

# Lithium Brine Extraction Technologies & Approaches

#### Takeaways:

- Brines from salars and salt lakes, as well as spodumene ores, are the primary source of lithium, while geothermal brines represent secondary sources.
- Produced water from oil & gas operations is an untapped source of lithium that may be more important in the future.
- Chemical precipitation, adsorption with inorganic ion exchange sorbents, solvent extraction and concentration with membrane technologies are the primary means of lithium recovery from brines.
- Each lithium extraction and recovery process has unique advantages and challenges that need to be considered when determining the best fit for any project.
- New advances in water treatment offer exciting improvements on the economics of using membrane technologies for lithium recovery.

Much of the world's commercial lithium is still recovered today in the way it has been for half a century: by evaporating brines collected from salars and salt lakes in evaporation ponds. Recovering lithium in evaporation ponds can take a year or more and leaves behind lots of salt waste, but there are new technologies and processes that offer exciting options for lithium extraction.



#### Summary of Major Lithium Brine Resources and Dominant Recovery Processes

Resource	Lithium (mg/L)	Dominant Process	Challenges	Opportunities
Salars (Lake Brines)	200- 7,000	Staged evaporation to atmosphere, concentrating and producing lithium.	Large land areas and significant quantities of water used to extract lithium from lake beds. Minimum 18 months from pond start-up to first production due to slow evaporation.	Massive resource with available natural evaporation energy. Opportunity to hybridize evaporation with concentration and purification technologies.
Groundwater Brines	20-200	Lithium absorption- desorption on a metal oxide, following by refining.	Tend to be richer in hardness than salars, making processing more challenging.	Vast resources in USA, close to major lithium utilization plays.
Oil & Gas Brines	50-100	No dominant process established.	Low concentration and extremely large volumes needed, while most produced waters are spread out and smaller volume.	Attractiveness of oil & gas wastewater adding value.





#### What are the Primary Sources of Lithium?

The demand for lithium is outpacing the rate lithium is being mined from brines, due to continuing advancements in mobile devices and electric cars. Lithium is an abundant element, however, there are very few commercial resources where lithium is found in concentrations sufficient for producing useful lithium compounds. The primary sources of lithium are in brines from salars and salt lakes, and lithium-bearing spodumene ores, while geothermal brines represent the second most productive sources of lithium. Lastly, produced waters from <u>oil & gas</u> fields are an untapped source of lithium resources, it is essential to have lithium recovery technology and processes that are optimized to the characteristics of each individual resource, such as the concentration of lithium, the ratio of lithium to magnesium and calcium ions, and relative concentrations of other ions.



#### Lithium Recovery via Chemical Precipitation

Lithium recovery via conventional chemical precipitation normally starts by subjecting lithium-rich brine to a series of solar pond evaporations. This will precipitate other salts such as sodium chloride and potassium chloride, while concentrating the lithium. Lime (calcium hydroxide) is then added to the concentrated lithium brine to further remove magnesium as magnesium hydroxide, and sulfate as calcium sulfate. Any calcium in the concentrated brine is removed as calcium carbonate by adding sodium carbonate. The brine that results from these chemical precipitations is then subjected to a carbonation process, where the lithium reacts with sodium carbonate at 80-90°C to produce technical-grade lithium carbonate. This can be further purified to produce battery-grade lithium by re-dissolving the lithium carbonate, and then using an ion exchange process to remove impurities.

To reduce the time required for solar evaporation concentration, lithium will sometimes be precipitated as lithium phosphate, which precipitates more quickly than lithium carbonate due to its roughly 30-fold lower solubility. Lithium phosphate is then converted into battery-grade lithium hydroxide through an electrochemical process.

### Lithium Recovery via Adsorption

Lithium selective ion exchange sorbents are a promising alternative for extracting lithium from brines. Inorganic ion exchange sorbents, such as lithium manganese oxides, spinel lithium titanium oxides, and lithium aluminum layered double hydroxide chloride, have been shown to have high lithium-selective uptake capacity. However, the recovery process requires the lithium to be in contact with these sorbents for long periods of time. Additionally, sorbents can be very expensive; they are mostly available as powders that require energy-intensive



processes for lithium recovery and can degrade during the acid-driven desorption process.

A novel technique based on an electrolytic cell that contains LiFePO<sub>4</sub>/FePO<sub>4</sub> as an electrode material has been studied to selectively recover lithium. Under an electrochemical process, lithium ions from a lithium-bearing brine are selectively intercalated into a cathode made from FePO<sub>4</sub> to form a lithium-saturated LiFePO<sub>4</sub>. Then, the current is reversed, turning the LiFePO<sub>4</sub> into an anode that can be used to recover lithium.

### Lithium Recovery via Solvent Extraction

One approach that has been tested to selectively recover lithium from brine involves using an organic phase comprising kerosene and an extractant, such as tributyl phosphate, trioctylphosphine oxide (TOPO), and beta-diketone compounds. Although these organic phases show very high selectivity toward lithium over sodium and magnesium ions under optimized conditions, the lithium stripping phase uses solvent extraction that can result in costly equipment corrosion. In addition, the residual brine that remains after lithium extraction may require posttreatment to remove the leached solvent before it can safely be sent for disposal.

## Lithium Recovery Using Membrane Technologies

Reverse osmosis (RO) and nanofiltration (NF) processes have been studied for pre-concentrating or separating lithium from a lithium-



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bearing brine. A typical lithium brine usually contains high concentrations (for example, more than 5.0 wt%) of salt ions. The maximum salt concentration that an RO/NF process can reach is linked to the osmotic pressure, as well as the membrane's selectivity and the mechanical stability of any associated equipment. There are automated chemical softening systems that can help membrane treatment systems reliably reach their treatment limits and improve yield, such as our <u>BrineRefine</u> system. Conventional NF processes cannot efficiently separate lithium without heavy pre-treatment of the brine, such as diluting the brine with a large amount of fresh water.

Electrodialysis systems that use monovalent-selective ion exchange membranes, such as <u>Flex EDR Selective</u>, have also been used to recover lithium from lithium brine containing divalent ions such as calcium, magnesium, and sulfate. The selectivity of the membranes for monovalent ions over multivalent ions is the key factor for determining the efficiency of the recovery process.