Lithium Extraction using Layered Double Hydroxide: A Kinetic Model-Based Optimization Approach

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ABSTRACT

This study develops a kinetic model for the LDH-DLE process using lab data and process simulation to optimize extraction. The validated model suggests that lab data, combined with thermodynamic simulations, can design, scale up, and optimize LDH DLE plants, assessing process variability impacts without additional experimentation.

INTRODUCTION

Direct lithium extraction (DLE) processes are currently the most effective method to extract lithium directly from geothermal and produced waters. Unlike traditional lithium extraction methods, which typically involve evaporation ponds and hard rock mining, DLE offers a more sustainable and environmentally friendly approach. DLE leverages advanced materials and technologies to selectively target and remove lithium ions from complex brine solutions, making it particularly suitable for resources with lower lithium concentrations or where rapid extraction is necessary.

Considerable research is underway evaluating emerging DLE technologies like membranes and sorbents. Membrane-based DLE methods utilize semi-permeable membranes that allow lithium ions to pass through while rejecting other ions, thereby concentrating the lithium. Sorbent-based methods involve materials that selectively adsorb lithium ions from brine solutions. One of the most promising materials in this category is Layered Double Hydroxides (LDHs), which have emerged as highly effective adsorbents due to their high selectivity, affinity for lithium ions, tunable structure, and potential for regeneration with minimal reagents.

Optimizing LDH-DLE processes for plant applications requires a comprehensive understanding of the interplay among several factors, such as brine chemistry, operating conditions, and kinetic behavior of the sorbent. Brine chemistry can vary significantly depending on the source, with factors like pH, temperature, and the presence of competing ions affecting lithium recovery. Operating conditions, including flow rates, contact time, and temperature, must be carefully controlled to maximize efficiency. The kinetic behavior of the sorbent, which describes how quickly lithium ions are adsorbed and desorbed, is crucial for designing effective extraction systems.

This study proposes a novel approach to combine sorption kinetic data with an electrolyte speciation model to simulate the behavior of DLE processes under changing feed and process conditions. By integrating kinetic data with speciation models, we can predict how variations in brine composition and operating parameters will impact lithium recovery. The DLE model is then combined with lithium purification for plant-wide optimization, allowing for a holistic view of the entire extraction and purification process.

This holistic approach aims to enhance understanding of process efficiency, cost considerations, and economic viability from lithium extraction through product purification. By optimizing each stage of the process, from initial extraction to final purification, we can improve overall performance, reduce operational costs, and ensure the economic sustainability of DLE technologies. This is particularly important as the demand for lithium continues to grow, driven by the expanding market for electric vehicles and renewable energy storage solutions.

CREATING A DATABASE FOR LITHIUM ALUMINUM DOUBLE HYDROXIDE LDH

We first constructed a proprietary database containing three LDH material structures. The database contains the material formula, mass and estimated thermodynamic properties (Gibb's Free Energy (G), enthalpy (H), entropy (S), molar volume (Vm), and heat capacity (Cp)). The crystalline LDH material includes two, three, or five Al(OH)$_3$ octahedra units designated as, $2Al(OH)_3.1H_2O$, $3Al(OH)_3.1H_2O$, $5Al(OH)_3.1.7H_2O$ with corresponding lithium salt-adsorbed material: $xLiCl.2Al(OH)_3.1H_2O$, $xLiCl.3Al(OH)_3.1H_2O$, $xLiCl.5Al(OH)_3.1.7H_2O$. The interaction of LDH material with lithium chloride can be written as the reversible reaction,

$$2Al(OH)_3.1H_2O + LiCl = 1LiCl.2Al(OH)_3.1H_2O \qquad [1]$$

The LDH material has similar properties to gibbsite, as it readily dissolves in strong acid and base. However, it's important that the LDH material is designated as its own chemical species such that it exhibits the intercalating behavior required for lithium extraction and does not compete with any pre-existing gibbsite mineral in the brine.

The stability of the LDH material was tested against gibbsite and boehmite (AlO(OH)) to ensure corresponding behavior with regards to temperature and pressure. Figure 1 shows the stability of the three LDH materials vs pH. Also plotted is the gibbsite stability, the LDH materials dissolve at a higher pH than gibbsite.

Figure 1. Gibbsite solubility versus pH compared to LDH material at 25C.
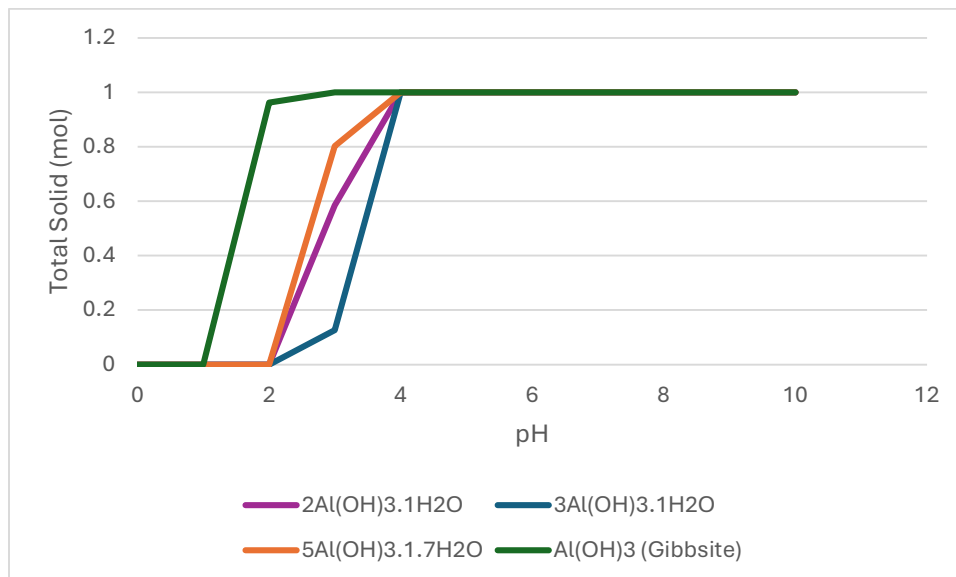
DEVELOPING A KINETIC RATE EXPRESSION

A kinetic rate expression was developed to describe the adsorption and desorption of LiCl with LDH material. Incorporating kinetics is crucial as the adsorption mechanism is rate limited and does not reach true equilibrium under typical operating conditions. A kinetic expression is not well-documented for the material as much of the information is proprietary, thus an expression was hypothesized based on what is known about the material. The forward reaction (adsorption) is likely driven by the lithium and chloride concentration in the feed brine as well as the availability of adsorption sites (designated as concentration) - more adsorption sites result in a higher adsorption rate. We postulate that desorption is driven by the osmotic differential between the stripping water and the chloride-containing interstitial space.

$$Rate\left(\frac{dLi^+}{dt}\right) = \left(\left[A_f * e^{B_f/T(K)} * \left((C_{Li^{+1}})^c * (C_{Cl^{-1}})^f * \left(C_{LDH3_{(s)}}\right)^g\right)\right] - \left[A_r * e^{B_r/T(K)} * \left(\left(C_{LiLDH3_{(s)}}\right)^h * \left(\frac{C_{LDH_{(s)}}}{IS}\right)^i\right)\right]\right)$$

FITTING ADSORPTION AND DESORPTION DATA USING KINETICS

LDH materials are synthesized by various manufacturers using different methods and raw materials. This leads to variations in their physical properties, performance, and stability. Even in similar chemical formulations, these differences impact the behavior and performance of the LDH materials in DLE applications, for this reason, a universal kinetic expression could not be derived. Instead, we fit the reaction orders to experimental data. We used experimental data published by Paranthaman et al., 2017 to obtain the constants.

The experiments described in Paranthaman, 2017 were recreated in a process simulation tool using the postulated kinetic equation. The reaction orders and rate constants were then derived by fitting the reported data. The process simulation, shown in Figure 2, was built using a steady-state simulation tool with each process unit representing a single measurement. The experiment was performed using 16 equivalent bed volumes, the amount of fluid that has passed through a single bed of sorption media. A measurement was taken each time 1 equivalent bed volume of fluid passed through the media. The full experiment consisted of 8 bed volumes (60 minutes) of

lithium-containing feed brine (loading), 2 bed volumes of wash water (washing), and 5 bed volumes of low ionic strength strip water (strip).

Figure 2. Process simulation of the LDH load, wash, and strip steps using a single theoretical stage for each bed volume of brine, washing, or stripping fluid processed in the unit.
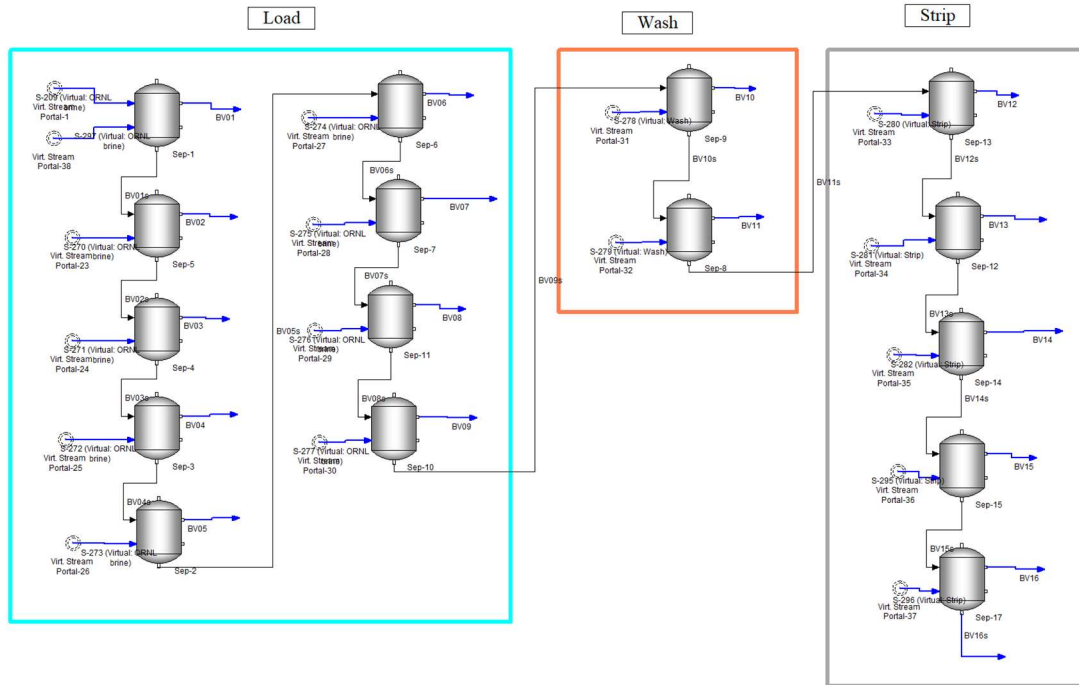

The data fit with the derived kinetic parameters are shown below in Figure 3. The resulting kinetics reveal that the combination of available LDH material and lithium chloride concentration in the brine is the primary driving force for the adsorption rate and extent of the reaction. While the total available lithium adsorption sites in the LDH significantly affect adsorption rate, it remains uncertain if this factor impacts desorption similarly. Conversely, the concentration of lithium-containing LDH material is the main influence in desorption. Surprisingly, desorption is minimally influenced by the ratio of LDH material to ionic strength with desorption mainly influenced by the chloride concentration in the adsorption term.

$$Rate\left(\frac{dLi^+}{dt}\right) = \left(\left[30000 * e^{3550/T(K)} * \left((C_{Li^{+1}})^{1.18} * (C_{Cl^{-1}})^{1.02} * \left(C_{LDH3_{(s)}}\right)^{1}\right)\right]\right.$$
$$\left. - \left[25 * e^{3550/T(K)} * \left(\left(C_{LiLDH3_{(s)}}\right)^{1} * \left(\frac{C_{LDH3_{(s)}}}{IS}\right)^{0.001}\right)\right]\right)$$

Figure 3 shows the results of the simulation with derived kinetic parameters compared against the Paranthaman 2017 experimental data. Good data fits were obtained except at BV 14, it is

unclear if this data point is an outlier, more data is required to fully validate the derived kinetics and test whether the above hypothesis regarding kinetic driving forces are true.

Figure 3. Simulation results with kinetics incorporated showing a comparison with published literature values from Paranthaman 2017.
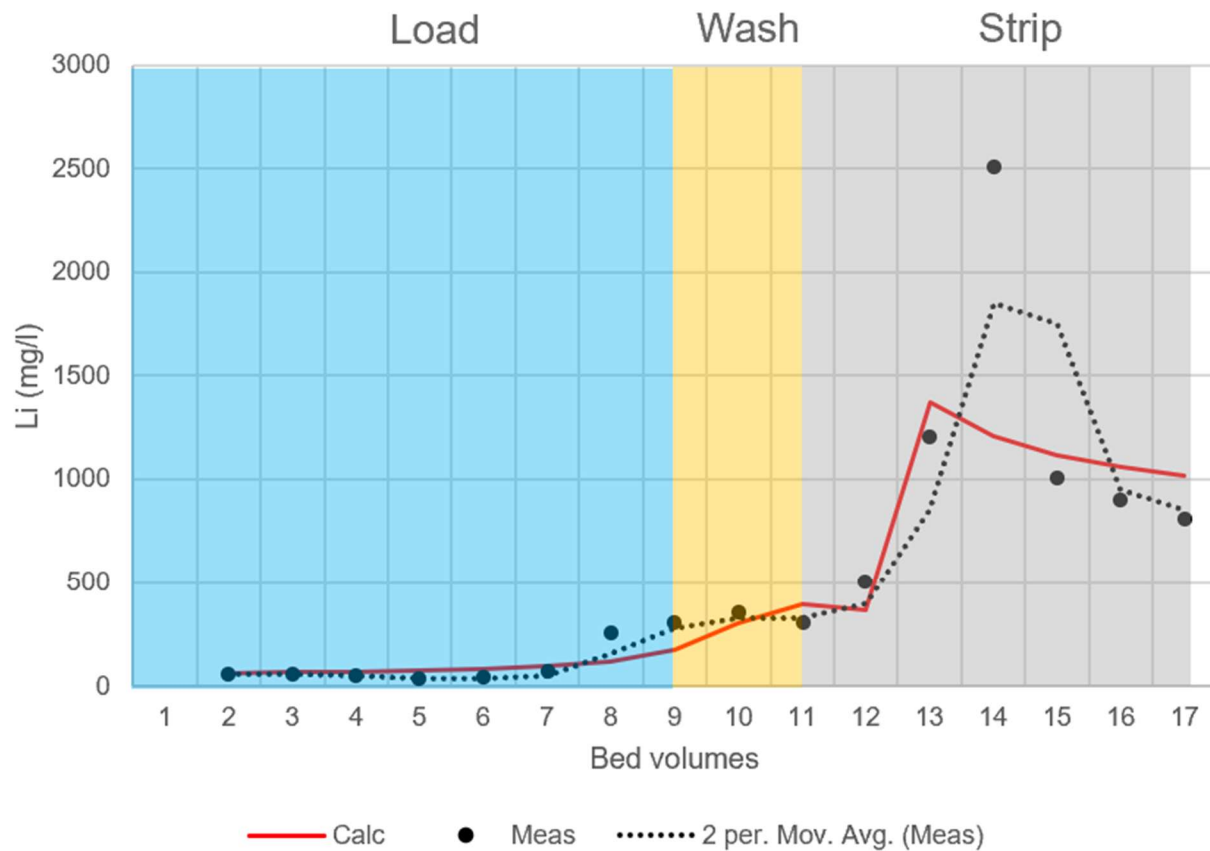
APPLYING THE KINETIC MODEL

With the kinetic equation derived, we now integrate the model within a process simulation tool to evaluate its performance across various brine compositions and flowsheet scenarios. This approach allows us to systematically analyze the model's predictive capabilities and optimize the DLE process under diverse operating conditions.

The derived kinetics were tested using a salar brine composition (Salar de Cauchari), while adjusting five conditions in the documented process simulation (feed to media ratio, residence time (per BV), brine feed temperature, salinity of strip solution, and strip solution temperature). The various operating conditions are documented in Table 1 and Table 2, showing the brine feed (adsorption) and strip solution conditions (desorption), respectively.

Table 1. Operating conditions tested in a process simulation tool using derived kinetics for the adsorption (brine feed) step.

	Feed to media Ratio	# of bed volumes	Residence Time (per BV)	Li conc.	Salinity	Column T
	g/g		*Minutes*	*ppm*	*ppm*	*C*
Start	**0.3**	9	**9 (1)**	360	186,100	**10**
End	**4**		**180 (20)**			**90**
Steps	**12**		**8**			**5**

Table 2. Operating conditions tested in a process simulation tool using derived kinetics for the desorption (stripping) step.

	Stripper to media ratio	# of bed volumes	Residence Time (per BV)	Li conc.	Salinity	Column T
	g/g	*9*	*Minutes*	*ppm*	*ppm*	*C*
Start	0.5		360 (30)	470	**3,600**	10
End					**14,400**	90
Steps					**3**	5

PERFORMANCE INDICATORS: CONTACT TIME AND OSMOTIC PRESSURE DIFFERENTIAL

Figures 4 and 5 present heat map results illustrating the impact of varying reactor retention time, brine-to-media ratio, and salinity of the strip solution on the concentration of lithium chloride in the product stream. These higher concentrations of lithium chloride in the product strip, denoted as "Li to RO," indicate more favorable operating conditions as this is the stream that will feed the lithium purification process and ultimately produce a lithium product.

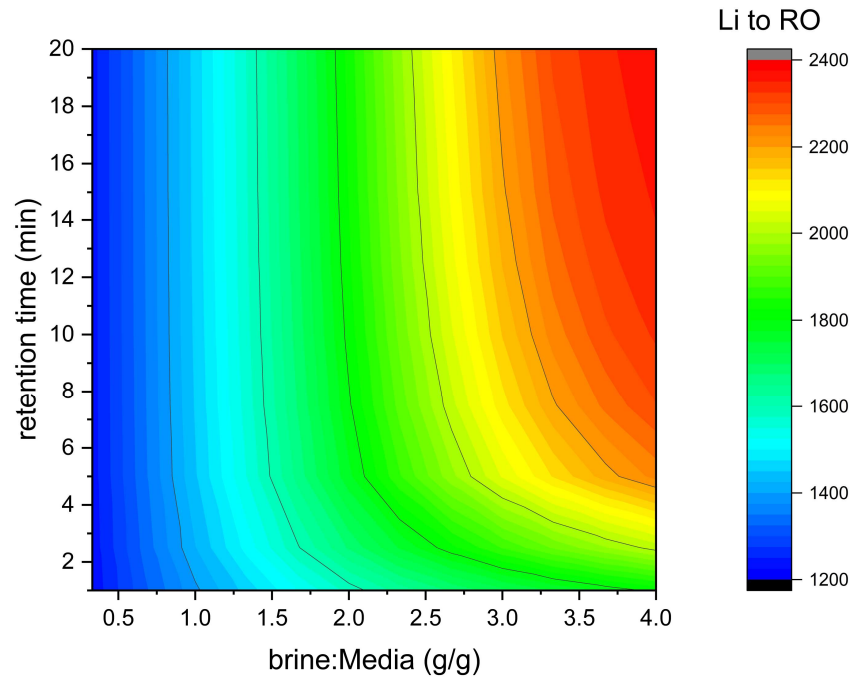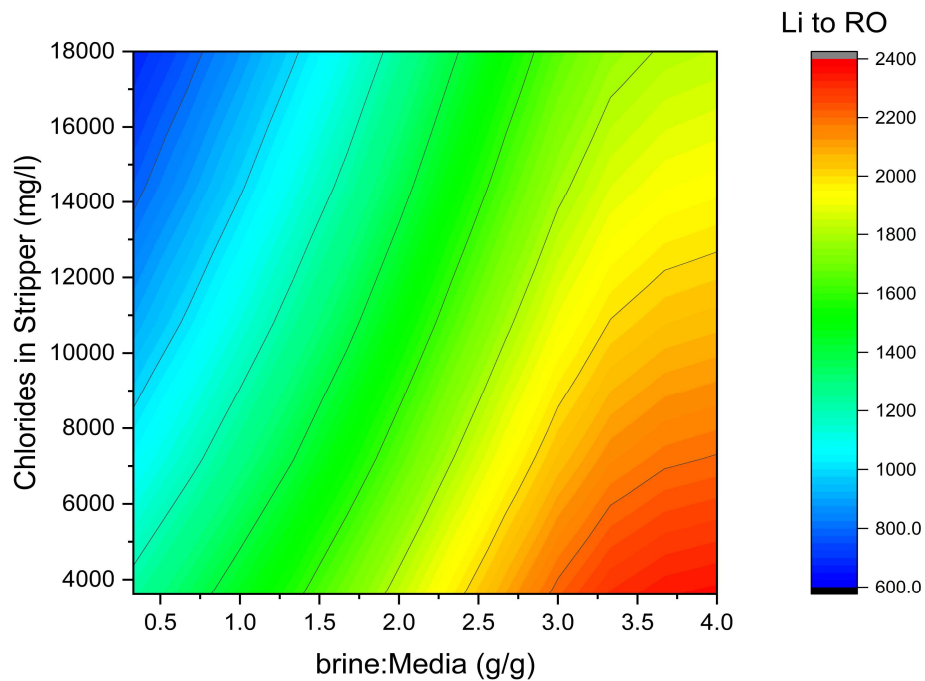**Figure 4. LiCl to RO vs. contact time and brine to media ratio**

Figure 5. LiCl to RO vs Chlorides in strip solution and Brine:media ratio

A longer retention time coupled with an elevated brine-to-media ratio (indicating an excess of brine) significantly enhances lithium concentrations in the product stream. Furthermore, the osmotic pressure of the stripping solution plays a crucial role in optimizing lithium concentration levels.

PERFORMANCE INDICATORS: LITHIUM RECOVERY AND LDH UTILIZATION

This section presents sensitivity analyses on the utilization of LDH material to optimize the mass of media used in the process, and overall lithium recovery from the feed brine. Figures 6 and 7 depict results showing the impact of retention time and brine to media ratio on the percent of lithium recovered from the brine, and temperature and brine to media ratio on lithium recovery, respectively.

As expected, a higher retention time improves lithium recovery up to a point at which there is not enough available media for adsorption to occur. In other words, the media is limiting the amount of lithium recovered. Regarding media utilization, temperature seems to have a minor effect on lithium adsorption and is largely driven by the brine to media ratio, favoring an excess of brine and an insufficient volume of media.

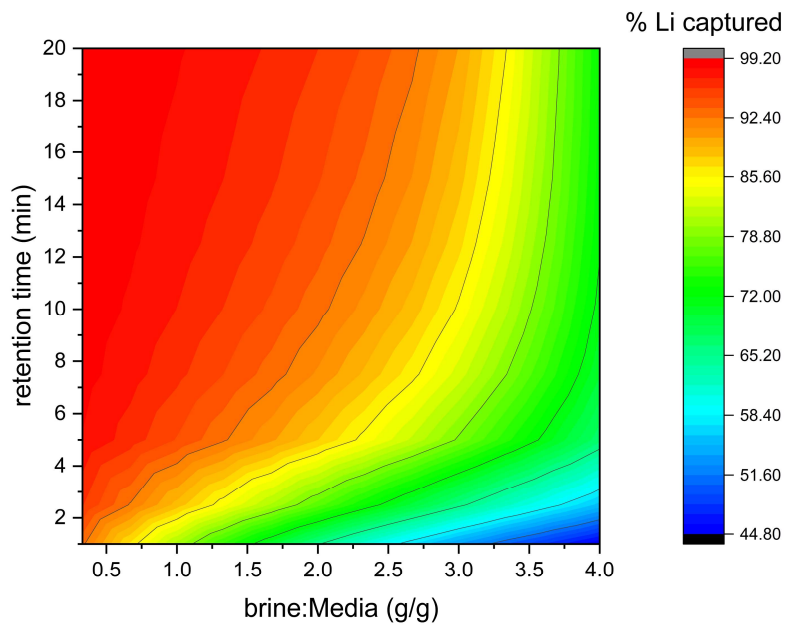**Figure 6. Li captured from brine vs. contact time and brine:media ratio**
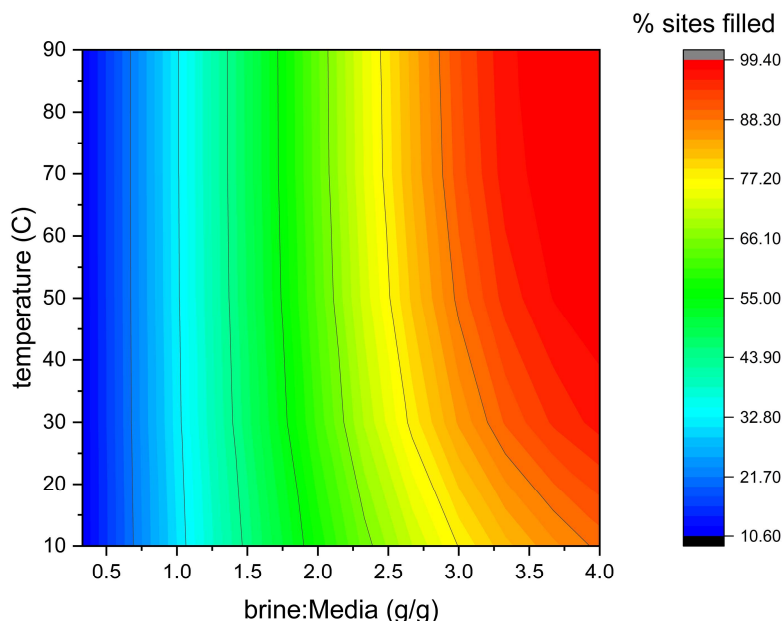
Figure 7. % of LDH sites filled vs. brine:media ratio and temperature

All the presented sensitivity results have economic implications, and the optimum operating conditions taking into account both performance and cost is operating temperature at ambient (no external heating), brine to media ratio of 2.0 – 3.25 g/g, 6–10-minute retention time, strip water below 8000 ppm Cl⁻. The two variables, brine to media ratio and retention time, are the hardest to analyze as there is a direct tradeoff between the amount of media used and the retention time, meaning an excess of media reduces the required residence times and resulting unit size, however excess media similarly increases process unit size by the volume it requires and is also costly. A more detailed technoeconomic analysis is required to understand the interconnectedness of these two variables.

INCORPORATING THE KINETIC MODEL WITH PURIFICATION PROCESSES

The development of a rigorous kinetic model is the first step in optimizing DLE when considering changing brine compositions. The next step in achieving a comprehensive model is understanding the impacts on downstream process units. In this section, a lithium purification process was modeled downstream of DLE process completing the model of a full plant. It was built with a steady state process simulation tool using the Mixed Solvent Electrolyte model (P. Wang, 2002; P. Wang, 2004; P. Wang, 2006) and combined with the already developed DLE process and kinetic model described above.

Figure 8 depicts the purification process recreated in the model. The inflow stream (LiCl from DLE) is the combined product stream from the DLE process model. The two simulations were connected such that the stripped lithium from DLE was combined and fed into the lithium purification process. The connection of the two models allows the user to understand how changes to the DLE process conditions directly impact the downstream purification process, enabling a detailed analysis of the overall process efficiency, cost implications, and potential

economic benefits, ensuring an optimized approach from extraction to final lithium product purification.

Figure 8. The lithium purification process recreated in a steady state simulation tool for lithium hydroxide monohydrate production.
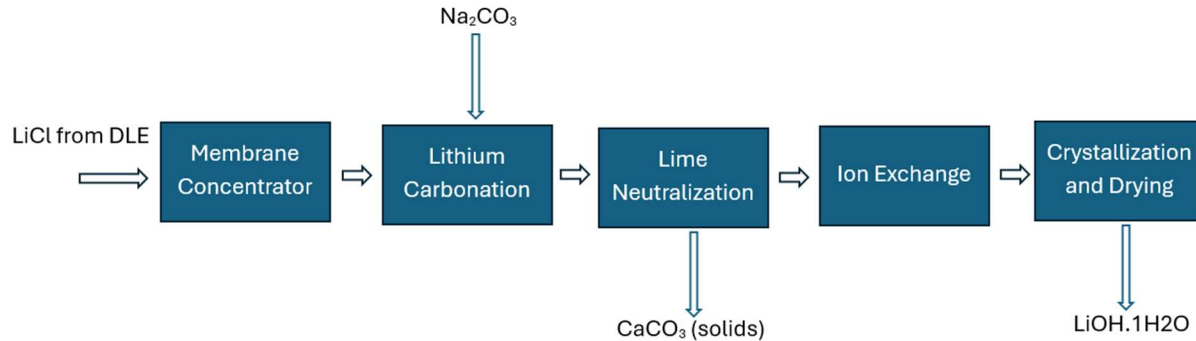
The purification process involves multiple steps. It begins by further concentrating the LiCl brine from the DLE process using nanofiltration (or similar membrane concentrator). Next, the concentrated stream undergoes carbonation to precipitate $LiCO_3$. The resulting precipitate is then mixed with water to form a slurry, which is neutralized with lime to eliminate carbonates and introduce hydroxides. Subsequently, the lithium is directed to an ion exchange polishing unit to remove any remaining impurities. Finally, it passes through several thermal evaporative and drying units to produce battery-grade lithium hydroxide (Wei, 2024).

EVALUATING THE IMPACT OF INCREASED STRIP WATER ON LITHIUM RECOVERY AND ENERGY USE

The process of purifying lithium demands a lot of energy, mainly due to the use of thermal evaporative and drying units. When evaluating combined DLE and lithium purification models, we studied how increasing strip water affects the process. Using more strip water boosts lithium recovery, but it also dilutes the lithium chloride stream heading into purification. This dilution means the process requires more energy and larger equipment to maintain efficiency.

Figures 9 and 10 illustrate the critical impacts of varying strip water flowrates on the lithium purification process. Figure 9 depicts the relationship between strip water flowrates and lithium recovery, highlighting how increasing strip water enhances recovery rates while also diluting the lithium chloride stream, thus affecting process efficiency. Also, Figure 9 outlines the corresponding energy requirements per lithium carbonate equivalent metric ton, showcasing the escalating energy demands associated with higher strip water usage. Moreover, to provide a comprehensive economic perspective, a cost analysis was conducted, with Figure 11 illustrating how the net revenue, factoring in the price of lithium minus energy costs, varies across different strip water flowrates. These charts collectively underscore the complex interplay between operational parameters, energy consumption, and economic outcomes in DLE and lithium purification processes.

Figure 9. Combined impact of varying strip water flowrates on lithium recovery and energy requirements per lithium carbonate equivalent tonne in the purification process.
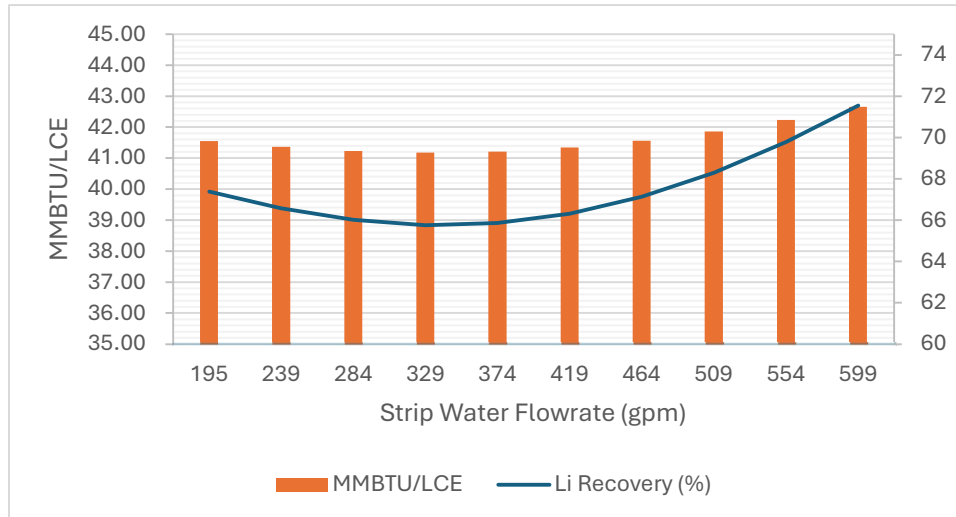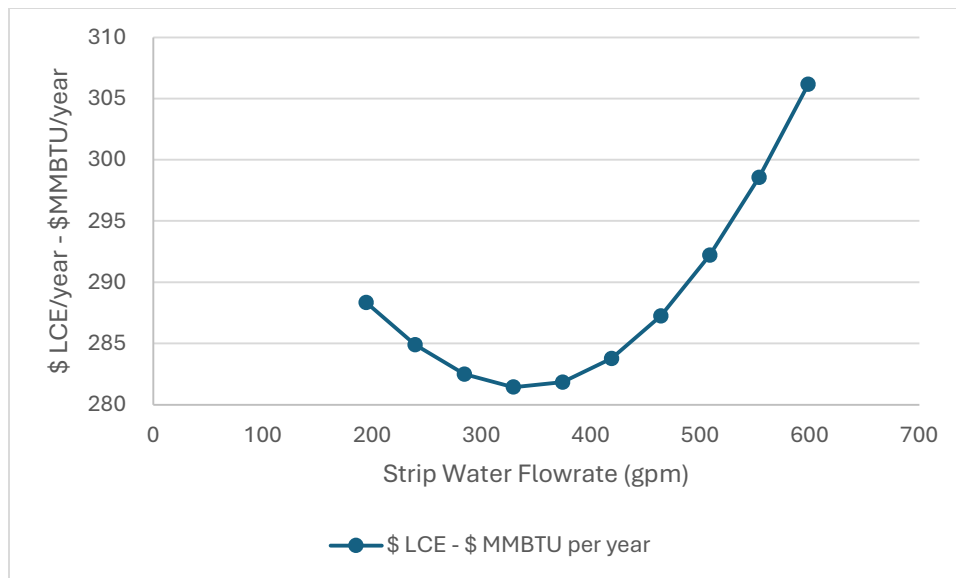

Figure 10. Cost analysis showing the net revenue implications of lithium price minus energy costs across different strip water flowrates.

Analyzing strip water management in the integrated DLE and lithium purification model reveals nuanced impacts on lithium recovery and energy use that are not fully apparent when analyzing only the DLE process (without considering purification downstream units). Despite the increased energy demand with higher strip water flowrates, the model shows clear benefits in terms of improved lithium recovery. This highlights the importance of optimizing strip water flowrates to enhance overall process efficiency. Further refining this cost analysis will provide valuable

insights for developing cost-effective and sustainable operational practices in the combined DLE and lithium purification process.

CONCLUSIONS AND RECOMMENDATIONS

This study developed a kinetic model for the Layered Double Hydroxide (LDH) Direct Lithium Extraction (DLE) process, incorporating chemical speciation, activity coefficients, and rate-limiting steps. This model accurately predicts the effects of operational parameters on media performance, facilitating the design, scale-up, and optimization of LDH DLE plants. Moving forward, additional validation under diverse brine compositions and operational scenarios is recommended to enhance reliability and accuracy.

The integration of a lithium purification process downstream of the DLE model completes the simulation of a full plant. This interconnected model enables comprehensive analysis of how variations in DLE conditions impact downstream purification efficiency, cost implications, and economic benefits. Future efforts should focus on optimizing operational conditions and integrating the DLE process with subsequent purification steps to maximize efficiency and ensure high-purity lithium production suitable for battery applications.

In evaluating combined DLE and lithium purification models, it's crucial to consider the energy-intensive nature of lithium purification, particularly due to thermal evaporation and drying units. Optimizing strip water management is one example of the nuanced interactions between DLE optimization and purification. Further refinement of cost analysis variables and methodologies will provide valuable insights for developing sustainable operational practices in DLE and lithium purification.

Recommendations:

1. **Further Validation:** While the kinetic model showed good agreement with experimental data, additional experimental validation, especially under different brine compositions and operational scenarios, is recommended to ensure robustness and accuracy.
2. **Process Optimization:** Detailed economic analysis and optimization should be conducted to determine the most cost-effective operating conditions. This includes optimizing retention time, brine-to-media ratio, and strip water salinity to maximize lithium recovery and minimize operational costs.
3. **Scale-Up Studies:** Conduct pilot-scale studies to assess the scalability of the LDH DLE process using the developed kinetic model. These studies should focus on evaluating the model's predictive capabilities in real-world scenarios and identifying any potential scale-up challenges.
4. **Integration with Lithium Purification:** Future work should explore the integration of the LDH DLE process with subsequent lithium purification steps. This will provide a comprehensive solution for lithium extraction and purification, ensuring high purity lithium production suitable for battery applications at the lowest cost.

By implementing these recommendations, the LDH DLE process can be further refined and optimized, paving the way for more efficient and sustainable lithium extraction technologies.

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