DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof. Reference herein to any social initiative (including but not limited to Diversity, Equity, and Inclusion (DEI); Community Benefits Plans (CBP); Justice 40; etc.) is made by the Author independent of any current requirement by the United States Government and does not constitute or imply endorsement, recommendation, or support by the United States Government or any agency thereof.

ANL/AMD-25/1

CRADA Report

Advanced Brine Processing to Enable U.S. Lithium Independence

Applied Materials Division

***Custom Text Heading**

Custom Text

About Argonne National Laboratory
Argonne is a U.S. Department of Energy laboratory managed by UChicago Argonne, LLC under contract DE-AC02-06CH11357. The Laboratory’s main facility is outside Chicago, at 9700 South Cass Avenue, Argonne, Illinois 60439. For information about Argonne and its pioneering science and technology programs, see www.anl.gov.

DOCUMENT AVAILABILITY

Online Access: U.S. Department of Energy (DOE) reports produced after 1991 and a growing number of pre-1991 documents are available free at OSTI.GOV (http://www.osti.gov/), a service of the U.S. Dept. of Energy's Office of Scientific and Technical Information

Reports not in digital format may be purchased by the public from the National Technical Information Service (NTIS):
U.S. Department of Commerce
National Technical Information Service
5301 Shawnee Rd
Alexandria, VA 22312
www.ntis.gov
Phone: (800) 553-NTIS (6847) or (703)
605-6000 Fax: (703) 605-6900
Email: **orders@ntis.gov**

Reports not in digital format are available to DOE and DOE contractors from the Office of Scientific and Technical Information (OSTI):
U.S. Department of Energy
Office of Scientific and Technical Information
P.O. Box 62
Oak Ridge, TN 37831-0062
www.osti.gov
Phone: (865) 576-8401
Fax: (865) 576-5728
Email: **reports@osti.gov**

Disclaimer
This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor UChicago Argonne, LLC, nor any of their employees or officers, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of document authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof, Argonne National Laboratory, or UChicago Argonne, LLC.

ANL/AMD-25/1

CRADA Report

Advanced Brine Processing to Enable U.S. Lithium Independence

prepared by
Albert Lipson, A H M Golam Hyder, and Mason Wasilk, Argonne National Laboratory
Collin Willoughby, Albemarle Corporation

Applied Materials Division, Argonne National Laboratory

7/30/2025

Introduction:

Current production of LiOH, which is needed to make Li-ion battery cathode active materials, utilizes a multistep process including solar evaporation, precipitation with Na_2CO_3 and then conversion to LiOH using $Ca(OH)_2$.[1, 2] This process requires a large amount of land area for solar evaporation, the right weather conditions, and chemicals for the conversion process that result in NaCl and $CaCO_3$ waste products. The production of $Ca(OH)_2$ is very energy intensive and evolves significant quantities of CO_2. An alternative process flow utilizing direct lithium extraction techniques, followed by a chemical free conversion process can have benefits in reducing the needed land requirements and chemicals for traditional brine processing. There are many potential direct lithium extraction technologies that are currently being developed.[2]

The direct lithium extraction process from typical brine sources will produce a LiCl solution with some impurities including typically high concentrations of Na. This brine then needs to be converted to LiOH for use in battery cathode production. Ideally this conversion could occur without the use of additional chemicals. Electrochemistry can do this conversion either via electrolysis or bipolar membrane electrodialysis (BPED) to produce LiOH and HCl in solution. BPED utilized bipolar membranes to split water, which has a reduced potential as compared to splitting water at electrodes into hydrogen and oxygen gas. This reduced potential required results in a significant energy savings for BPED over electrolysis methods.

This CRADA project aimed to develop such an integrated process using direct lithium extraction followed by BPED to produce a LiOH solution. That solution can then be crystallized into battery grade LiOH. In particular, Albemarle utilized a direct lithium extraction process to produce a concentrated LiCl solution that could be used for the BPED process. The BPED process was first tested using various LiCl solutions with impurity ions added at bench scale to understand the effects of impurities and determine processing parameters. Then testing was performed using the direct lithium extracted brine at the bench scale before scaling the process up. After the process was scaled up a long duration test was carried out to estimate the lifetime of the membranes, which is key to the economics of the BPED process.

Results and Discussion:

The BPED process is schematically shown in Figure 1. There are three main solution loops and a separate loop for the electrode rinse solution. The three main loops are the feed (LiCl solution), base (LiOH solution) and acid (HCl solution). The LiCl is split into Li^+ and Cl^- through the electric field forcing them through a cation and anion exchange membrane to the base and acid loops, respectively. Meanwhile, the bipolar membranes split H_2O into OH^- and H^+, which move into the base and acid loops, respectively. This leaves the base compartment concentrating in LiOH, and the acid compartment concentrating in HCl while the feed salt is depleted. Typically, the process is run until a fraction of the salt remains (≈50%), and then the diluted salt is reconcentrated with fresh LiCl feed solution. The acid and base final solutions can be concentrated up to about 2 M during the process. Higher concentrations in the HCl acid loop begin to reduce the energy efficiency due to proton diffusion across the anion exchange membrane from the acid compartment to the feed compartment.

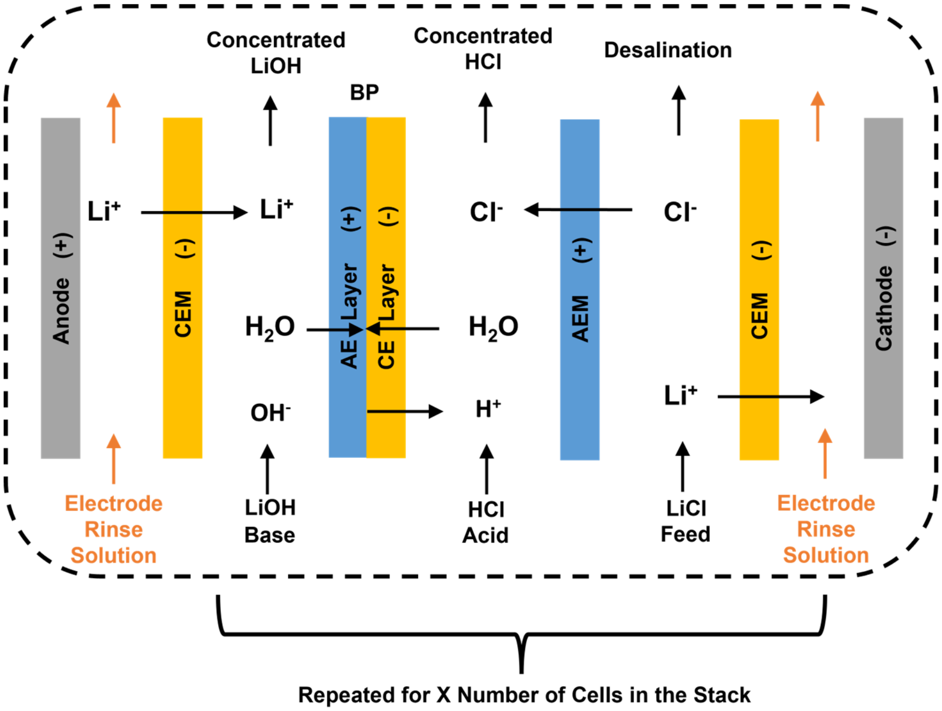
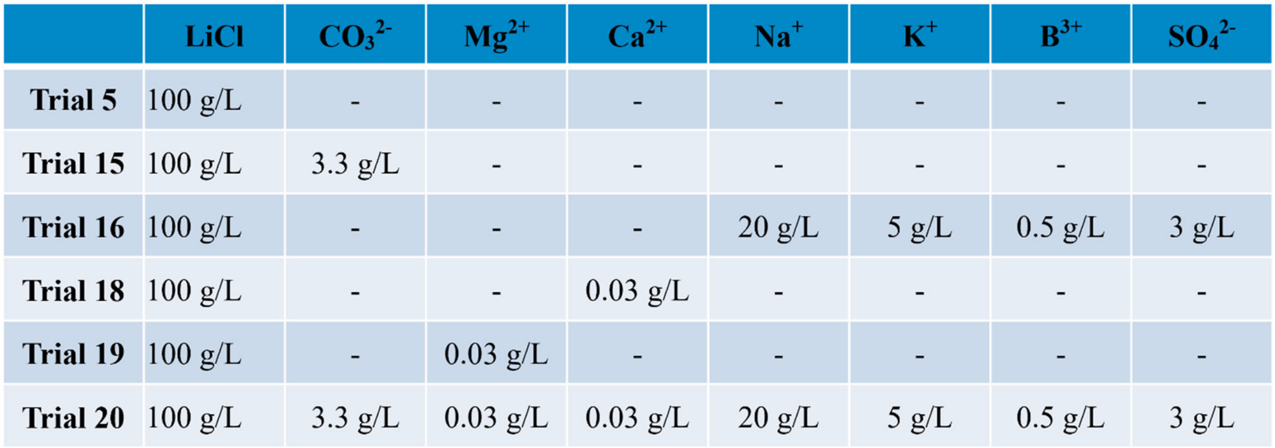


Figure 1. Schematic of the BPED process.

The BPED process was initially performed on the bench-scale system with artificial solutions created by mixing pure salts (e.g., LiCl and $LiOH.H_2O$) in DI water (Trial 5, 15, 16, and 18-20. The results of those initial studies are shown in Figure 2. Overall, the impurities did not make a very large impact on the performance of the BPED process. Although it should be noted that the efficiencies are calculated based on total base produced (sum of LiOH, NaOH, and KOH) and do not factor in the loss associated with producing NaOH and KOH. While the differences are slight there is a notable decrease in specific energy consumption for trial 16, which is predominantly due to the increased conductivity of the feed solution.



	LiCl	CO_3^{2-}	Mg^{2+}	Ca^{2+}	Na^+	K^+	B^{3+}	SO_4^{2-}
Trial 5	100 g/L	-	-	-	-	-	-	-
Trial 15	100 g/L	3.3 g/L	-	-	-	-	-	-
Trial 16	100 g/L	-	-	-	20 g/L	5 g/L	0.5 g/L	3 g/L
Trial 18	100 g/L	-	-	0.03 g/L	-	-	-	-
Trial 19	100 g/L	-	0.03 g/L	-	-	-	-	-
Trial 20	100 g/L	3.3 g/L	0.03 g/L	0.03 g/L	20 g/L	5 g/L	0.5 g/L	3 g/L

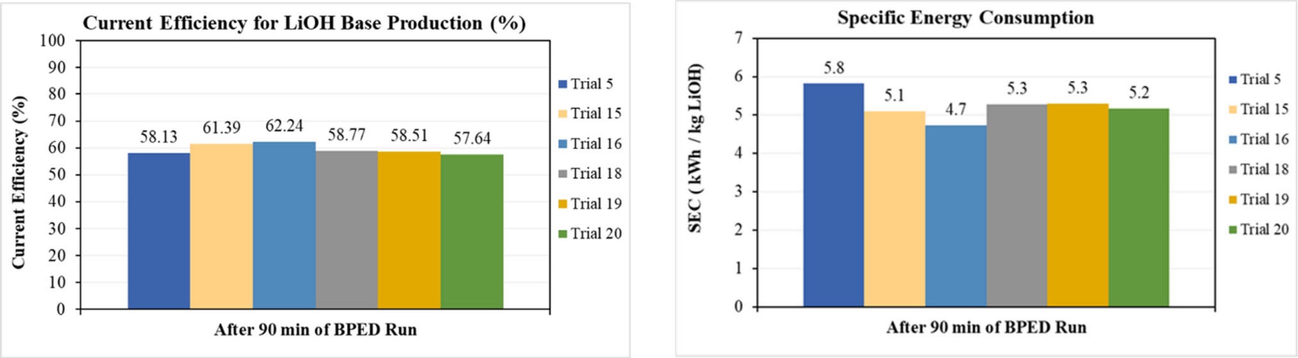


Figure 2. Trial concentrations and the resulting Coulombic and specific energy consumption from running the BPED process with those feed solutions.

To better understand the process and look for ions that may be lost in the membranes the concentration of ions were tracked via inductively coupled plasma (ICP) analysis. The resulting concentrations through time are shown in Figure 3. As expected Li, Na, and K transfer from the feed loop into the base loop with no discernible loss. However, Mg does not transfer to the base loop indicating that all of the Mg^{2+} is precipitating as $Mg(OH)_2$ inside the membranes, which can create fouling. Some Ca does transfer to the base compartment, however, the concentration is lower than would be expected indicating some precipitation of Ca^{2+} as $Ca(OH)_2$ inside the membrane, but not all of the Ca^{2+} does this. The process should be somewhat more resilient to Ca than Mg impurities as a result.

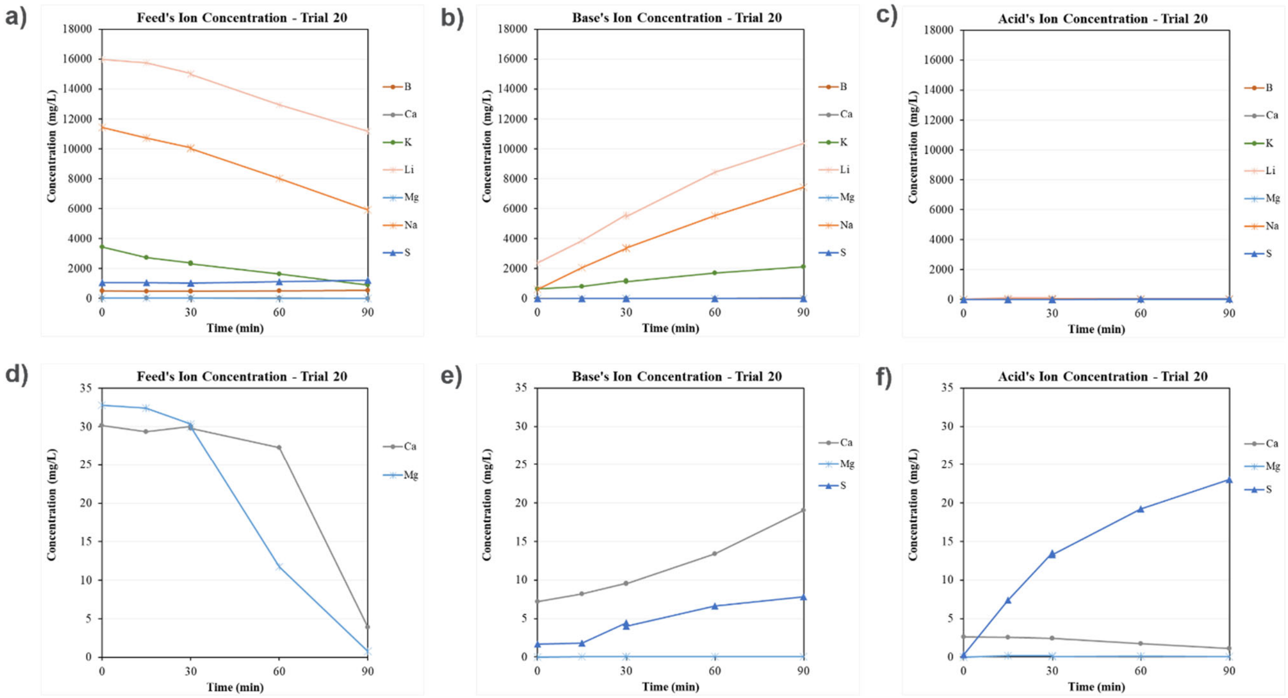


Figure 3. a, b, c) Elemental concentrations of various elements for the feed, base, and acid compartments, respectively. d, e, f) Elemental concentrations of various elements for the feed, base, and acid compartments, respectively showing only the low concentration elements.

To better determine the realistic operating parameters of the BPED process, we scaled the process up to a larger scale. In particular, we used a system with 0.06 m^2 active membrane area with 25 cells in two stacks placed in parallel as shown in Figure 4a. The system is capable of initially producing about 1 kg of $LiOH{\cdot}H_2O$ per hour. Initial testing using this scaled up system showed an energy reduction of about 20% as compared to the bench scale system. This is due to two changes in the system: (i) using proton blocking anion exchange membranes, and (ii) the increase in the number of cells thereby reducing the amount of hydrogen and oxygen produced per LiOH.

The other key parameter needed to properly model the cost of the system is to determine the change of the energy efficiency with membrane degradation. This type of test requires hundreds of hours of runtime on the membranes to determine the degradation of those membranes. In order to complete such a test either a large quantity of feed would be needed or the feed would need to be regenerated from the products. To minimize the quantity needed and reduce the logistical hurdles of handling such a large volume of feed it was chosen to regenerate the feed. 500 gallons of brine were prepared by Albemarle and sent to Argonne for processing. The brine was processed through the BPED system creating a dilute LiCl brine, HCl acid, and LiOH base. The dilute brine was reconcentrated using a reverse osmosis system in closed loop operation to approximately 9 wt.% dissolved solids, which is about 1 wt.% less than the original LiCl feed solution. The HCl acid and LiOH were remixed and then fed into the dilute feed for concentration using the reverse osmosis system. The reconcentrated feed was then fed back into the BPED plant for reprocessing. After 500 hours of runtime on the BPED system the resulting energy efficiency through time can be examined. It is clear that performance is degrading at the end of the 500 hr trial. The cause of this decline is mostly due to a loss in LiOH production rate. This appears to be caused by the need to keep the LiCl feed solution acidic to maintain the conductivity of the proton blocking anion exchange membrane. The amount of acid required to accomplish this increased with runtime on the membranes. There are two potential methods to alleviate this issue. One option is to not use proton blocking membranes, which will reduce the initial energy efficiency, but might improve the stability of the system through time. Another option is to run the BPED system with higher initial HCl acid concentrations in the acid compartment thereby providing the protons needed for conductivity from the acid compartment. This was not done in these experiments as corrosion of sensors needed to operate this particular system would be too high, which would cause impurities in the stream and eventually loss of the sensor. Redesigning the system to use HCl compatible sensors could be done. In addition, there is corrosion of the isopotential electrodes that would also need to be mitigated. Without these modifications it appears that the anion exchange membranes should be replaced at about 500 hours or sooner depending on the energy cost versus the membrane cost balance.

Albemarle took a portion of the final LiOH product from the pilot scale BPED test and crystallized battery grade LiOH from that LiOH product. In performing a high-level technoeconomic analysis of the entire process, it was found that the capital expenditure for the flowsheet increased by roughly 50%. While operational cost savings are found for the LiOH conversion step, upstream purification and downstream handling and treatment of dilute streams lead to a flowsheet of comparable operating costs to a traditional LiOH conversion process. Pairing this with the risk associated with a little to no commercial demonstration of this technology in the lithium industry lends this to be an unattractive business case at this point in time without further process improvements.

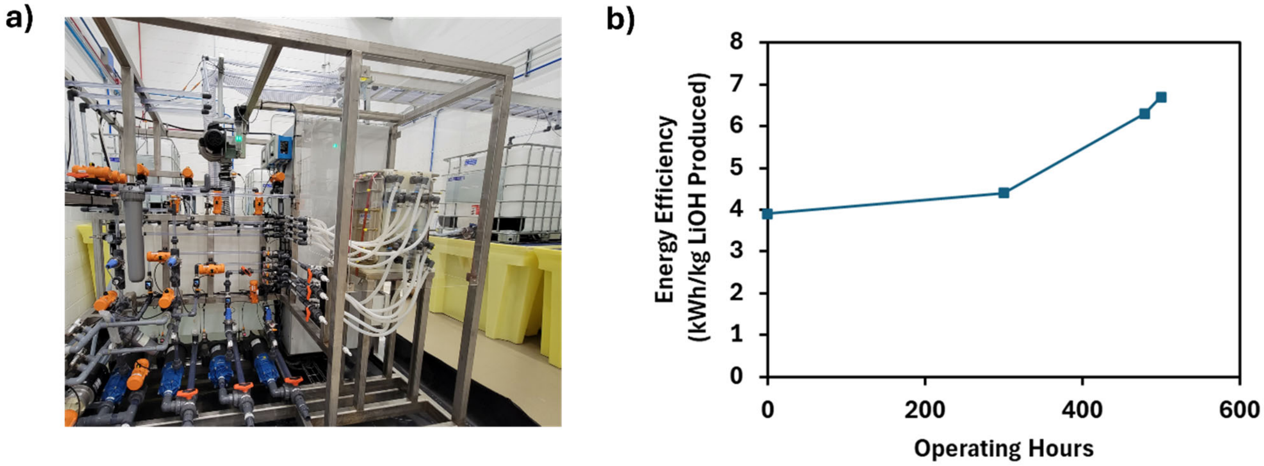


Figure 4. a) Picture of the scaled up BPED system. b) Energy usage to create 1 kg of LiOH over the course of a long duration trial.

Conclusions:

We have demonstrated that BPED can be used to convert a LiCl brine produced from natural sources into LiOH. The initial efficiency using a scaled-up system was less than 4 kWh/kg LiOH, however, that efficiency reduced with time due to degradation of the proton blocking anion exchange membranes. The movement of ions through the bench scale system indicates that Mg impurities are likely the biggest concern in the feedstock, but any cation that forms a relatively insoluble hydroxide should be eliminated prior to this process. Further improvements are needed in the upstream and downstream processes to improve the economics of the process. In addition, improving the processing conditions or the anion exchange membrane lifetime with the current conditions can improve the overall economics.

References:

(1) Flexer, V.; Baspineiro, C. F.; Galli, C. I. Lithium recovery from brines: A vital raw material for green energies with a potential environmental impact in its mining and processing. *Science of The Total Environment* **2018**, *639*, 1188-1204. DOI: https://doi.org/10.1016/j.scitotenv.2018.05.223.

(2) Murphy, O.; Haji, M. N. A review of technologies for direct lithium extraction from low Li+ concentration aqueous solutions. *Frontiers in Chemical Engineering* **2022**, *4*, Review. DOI: 10.3389/fceng.2022.1008680.

Applied Materials Division
Argonne National Laboratory
9700 South Cass Avenue
Lemont, IL 60439

www.anl.gov

Argonne National Laboratory is a U.S. Department of Energy
laboratory managed by UChicago Argonne, LLC