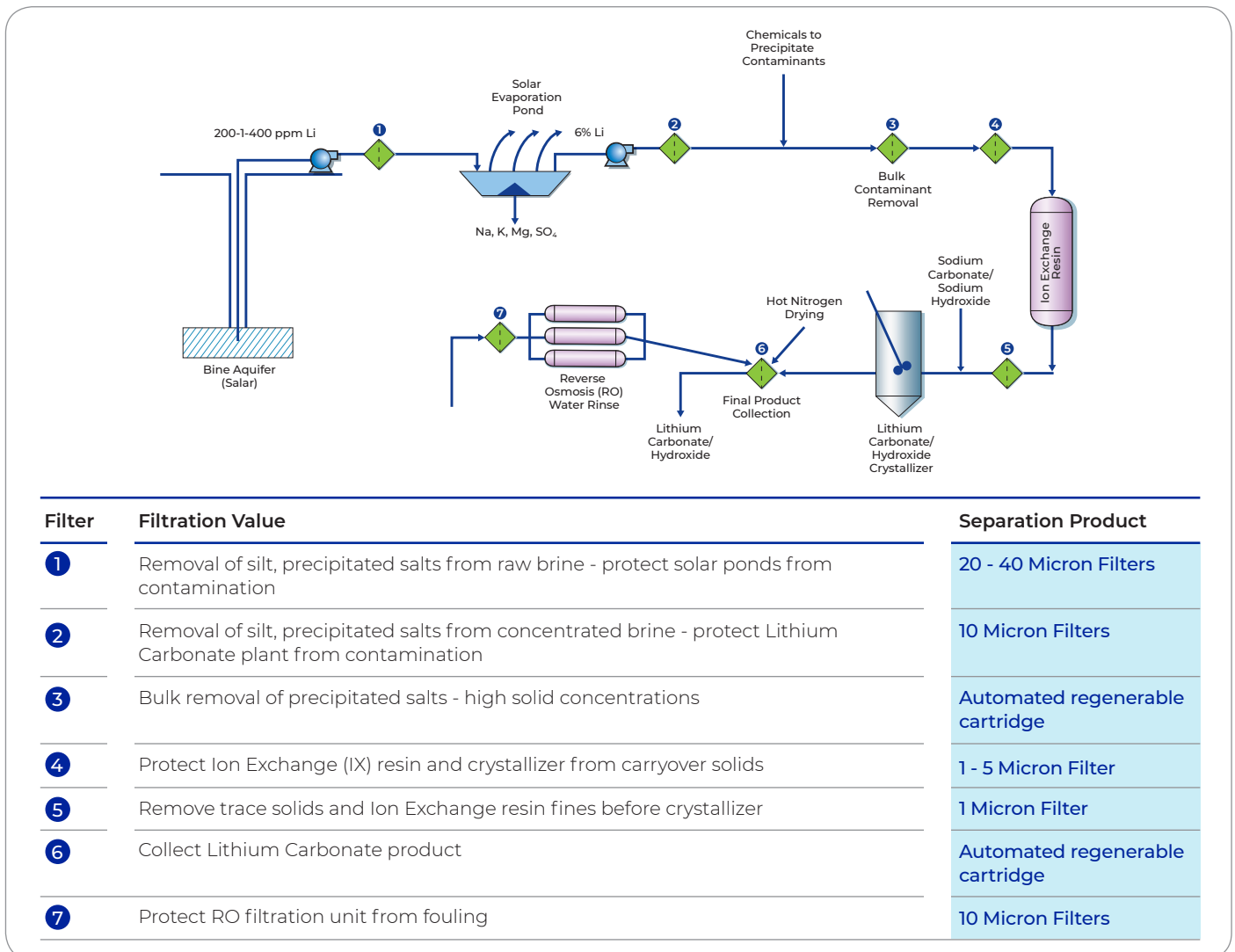


Figure 2. Lithium Carbonate Process Using Evaporation Ponds

Lithium Processing – DLE

Lithium brine can also be converted into Lithium Carbonate by Direct Lithium Extraction (DLE) using an adsorption bed to separate out the Lithium from the brine. A schematic for making Lithium Carbonate is illustrated in Figure 3. A similar flow schematic with different chemical reagents can be used to make Lithium Hydroxide.

The first step is pumping the brine (200 -1,400 ppm Li) up from underground lakes called Salars. The raw brine is filtered at location (1) with 20-40 micron filter cartridges to remove silt and undissolved salts before it goes to adsorption beds made up of specialized resins that are intended to adsorb the Lithium and allow the other contaminants (Calcium, Magnesium, Potassium, and others) to remain in the brine which is then sent back to the underground Salar.

When the adsorption bed becomes saturated with Lithium, it is taken offline, and Deionized Water (DI) is used to elute the Lithium from the adsorption bed (2,500 ppm Li). A filter cartridge rated at 10 micron is used at location (6) to protect the Reverse Osmosis Membrane System from fouling prematurely. The elution stream from the adsorbent bed is then sent to evaporation ponds to concentrate. These ponds are much smaller than the ones depicted in Figure 2 for purifying the brine through mostly evaporation.

When the eluted Lithium solution evaporation progresses to 6% Lithium concentration, it is further processed by adding chemicals to precipitate out any remaining contaminants. These precipitates are separated from

the stream at location (2) typically through use of either a filter press or a centrifuge type separator. An improved method for this separation step has been developed using automated regenerable cartridge filtration.

Following this step, any remaining fine contaminants are separated at location (3), using filter cartridges rated at 1-5 micron to protect the Ion-Exchange bed from fouling. The Ion-Exchange bed is primarily used to remove divalent dissolved contaminants remaining such as Ca^{2+} and Mg^{2+} .

Downstream of the Ion-Exchange resin bed, a cartridge filter rated at 1 micron is used at location (4) to prevent fine particulates from contaminating the final product. Sodium Carbonate is added to convert the Lithium brine to the desired Lithium Carbonate product which is separated from the liquid stream using a crystallizer. The solid Lithium Carbonate product is collected typically using either a centrifuge or filter press at location (5).

A belt press filter is then used to further separate out and process the Lithium Carbonate particles through a rinse stage using deionized water. An improved method has been developed using automated regenerable cartridge filtration that can replace the centrifuge, filter press and belt filter. A filter cartridge rated at 10 micron is used at location (6) to protect the Reverse Osmosis Membrane System from fouling prematurely.

To achieve battery grade final Lithium products, multiple crystallization, re-dissolution and rinsing stages are often required that are not shown in this flow schematic for simplicity. Also, the process depicted is based on conventional operating plants and there are many new methods in development in this emerging industry.

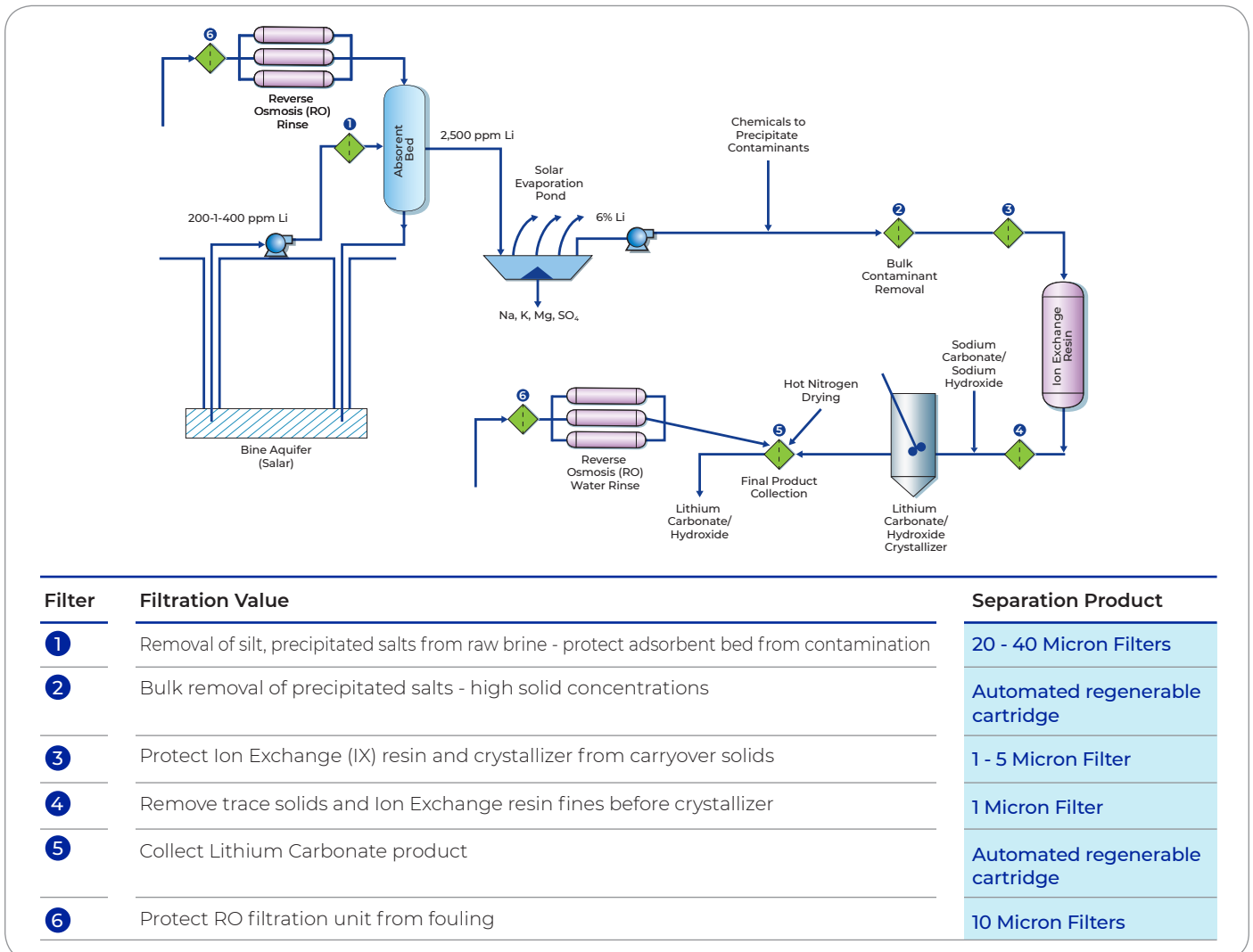


Figure 3. Lithium Carbonate Process Using Direct Lithium Extraction (DLE)

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.

Optimized 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.

| | | |
|---|-------|-----|
| Li ₂ CO ₃ , wt. % | 99.5 | min |
| Loss @ 500° C | 0.5 | max |
| Na, wt. % | 0.050 | max |
| Ca, wt. % | 0.040 | max |
| SO ₄ , wt. % | 0.1 | max |
| Fe, wppm | 5 | max |
| Zn, wppm | 5 | max |
| Al, wppm | 10 | max |
| Cu, wppm | 5 | max |
| Ni, wppm | 6 | max |
| Cl, wt. % | 0.01 | max |
| Acid Insolubles, wt. % | 0.02 | max |
| Malvern D100, µm | 40 | max |
| Malvern D90, µm | 13 | max |
| Malvern D50, µm | 4-6 | max |
| H ₂ O*, wt. % | 0.5 | max |

* Value (as weight percent loss) determined by drying at 500°C for 30 minutes

Table 2. Battery Grade Purity Specifications²

EV Battery Value Chain

The various stages in the Electric Battery (EV) value chain are given in Figure 4. 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.

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.

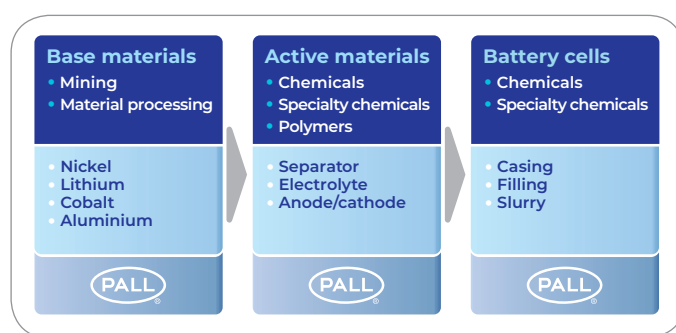


Figure 4. Applications in the EV Battery Value Chain

References

1. Phillips, Piedmont Lithium Company Presentation (Nov 2020) <https://www.piedmontlithium.com/>
2. <https://livent.com/wp-content/uploads/2018/09/QS-PDS-1021-r3.pdf>

Dr. Thomas H. Wines is a Director at Pall Corporation's Technology Development Team with over 35 years' experience in Separation Technologies. He is focused on the Energy Market including Lithium-Ion Batteries, Upstream and Midstream Oil & Gas Processes, and Downstream Refining Operations. For more information, Dr. Wines can be reached by email at tom_wines@pall.com.



PALL CORPORATION

Corporate Headquarters

Port Washington, NY, USA
+1-800-717-7255 toll free (USA)
+1-516-484-5400 phone

European Headquarters

Fribourg, Switzerland
+41 (0)26 350 53 00 phone

Asia-Pacific Headquarters

Singapore
+65 6389 6500 phone

Visit us on the Web at www.pall.com/industry

Contact us at www.pall.com/contact

Pall Corporation has offices and plants throughout the world. To locate the Pall office or distributor nearest you, visit www.pall.com/contact.

The information provided in this literature was reviewed for accuracy at the time of publication. Product data may be subject to change without notice. For current information consult your local Pall distributor or contact Pall directly.

IF APPLICABLE Please contact Pall Corporation to verify that the product conforms to your national legislation and/or regional regulatory requirements for water and food contact use.

© Copyright 2024, Pall Corporation. Pall and are trademarks of Pall Corporation. ® Indicates a trademark registered in the USA.