Design of a Processing Plant for the Extraction of Lithium and Other Minerals from Geothermal Brines in the Salton Sea, California

Case studies of lithium-ion battery disposal methods

A Thesis Prospectus In STS 4500 Presented to The Faculty of the School of Engineering and Applied Science University of Virginia In Partial Fulfillment of the Requirements for the Degree Bachelor of Science in Chemical Engineering

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On my honor as a University student, I have neither given nor received unauthorized aid on this assignment as defined by the Honor Guidelines for Thesis-Related Assignments.

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General Research Problem: Transitioning to Electric Cars

How can production of lithium-ion batteries support the transition to electric cars?

As the world finds ways to reduce carbon emissions to slow the pace of climate change, the clean energy transition of the transportation sector is a key part of the solution. For many countries, their transportation sector's carbon dioxide emissions account for at least a third of total emissions. Governments around the world are enacting policies to drive the personal mobility transportation towards electric cars and major automobile companies are announcing their steps towards electric vehicles. Most notably, General Motors plans to stop selling petrol-powered and diesel models by 2035 and Audi plans to stop producing these vehicles by 2033 (Castelvecchi, n.d.). Electric vehicle sales will continue to increase with sales up by three quarters in the first quarter of 2022 compared to 2021, eventually leading to half of all global passenger-vehicle sales in 2035 being electric according to the BloombergNEF consultancy. In order to meet the demand created by millions of electric cars on the roads, lithium-ion battery production must keep pace.

Lithium-ion batteries are now more accessible to electric car manufacturers and drivers since the cost has continue to decline (Nykvist & Nilsson, 2015) and its technology has greatly improved since they first entered the market in the 1990s. A predicted price of \$100 per kilowatt-hour by 2023 will make it possible for electric cars to reach price parity with conventional cars by the mid-2020s (Castelvecchi, n.d.). Price is still highly dependent on the prices for lithium, a key component of the lithium-ion battery used in electric cars, which may fluctuate greatly depending if production is able to meet demand. Currently, new extraction technologies utilizing innovative sources are allowing for increased lithium production. Greater access to lithium has

paved the way for improved battery technology and ultimately more electric cars; longer battery lifetime is a key measure of this improvement. Every electric car battery sold in the U.S. comes with a warranty of eight years or up to 100,000 miles according to CarFax. With this increased lifetime, end-of-life disposal and lithium recovery process of the battery still is a question that looms large. As lithium-ion batteries continue to improve their technology and the infrastructure surrounding their production and disposal improves, the use of electric cars will increase.

Technical Research Problem: Design of a Processing Plant for the Extraction of Lithium and Other Minerals from Geothermal Brines in the Salton Sea, California

With technological advancements in electric vehicles and batteries, global demand for high-energy density materials, such as lithium, has increased significantly. It is estimated that rising demand will push production of lithium from 447 thousand tons of lithium carbonate equivalent in 2018 to over 2 million tons by 2050 (Stringfellow & Dobson, 2021).

Currently, the United States relies on lithium imported from Chile and Argentina, where an energy intensive and environmentally damaging process known as evaporative extraction is utilized (Warren, 2021). Geothermal brines from the Salton Sea in California contain a significant amount of lithium along with trace quantities of other valuable elements, such as rubidium and cesium. Directly adsorbing lithium from Salton Sea brines offers an attractive, environmentally conscious alternative to meet increasing lithium demands. With eleven geothermal wells drawing from the Salton Sea in California, lithium extraction holds the potential to produce \$5 billion annually (Jones et al., 2022). For this project, we propose a plant design to extract lithium and other valuable metals from an existing 6000 gal/min well located in the Salton Sea (Ventura et al., 2020). A single well has the potential to produce 2500 mt/yr of lithium. The plant can be separated into three distinct sections: pre-treatment, lithium extraction, and alternative products capture. Pretreatment of the feed involves the removal of silicates from brine by introducing calcium hydroxide to precipitate iron silicates, which are then physically filtered from the solution (Koenig, personal communication, 2022). Once silicates are removed, the stream is passed through a boiler, where the hot brine is used to produce high pressure vapor for geothermal power plants.

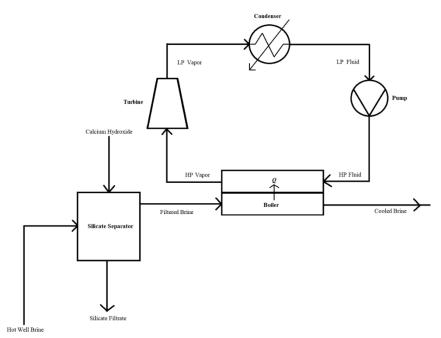


Figure 1. Processed Flow Diagram of Brine Pretreatment Process

After passing through the power plant, cooled brine is processed using a series of packed bed reactors containing iron (III) phosphate, which selectively adsorbs lithium through a reductionoxidation (redox) reaction (Geise, personal communication, 2022). The spent brine is then sent away for further product extraction. After reaching sorption capacity, iron (III) chloride is then fed to the reactor, which reacts with the lithium iron (II) phosphate to regenerate iron (III) phosphate and lithium chloride. The packed bed reactors are operated such that half are in adsorption mode and half are in regeneration mode to ensure the process is continuous.

Lithium rich brine is then sent to an electrolysis unit, which selectively isolates lithium ions from chloride and iron ions via a redox reaction. Chloride ions from brine (Cl-) are oxidized at the anode to form chlorine gas (Cl₂), while water is reduced at the cathode to form hydroxide ions (OH-). Lithium ions pass from the anode to the cathode to form lithium hydroxide monohydrate (LiOH·H₂O), which is sent to a crystallization unit for further purification. Oxygen (O₂) and hydrogen (H₂) gas are produced as side products as well as iron (III) chloride, which can be reused in the reactor.

Additional product capture involves the extraction of alkali metals from spent brines. While only present in small concentrations, rubidium (32 ppm) and cesium (6 ppm) have high market values (Warren, 2021). Rubidium and cesium can be selectively separated from other minerals via an ion exchange process using zeolite-based sorbents (Neupane & Wendt, 2017). A similar operation structure to the lithium extraction process could be implemented to extract rubidium and cesium products.

For proprietary adsorption and electrolysis unit operations, experimental design data will be sourced from professors Gaurav Giri, Gary Koenig, and Geoff Geise. Additional information regarding other components of the process, such as other alkali metals capture, will be acquired through peer reviewed journals. Data will be consolidated into a thermodynamic model using Aspen Plus design software with the Electrolyte-Nonrandom Two-Liquid equations activity model (ELECNRTL) which has shown to be successful in simulating high temperature and pressure brines in previous literature (Ye et al., 2019). Over the course of two semesters in CHE 4474 and CHE 4476, this project will be completed as a team of five members. Work will be divided equally where each member will focus on a specific unit operation's design and economic analysis; a project management tool, such as a Gantt chart, will be used to assess group progress.

STS Research Problem: Case studies of lithium-ion battery disposal methods

What do case studies of lithium-ion battery end-of-life pathways show about the move towards a circular economy?

The number of electric vehicle batteries is predicted to increase to 150 million by 2035 (Kotak et al., 2021) which makes determining the end-of-life pathway of lithium-ion batteries within these vehicles increasingly important to figure out. After a battery drops below its capacity retention rate, it must be retired from its use in an electric vehicle and moved on to its disposal lifecycle. Batteries in decent condition can be implemented into other applications that require less power than electric cars such as electric bikes, energy storage and even street lights and then recycled once their capacity falls below 30% if its original potential (Liu et al., 2020). If batteries are not placed into a specific disposal pathway and instead abandoned in landfills, precious minerals may cause environmental harm and increase the demand to mine for virgin materials that are already limited in supply. A circular economy model would eliminate waste and pollution and allow for products and materials to be kept in use at their highest value.

One end-of-life pathway for a lithium-ion battery is usage in e-bikes in China. While this method holds great potential for reuse, a challenge facing this pathway is the heterogeneity of the retired batteries. Though a manufacturer may recommend a new battery for an electric vehicle when it reaches a 70% capacity of it's original health, drivers make the decision on when to get a new battery which will result in a wide range of battery health coming into a reuse program

(Kotak et al., 2021). For this reason, until conditions become more stabilized, recycling methods may be the most reliable option.

Recycling has a high initial investment cost and returns have been constant with the use of pyrometallurgy/smelting and hydrometallurgy to accomplish the process (Kotak et al., 2021). Regaining precious metals such as nickel and cobalt have economically driven the technology forward and will continue to do so. The move towards a circular economy in which products are reused and valuable resources are regained is a main motivating factor in the disposal of lithiumion batteries. Recycling rates are currently very low worldwide and the incoming boom of lithium-ion batteries as more electric cars hit the streets will impact these numbers (Pagliaro & Meneguzzo, 2019).

Currently the economics of recycling lithium from lithium-ion batteries is much more expensive than mining it. The market for recycled lithium will increase as more batteries come to their end-of-life and companies must figure out how to dispose of them. Companies are started and expanded as these markets are created and many government policies push innovation and business in the necessary areas. China's economy and how the government is supporting the recycling of precious metals is one case study of how the lithium recycling industry may expand in the coming years. Circular economy companies are working with battery manufacturers in order to make this process easier in the future and this will greatly increase the recycling rate of the future (Pagliaro & Meneguzzo, 2019).

Case studies of different disposal pathways for lithium-ion batteries will focus on the actors in each application, whether this be a reuse or recycling program. Evidence showing how the disposal pathway impacts the surrounding economy and is shaped by the policies of the area

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will indicate if this method is a path towards the circular economy model in the area. Actors in each of the disposal pathways will be examined including the health of the battery in the end-oflife use, the company or government actor running the program, and the policy and economic implications of the program. Statistical data will be collected from journal articles and support the case study analysis in regions including the U.S., China and the E.U. Through the comparison of these case studies, an overview of the how disposal pathways move towards the circular economy and ultimately benefit the environment will be explored.

Conclusion

By determining the actors that play into disposal methods and comparing different case studies around the world, an understanding of the status of the circular economy can be concluded. With the need the preserve and increase the supply of lithium, new lithium extraction technologies will be explored through extraction from geothermal brines. The environmental impact of these new technologies developed for both production and disposal will impact the benefits of these technologies within the circular economy and influence how strong they are. Finally, with 95% of the demand for lithium coming from the need to power lithium-ion batteries for electric vehicles, this paper will unpack how the world will transition to electric.

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