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Energy Research and Development Division

## **FINAL PROJECT REPORT**

# **Selective Recovery of Lithium from Geothermal Brines**

**Gavin Newsom, Governor  
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## PREFACE

The California Energy Commission's (CEC) Energy Research and Development Division supports energy research and development programs to spur innovation in energy efficiency, renewable energy and advanced clean generation, energy-related environmental protection, energy transmission and distribution, and transportation.

In 2012, the Electric Program Investment Charge (EPIC) was established by the California Public Utilities Commission to fund public investments in research to create and advance new energy solutions, foster regional innovation and bring ideas from the lab to the marketplace. The CEC and the state's three largest investor-owned utilities—Pacific Gas and Electric Company, San Diego Gas & Electric Company, and Southern California Edison Company—were selected to administer the EPIC funds and advance novel technologies, tools, and strategies that provide benefits to their electric ratepayers.

The CEC is committed to ensuring public participation in its research and development programs that promote greater reliability, lower costs, and increase safety for the California electric ratepayer and include:

- Providing societal benefits.
- Reducing greenhouse gas emissions in the electricity sector at the lowest possible cost.
- Supporting California's loading order to meet energy needs first with energy efficiency and demand response, next with renewable energy (distributed generation and utility scale), and finally with clean, conventional electricity supply.
- Supporting low-emission vehicles and transportation.
- Providing economic development.
- Using ratepayer funds efficiently.

"Selective Recovery of Lithium from Geothermal Brines" is the final report for the "Recovery of Lithium from Geothermal Brines" project (Grant Number EPC-16-020) conducted by SRI International. The information from this project contributes to the Energy Research and Development Division's EPIC Program.

For more information about the Energy Research and Development Division, please visit the [CEC's research website](http://www.energy.ca.gov/research/) (www.energy.ca.gov/research/) or contact the CEC at 916-327-1551.

## ABSTRACT

SRI International demonstrated a new process for the extraction of lithium from geothermal brines based on new high-capacity selective sorbents (material used to absorb or adsorb liquids or gases) and a new sorbent regeneration process. Recovery of lithium from geothermal brines is expected to help the economics of geothermal energy production in California by generating revenue from the production and sale of lithium carbonate. Lithium recovery is also expected to create thousands of new jobs in the United States.

Lithium is a high-value metal used in lithium-rechargeable batteries. It is found in low but significant concentrations in geothermal waters (specifically a few hundred parts per million). Because of the very large volume of brine processed in a geothermal power plant (hundreds of cubic meters per hour), even low-lithium brines represent a valuable resource. SRI International's technology enables lithium carbonate producers to extract lithium from brines using a fast, cost-effective, and selective process adaptable to a variety of brines, including geothermal brines. Compared to traditional methods of lithium recovery from brines, SRI International's sorbents and regeneration processes are expected to lower the cost of lithium production by allowing online separation with higher recovery efficiency and using smaller volumes of sorbent, minimizing processing time. The project team demonstrated extraction of lithium with efficiency as high as 90 percent and detected no significant loss in capacity after repeated lithium adsorption-desorption cycles.

The co-production of geothermal power and lithium carbonate will effectively lower the cost of geothermal power in California, making geothermal energy competitive with other sources of renewable energy.

**Keywords:** *Lithium, geothermal brine, geothermal power, sorbent, solid-phase extraction*

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# EXECUTIVE SUMMARY

## Background

Geothermal energy is an important source of renewable energy in California. In 2018, geothermal energy in the state produced 11,528 gigawatt-hours of electricity, contributing almost 6 percent of the state's total system power.

Expanding geothermal energy production in California will help the state achieve its goals of 60 percent renewable electricity and a 40 percent reduction in greenhouse gas emissions below 1990 levels by 2030. Developing new low-cost processes for the extraction of critical metals from geothermal fluids will greatly benefit the economics of geothermal power production by creating a value stream from the sale of these metals.

Hot geothermal fluids can reach temperatures higher than 482°F (250°C) to 572°F (300°C) and, while in contact with underground rock formations, these fluids can dissolve minerals and metals depending on mineral deposits found in specific geographical areas. After using the heat from the geothermal fluids to produce geothermal power and before reinjecting the fluid, it is possible to extract metals present in the geothermal fluid.

High-temperature geothermal fluids like those found in the Salton Sea Known Geothermal Resource Area are rich in a variety of critical metals, such as lithium, manganese, zinc, and others. Extraction of lithium from brines is of considerable commercial interest. Production of lithium carbonate and lithium hydroxide has increased rapidly over the past few years because of the high demand for lithium batteries used in portable devices, electric vehicles, and electric grid storage. The current price of lithium carbonate is about \$12,000 per ton, and the Salton Sea Known Geothermal Resource Area is capable of producing an estimated 600,000 tons per year of lithium carbonate with a value of \$7.2 billion.

## Project Purpose

Extracting lithium from brines found below the surface of dried lakebeds (known as salar) and from mineral deposits has been the dominant method of producing lithium. High grade lithium compounds are processed mostly by solar evaporation of salar brines in Argentina, Chile, and Bolivia. Lithium is present in very high concentrations in these brines (typically more than 500 milligrams of lithium per liter of brine), and processing costs are low. However, lithium separation from salar brines has several disadvantages. Separation is slow (taking up to 24 months), weather-dependent, and has an extraction efficiency of only about 50 percent. After lithium is concentrated by solar evaporation, it still requires multiple purification steps.

Because geothermal brines often have high concentrations of lithium, they are an attractive source. There is considerable interest in new low-cost technologies for rapid and efficient extraction of lithium from a variety of brines to meet market demand.

The goal of this project was to demonstrate a new low-cost process for the rapid and selective extraction of lithium from geothermal brines using two technologies:

1. A new selective high capacity sorbent (a substance that takes up and holds another substance by either absorption or adsorption) to capture lithium from the brine.
2. A new sorbent regeneration process that releases the lithium from the solid phase.

SRI International's (SRI) sorbent and process should allow the rapid processing of brines and extraction of lithium with high recovery efficiency that requires hours instead of months. The end product of the process is a high purity grade lithium carbonate for use in manufacturing lithium batteries.

The coproduction of geothermal power and lithium carbonate will lower the levelized cost of energy of geothermal power in California, making geothermal energy competitive with other sources of renewable energy.

## **Project Approach**

This project was performed at SRI International's Chemistry and Materials Laboratory. EnergySource and Ormat supported SRI International in an advisory capacity by providing brine samples and technical background information on geothermal fluids, offering expertise on issues relevant to using SRI International's new sorbents in a commercial operation, and assessing capital and operational costs. The project was also supported by California's Imperial Irrigation District in which the Salton Sea Known Geothermal Resource Area is located. Metal recovery has the potential to improve the cost-effectiveness of geothermal energy production and expand economic opportunities in this area.

This project demonstrated the new process of lithium extraction using synthetic and actual brines at the laboratory scale. Initial work was performed on developing methods to prepare hybrid sorbent-containing nanostructured ion sieves and lithium-imprinted polymers. The sorbent was prepared in the form of small beads for use in a packed bed configuration for continuous online processing of the brine. Researchers prepared and evaluated several sorbent formulations for a variety of performance parameters before selecting the most promising one. The research team performed an initial test of the durability of the sorbent running continuous adsorption-regeneration cycles for more than 100 hours.

Based on laboratory results, SRI International designed a process for the production of a 20,000-ton-per-year lithium carbonate equivalent. This plant capacity corresponds to the amount of lithium carbonate equivalent that could be produced by a 50-megawatt geothermal plant operating at a brine flow rate of 6,000 gallons per minute and lithium concentration of 400 milligrams per liter.

## **Project Results**

The project demonstrated that the new hybrid sorbent had high lithium capacity and selectivity for lithium adsorption, even in the presence of high concentrations of sodium, potassium, magnesium, calcium, and other metals. The adsorption of lithium by the sorbent beads was very fast and allowed SRI International to use the sorbent in a packed-bed configuration and efficiently extract lithium even when the brine was passed through the sorbent bed at high flow rates. The project team demonstrated extraction of lithium with efficiency as high as 90 percent under selected conditions. The carbon dioxide regeneration process was found to be efficient, and lithium was stripped from the sorbent as a solution of lithium bicarbonate.

The team designed and set up a computer-controlled system to perform automated multiple adsorption-desorption cycles to test sorbent capacity and performance and determine the stability of the sorbent. Using a geothermal brine, the team detected no significant loss in capacity for repeated lithium adsorption-desorption steps during 100 hours of operation.

This initial demonstration at laboratory scale validates the new sorbent and lithium recovery process. Additional work still needs to be performed to (1) demonstrate sorbent durability over thousands of hours of operation at variable temperatures, and (2) scale-up the process to a skid-mounted system for lithium extraction. Process operation at specific sites will help to identify any brine pre-treatment needed before lithium extraction.

The estimated production cost of lithium carbonate for a 20,000-ton-per-year plant is less than \$4,000 per ton and therefore competitive with that of traditional processes, such as mining and evaporation.

## **Technology/Knowledge Transfer/Market Adoption (Advancing the Research to Market)**

SRI International's lithium-extraction process is based on a patent pending, selective, low-cost, and reusable sorbent processed in the form of microporous beads that allow rapid and selective capture of lithium ions from brines. The sorbent is then regenerated to produce lithium carbonate.

SRI International's technical and business development project staff worked closely to promote outreach of the newly developed process with the public and commercial entities. The team planned public outreach by online dissemination of project information and presenting technical progress to geothermal stakeholders at appropriate scientific meetings.

SRI International's webpage highlighted the project (<https://www.sri.com/work/projects/lithium-recovery-geothermal-operations>).

In 2018, SRI International presented a paper on the technology developed under this contract at the 43rd Workshop on Geothermal Reservoir Engineering at Stanford University held on February 12 – 14. The paper entitled "Selective Recovery of Lithium From Brines" was published online in the workshop proceedings shortly after the workshop ended.

SRI International filed two pending patents that cover the lithium-extraction process technology: "Metal ion extraction from brines" and "Concentrating lithium carbonate after regeneration of lithium sorbent," in 2017 and 2018 respectively.

The lithium-extraction technology was licensed for commercialization to ExSorbition, Inc. which intends to further develop this technology with the demonstration of a skid-mounted system for the extraction of lithium from various brine sources, including geothermal brines.

## **Benefits to California**

The technology will lower the cost of geothermal production by coproducing lithium carbonate from geothermal fluids. It is estimated that the Salton Sea Known Geothermal Resource Area can produce more than 600,000 tons per year of lithium carbonate with a value of \$7.2 billion based on the lithium carbonate price of \$12,000 per ton.

Developing additional geothermal energy sources is an important part of the Imperial Irrigation District's Salton Sea Restoration and Renewable Energy Initiative and will provide environmental benefits to the region, including reduced greenhouse gas emissions. Revenue from the land leases and mineral recovery is expected to support restoration projects, which some sources estimate may cost between \$3 billion and \$9 billion.

Greenhouse gas emission reductions will depend on the extent to which this technology enables the building of new geothermal plants instead of (or to replace) natural gas-fired power plants. A typical geothermal plant emits 7.5 kilograms of greenhouse gases per megawatt-hour, while the carbon dioxide emission rate for the marginal natural gas power plant is 382 kilograms per megawatt-hour.

According to a 2008 feasibility study sponsored by the Imperial Irrigation District, developing geothermal resources could create 7,000 to 9,000 jobs. Many of these jobs are likely to be in communities to the north, east, and south of the Salton Sea—areas that meet the disadvantaged community designation in CalEnviroScreen, a mapping tool that helps identify California communities most affected by sources of pollution and where people are especially vulnerable to pollution effects.

# CHAPTER 1:

## Introduction

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### Background

Expansion of geothermal energy production in California will greatly benefit from the creation of a value stream produced by the recovery of critical metals from geothermal fluids. The efficient separation of metals, such as lithium, from geothermal brines promises to make the production of geothermal power economically favorable, even from low-temperature geothermal fluids. Revenue will be produced from the sale of the marketable metals, and the scaling and re-injection issues associated with high-solid-content brines will be minimized.

Lithium is a high-value metal used in the production of lithium rechargeable batteries, and it is found in low but significant concentrations in geothermal waters (that is, a few hundred milligrams per liter [mg/L]). Because of the very large volume of brine processed in a geothermal power plant (greater than 6,000 gal per min), even low-lithium brines represent a valuable resource. To support the rapid market growth of lithium rechargeable batteries, there is a strong demand for new lithium recovery methods.

Extraction of lithium from brines is currently the dominant method of lithium production because of the higher cost efficiency of extraction compared to processing of mineral deposits. High-grade lithium compounds are mostly processed from salar brines in Argentina, Chile, and Bolivia due to low operation costs. However, lithium separation from salar brines is typically slow (months), since it is based on solar evaporation of the brines in ponds. The lithium then requires multiple purification steps. Solvent extraction processes and solid-phase extraction processes are currently being evaluated for lithium recovery from brines (Neupane & Wendt 2017).

Geothermal fluids can reach temperatures in excess of 482°F (250°C) while in contact with underground rock formations, and they dissolve a variety of natural mineral and metal deposits found in specific geographical areas. The heat content of geothermal fluids is typically used to produce geothermal power. Before reinjection of the fluid, metals present in the geothermal fluid can be isolated by extraction according to an operation that can be envisioned as “liquid mining.” High temperature geothermal fluids like those found in the Salton Sea are rich in a variety of minerals and metals, including sodium, potassium, calcium, potassium, silica, iron, manganese, zinc, lead, and lithium (Neupane & Wendt 2017).

Table 1 shows the typical composition of the hypersaline geothermal fluids from the Imperial Valley Known Geothermal Resource Areas (KGRA).

**Table 1: Typical Geothermal Brine Compositions in the Imperial Valley**

<b>Dissolved solids (mg/L)</b>	<b>Salton Sea</b>	<b>Westmorland</b>	<b>Brawley</b>	<b>Heber</b>	<b>East Mesa</b>
Lithium (Li)	211.00	48.00	100.00	9.50	6.30
Sodium (Na)	52,000.00	10,000.00	22,000.00	4,200.00	2,600.00
Potassium (K)	14,000.00	1,400.00	3,800.00	260.00	190.00
Magnesium (Mg)	160.00	188.00	34.00	5.40	3.40
Calcium (Ca <sub>2+</sub> )	24,000.00	690.00	8,100.00	880.00	130.00
Strontium (Sr)	500.00	-	340.00	53.00	38.00
Barium (Ba)	433.00	-	363.00	3.80	2.20
Arsenic (As)	11.00	-	2.60	0.10	0.16
Boron (B)	350.00	63.00	140.00	14.00	5.40
Copper (Cu)	4.00	0.07	0.11	0.53	0.03
Iron (Fe)	2,300.00	0.30	65.00	22.00	2.20
Manganese (Mn)	1,200.00	2.80	190.00	2.70	0.42
Nickel (Ni)	4.00	-	-	0.03	-
Lead (Pb)	100.00	3.80	1.10	1.90	0.09
Zinc (Zn)	660.00	0.04	14.00	0.83	0.07
Chloride (Cl)	145,000.00	18,000.00	46,000.00	7,900.00	3,900.00
Sulfate (SO <sub>4</sub> )	84.00	57.00	-	99.00	155.00
Bicarbonate (HCO <sub>3</sub> )	140.00	2,900.00	49.00	27.00	490.00
Fluoride (F)	9.00	2.24	-	1.60	2.00

Source: D. Gagne et al., *The Potential for Renewable Energy Development to Benefit Restoration of the Salton Sea: Analysis of Technical and Market Potential* Technical Report NREL/TP-7A4.

Extraction of lithium from geothermal brines from the Salton Sea area is of great interest because their lithium concentrations are as high as 400 mg/L. Furthermore, Salton Sea KGRA geothermal brines contain other salable metals such as manganese, zinc, and potassium.

Geothermal brines have several characteristics that present challenges for any process that aims to recover lithium in an economical fashion:

- Very large volumes of brine are processed. Any lithium recovery process that requires pre-treatment of the brine or chemical modification of the entire brine flow is likely to require large quantities of consumable reagents, which are relatively expensive. Even simple processes like heating or cooling the brines may be costly.

- Brines contain high concentrations of low-value dissolved solids. The recovery process must be highly selective for lithium, without first requiring removal of any by-products such as sodium chloride (NaCl), potassium chloride (KCl), calcium chloride (CaCl<sub>2</sub>), magnesium chloride (MgCl<sub>2</sub>), and others.
- The lithium concentrations are low. The process must be efficient, that is, able to capture lithium down to low parts per million (ppm) concentrations.

Furthermore, the metal extraction process should not alter the chemical characteristics of the geothermal fluid, since it is necessary to reinject it to sustain the geothermal reservoir.

## **Goals and Objectives**

The project objective was to demonstrate a cost-effective, solid-phase extraction process for the recovery of lithium from geothermal brines based on: (1) a new high-capacity selective composite sorbent that uses inorganic lithium-ion sieves and lithium-ion-imprinted polymers; and (2) a new sorbent regeneration process using eco-friendly carbon dioxide to directly form high purity lithium carbonate (Li<sub>2</sub>CO<sub>3</sub>).

To demonstrate the proposed process, SRI used synthetic brines as well as geothermal brines supplied by Ormat Technologies Inc. (Reno, Nevada) and EnergySource LLC (Calipatria, California), two geothermal power companies with operations in California. Mr. Derek Benson from EnergySource LLC, and Mr. Bob Sullivan from Ormat Technologies Inc., also served as the project technology advisors. They helped SRI's technical team to identify the challenges, such as high temperature operation and complex chemical composition, associated with geothermal brines.

# CHAPTER 2:

## Project Approach

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### Project Organization

The project was organized according to the following technical tasks.

#### Task 1. Sorbent Preparation

The objective of this task was to develop synthetic methods for the preparation of hybrid sorbent beads containing an inorganic ion sieve and a lithium-imprinted polymer. As starting material, SRI chose to use spinel lithium manganese oxide as the inorganic ion sieve because of its well-known high lithium uptake capacity and selectivity, and the team combined it with a formulation of lithium-imprinted polymer. The team prepared batches of hybrid sorbent beads of variable composition and screened their properties.

The period of performance of this task was 12 months. A confidential sorbent preparation report was prepared to summarize the work done.

#### Task 2. Sorbent Qualification Test in Lab-Scale Column

The goal of this task was to characterize the adsorption properties of the sorbent prepared in Task 1 by testing the performance of the hybrid sorbent beads in small lab-scale flow-through columns. The team planned to evaluate the sorbent lithium uptake capacity, selectivity, and kinetics of adsorption.

The period of performance of this task was nine months. A confidential test plan and sorbent qualification report were prepared.

#### Task 3. Sorbent Regeneration Testing

The goal of this task was to demonstrate regeneration of the lithiated sorbent with CO<sub>2</sub> (gas). The modality of using carbon dioxide (CO<sub>2</sub>), and various experimental conditions were tested to optimize the regeneration process.

The period of performance of this task was nine months. A confidential test plan and regeneration test reports were prepared at the end of this task.

#### Task 4. Additional Sorbent Preparation

The goal of this task was to prepare additional sorbent to support the second half of the project. The focus was to continue development of new formulations to enhance performance of the hybrid sorbent beads.

This task was performed for nine months. An additional confidential sorbent preparation report was prepared at the end of this task.

#### Task 5. Process Integration and Testing

The goal of this task was to integrate adsorption and regeneration cycles and use automated testing equipment to evaluate the performance of the sorbent upon continued cycling.

This task was conducted over a period of 12 months. A confidential test plan and process integration report were prepared at the end of this task.

### **Task 6. Evaluation of Project Benefits**

The goal of this task was to report anticipated benefits resulting from this project. In particular, SRI planned to report on the targeted market sector and its potential job creation and economic development. The potential for greenhouse gas emission reduction was also to be estimated.

The outcome of this task was summarized in three project benefits questionnaires at the project kick-off meeting, project mid-term, and end of the project.

### **Task 7. Technology Transfer Activities**

The goal of this task was to develop and implement a plan to make the knowledge gained, the experimental results, and the lessons learned available to the public and key decision makers.

A technology/knowledge transfer report was prepared at the end of this task.

### **Task 8. Production Readiness Plan**

The goal of this task was to determine the steps that will lead to the commercialization and manufacturing of the lithium recovery technology developed in this project.

A confidential production readiness plan was prepared at the end of this task.

# CHAPTER 3:

## Project Results

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### Preparation of Sorbents for Selective Extraction of Lithium

Low-cost recovery of lithium from brines demands the use of selective high-capacity reusable sorbents. The goal of this task was to prepare a new advanced sorbent for the selective extraction of lithium from brines containing high concentrations of other metals.

The SRI team prepared a new hybrid sorbent consisting of nanostructured hydrous manganese oxide (HMO) embedded within a lithium-imprinted polymer in the form of porous beads that has demonstrated selective lithium extraction in a continuous solid-phase extraction process. The team chose to use nanostructured HMO to enhance lithium sorption kinetics, and to embed the inorganic sieve into larger beads to enable operational flow-through and solid-phase extraction at high flow rates.

### Inorganic Ion Sieves

Inorganic sorbents, such as aluminum hydroxide, manganese oxide, or titanium oxide are relatively inexpensive, stable over a high-temperature range, and have shown promising properties for the selective adsorption of lithium. The team chose to use HMO because of its high lithium selectivity and ability to remove lithium in the presence of very large concentrations of sodium (Na), potassium (K), calcium (Ca), magnesium (Mg), and other metal ions (Zandevakili, S. et al. 2014; Sun, S.-Y. et al. 2014; Chitrakar, R. et al. 2001; Shi, X. et al. 2011).

The HMO lithium-ion sieves are prepared in a two-step method. First, spinel-type lithium manganese oxide, such as  $\text{Li}_{1.35} \text{Mn}_{1.61} \text{O}_4$ , is prepared. Next, lithium ions ( $\text{Li}^+$ ) are extracted by treatment with an acidic aqueous solution such as hydrochloric acid ( $\text{HCl}[\text{aq}]$ ) so that  $\text{Li}^+$  are replaced by hydrogen ions ( $\text{H}^+$ ) forming the correspondent HMO. The HMO retains the framework of the parent compound and is characterized by pore structures and vacant sites in the spinel phase that are uniquely suited for the insertion and de-insertion of  $\text{Li}^+$  (Shi, X. et al. 2011). The mechanism for the lithium-ion sieve adsorption of  $\text{Li}^+$  can therefore be explained by an ion-exchange process as follows:



The bars refer to the ion species in the adsorbent.

### Hybrid Sorbent Beads

It is highly desirable to prepare HMO nanoparticles to enhance lithium sorption kinetics, but sorbents in the form of nanopowders are not suited for the flow-through separation processes because of large pressure drops in column operations and high-energy consumption. To provide a solution to this problem, the team chose to prepare a hybrid nanocomposite sorbent consisting of nanostructured particles of an inorganic ion sieve embedded into a porous polymer support. Polymers, such as polyvinylchloride (PVC), polyacrylonitrile (PAN), or polyacrylamide (PAM), have been used as binders of micron or sub-micron size ion sieves (Xiao, G. et al., 2012; Xiao, J.-L. et al., 2015). However, these polymers do not have any

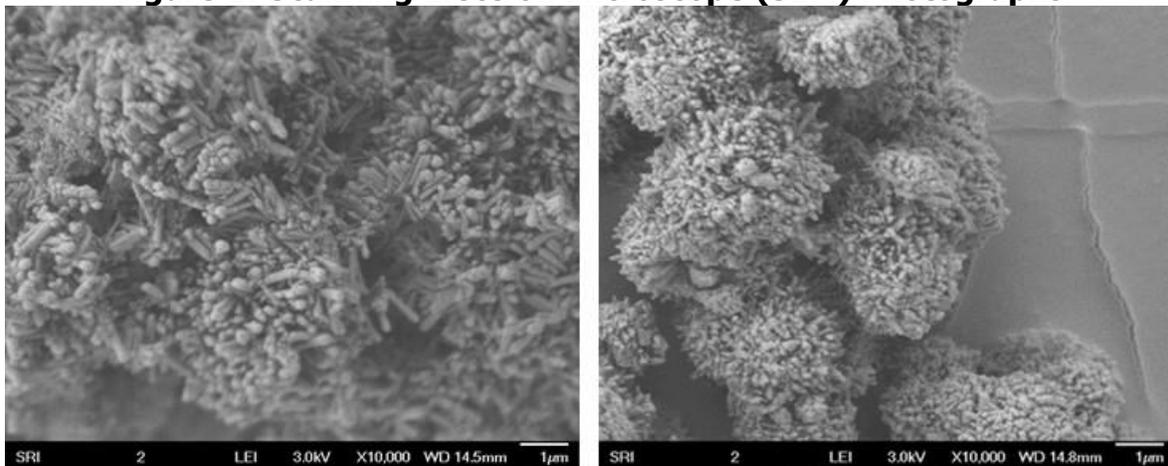
lithium ion transport properties and may end up blocking access to the inorganic lithium adsorbent.

Inorganic ion sieves, such as HMO, have well-known high lithium uptake capacity, while the lithium-imprinted polymer binds  $\text{Li}^+$  and enhances its concentration at the HMO-polymer interface, improving the lithium uptake kinetics.

### Preparation and Characterization of Nanostructured LMO

Nanostructured lithium manganese oxide (LMO) was prepared via hydrothermal synthesis. First, manganese dioxide ( $\text{MnO}_2$ ) is prepared from equimolar amounts of manganese nitrate tetrahydrate [ $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ] and sodium persulfate ( $\text{Na}_2\text{S}_2\text{O}_8$ ) dissolved in deionized water. The aqueous solution is transferred into a stainless-steel autoclave and heated for 12 hours at  $248^\circ\text{F}$  ( $120^\circ\text{C}$ ). The resulting black solid is filtered, washed thoroughly with deionized water, and dried overnight at  $212^\circ\text{F}$  ( $100^\circ\text{C}$ ). Next, the manganese oxide powder is thoroughly mixed with a suitable amount of 0.5 molar (M) lithium nitrate [ $\text{LiNO}_3$  (aq)] in the desired Li/Mn molar ratio. This mixture is then heated in the oven for 12 hours at  $212^\circ\text{F}$  ( $100^\circ\text{C}$ ) to remove water. Finally, the resulting mixture is calcined in a furnace at  $842^\circ\text{F}$  ( $450^\circ\text{C}$ ) for six hours to obtain the LMO nanopowder. The nanostructure of the resulting LMO powder is confirmed by scanning electron microscope (SEM) analysis. The photographs in Figure 1 show the needle-like nanostructure of the LMO that has a width of 100 nm and length less than 1 micron.

**Figure 1: Scanning Electron Microscope (SEM) Photographs**



(a)

(b)

The SEM images above show (a) manganese oxide and (b) lithium manganese oxide.

Source: SRI International

Nanostructured HMO was prepared by stirring the LMO powder in a solution of 0.5 M HCl for a predetermined period of time to exchange the  $\text{Li}^+$  in the inorganic sorbent with  $\text{H}^+$ . The resulting HMO was then filtered and thoroughly washed with water. The lithium uptake capacity of the nanostructured HMO was initially evaluated in a batch test by contacting the inorganic sorbent with a solution containing  $\text{Li}$  360 mg/L,  $\text{Na}$  15000 mg/L and  $\text{K}$  9000 mg/L at  $122^\circ\text{F}$  ( $50^\circ\text{C}$ ) for 30 minutes.

## Synthesis of the Hybrid Nanocomposite Sorbent

Hybrid nanocomposite sorbent beads were prepared by suspension and radical polymerization of the lithiated monomer with a crosslinking agent in the presence of LMO powder. Once the polymerization was completed, the hybrid sorbent beads were collected by filtration, washed, and dried. Sorbent beads typically had a diameter greater than 250 microns. The sorbent beads were treated with an acidic solution to extract lithium, before they were tested for their lithium extraction properties.

Hybrid sorbent beads with different compositions were prepared. The composition of the lithium-imprinted polymer and the ratio of the inorganic ion sieve versus lithium-imprinted polymer were varied. The resulting hybrid sorbent beads were evaluated for their physical and chemical properties, and then for their ability to extract lithium from brines.

During the program, SRI developed two main hybrid sorbent formulations. The second-generation sorbent beads, prepared using a simplified synthetic procedure, were found to have enhanced lithium capacity. For both sorbent formulations SRI demonstrated that the sorbent beads can be reproducibly prepared at the lab scale in tens of gram quantities.

## Lithium Extraction Tests

The goal of this task was to perform an initial evaluation of the newly prepared hybrid sorbent beads and assess their lithium extraction properties.

The hybrid sorbent beads were tested in a fixed-bed configuration to determine its capacity and selectivity. Initial tests were performed using an aqueous solution of hydrochloric acid to regenerate the sorbent.

In these experiments, a lithium-containing brine is fed into a column of sorbent, and the composition of the exiting brine is measured as a function of time, until the exit composition matches the feed composition. Taking into consideration the fact that the composition of geothermal brines can vary widely depending on the source reservoir, SRI tested the sorbent performance at various temperatures, pH values, and concentrations of competing metals using synthetic brines. Synthetic brines were prepared using the specified metal chlorides. The pH values of the brines were controlled using buffer solutions from pH 5 up to pH 7.

The sorbent beads were suspended in water and loaded into a jacketed column with a diameter of 1 centimeter (cm) and height of 30 cm. The actual height of the packed bed depended on the amount of sorbent loaded. The column temperature was controlled by circulating water at a constant temperature through the column jacket. The brine flow rate was controlled by a constant-displacement pump.

The outlet solution was collected in consecutive fractions, and each fraction was analyzed for its lithium concentration using ion-exchange chromatography. After the adsorption was complete, the sorbent was regenerated using an aqueous solution of hydrochloric acid. The regenerated solution was collected and analyzed for total lithium content to provide a measurement of lithium capacity.

The lithium separation coefficients were calculated as follows:

$$\alpha_{Li/M} = Q_{Li}/C_{Li} * C_M / Q_M$$

Where  $Q_{Li}$  and  $Q_M$  represent the concentration of lithium and a generic metal ion M in the regeneration solution (mg Li or M /L regeneration solution), and  $C_{Li}$  and  $C_{Me}$  are the concentrations of lithium and metal ion M in the brine (mg Li or M/L brine) tested.

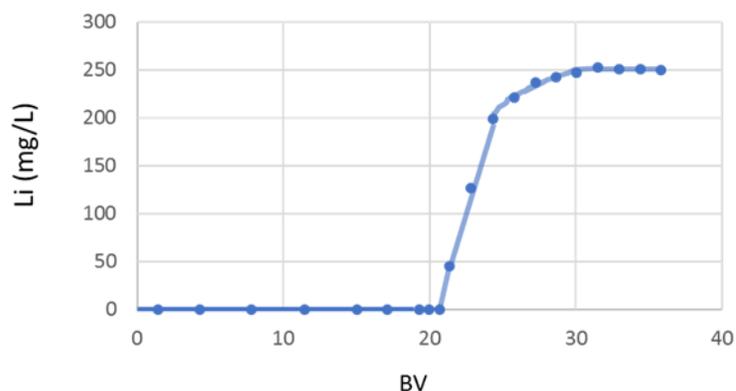
The concentrations of lithium ion and other metal ions in the aqueous solutions were tested by ion-exchange chromatography.

### Lithium Adsorption Capacity and Selectivity Using Synthetic Brines

The hybrid sorbent generation was tested for its lithium adsorption and selectivity under variable conditions, including pH, composition, and temperature.

In a typical experiment, the hybrid nanocomposite fixed bed was tested for its adsorption of  $Li^+$  from a synthetic brine containing 255 ppm Li, 10,570 ppm Na, and 10,400 ppm of K in a pH 6 sodium phosphate buffer solution at 50°C. The brine was passed through the column at a flow rate of 27 BV per hour (in which BV is the bed volume defined as  $BV = L\pi r^2$  with L equal to the length of the sorbent packed bed and r is the radius of the column), and the exiting brine was collected in small fractions. The lithium content of each fraction was measured, and the adsorption experiment was continued until the sorbent was saturated and the exiting brine had the same lithium content as the feed. The sharp breakthrough adsorption curve (Figure 2) indicates that the lithium uptake is fast.

**Figure 2: Breakthrough Curve of  $Li^+$**



The graph above shows data from a fixed column packed with hybrid nanocomposite sorbent. The brine's tested composition was: 255 ppm Li, 10,570 ppm Na and 10,400 ppm of K in a pH 6 0.4 M sodium phosphate buffer solution (T= 70°C, flow rate 27 BV/hr).

Source: SRI International

The lithium capacity and selectivity in the presence of high concentrations of Na and K ion are shown in Table 2. The lithium capacity is calculated from the amount of the lithium released by treatment with 0.5 M HCl, after the sorbent was saturated with lithium.

**Table 2: Sorbent Lithium Capacity and Selectivity in Synthetic Brines at Variable pH**

pH	Li brine conc. (mg/L)	Na brine conc. (mg/L)	K brine conc. (mg/L)	Mg brine conc. (mg/L)	Ca brine conc. (mg/L)	Li capacity (mg Li/g sorbent)	Sep. coeff. $\alpha_{Li/Na}$	Sep. coeff. $\alpha_{Li/K}$	Sep. coeff. $\alpha_{Li/Mg}$	Sep. coeff. $\alpha_{Li/Ca}$
7.2	250	17134	10749	-	-	16.2	323	107	-	-
6	255	10570	10400	-	-	14.2	211	77	-	-
5	242	10059	-	964	9250	10.8	198	-	High *	71

Experimental conditions: flow rate 27BV/hr, temperature 70°C. (\*) no Mg uptake was detected.

Source: SRI International

The binding capacity of Mg from synthetic brines containing 964 mg/L of Mg<sup>2+</sup> was found to be negligible, with no detected Mg uptake under the experimental conditions summarized in Table 2; therefore, the team could not reliably calculate an actual separation coefficient.

The three synthetic brines in Table 2 were prepared from buffer solutions to simulate the pH of geothermal brines. Sodium phosphate solutions were used for the pH 7.2 and 6 buffers, while an acetic acid/sodium acetate solution was used for the pH 5 buffer. The sorbent lithium capacity for all three brines was greater than 10 mg Li/g sorbent, and as high as 16.2 mg Li/g sorbent for the brine at pH 7.2.

Higher lithium separation coefficients were obtained for the second-generation sorbent. Adsorption tests were performed by varying the adsorption temperature and using a synthetic brine at pH 5 that contained concentrations of Li, Na, K, and Ca comparable to those found in California’s Salton Sea geothermal brines (Table 3). Thus, the brine tested contained 377 mg/L of Li, 57,777 mg/L of Na, 14,448 mg/L of K, and 26,766 mg/L of Ca. Even in the presence of a high concentration of other metal ions, the sorbent lithium capacity was greater than 11mg Li/g sorbent at 158°F (70°C) with a Li separation coefficient of 3,855 compared to Na, 211 compared to K, and 119 compared to Ca. When the adsorption process was conducted at 122°F (50°C) and 86°F (30°C), the lithium capacity of the sorbent was still greater than 10 mg Li/g sorbent with high selectivity.

**Table 3: Sorbent Lithium Capacity and Separation Coefficient in Complex Simulated Brine**

T (°C)	Li capacity (mg Li/g sorbent)	Li Separation Coefficient	Li Separation Coefficient	Li Separation Coefficient
		$\alpha_{Li/Na}$	$\alpha_{Li/K}$	$\alpha_{Li/Ca}$
70	11.25	3855	211	119
50	10.12	3876	185	109
30	10.16	1351	164	136

Brine composition: Li 377 mg/L, Na 57777 mg/L, K 14448 mg/L, Ca 26766 mg/L. Experimental conditions: flow rate 30 BV/hr, pH 5

Source: SRI International

## Sorbent Regeneration Tests

Regeneration tests were performed on sorbent beads that had been loaded with lithium during an adsorption test. Before regeneration, the loaded sorbent was washed with water to remove the brine surrounding the sorbent beads.

The regeneration temperature was controlled by circulating water from a constant temperature bath, through the column jacket. Regeneration tests were performed as a function of column temperature and applied CO<sub>2</sub> pressure. The regeneration solution was collected in fractions and analyzed by ion chromatography for lithium and other metals.

The loading of lithium in the sorbent was fixed by saturating the sorbent using a brine containing 406 mg/L of lithium, 16,218 mg/L of sodium, and 10,705 mg/L of potassium. The flow rate of regeneration solution was fixed, and the regeneration temperature and the CO<sub>2</sub> pressure were varied.

After testing sorbent regeneration at three different temperatures and three CO<sub>2</sub> pressures, the team selected the experimental conditions that provided the highest sorbent regeneration capacity.

The CO<sub>2</sub> regeneration process was found to be efficient in desorbing lithium from the sorbent beads without causing dissolution of manganese from the LMO spinel. This is an important aspect of the regeneration technology since it is well known that manganese readily dissolves in contact with HCl(aq), thus limiting its usefulness as a regenerating solution.

## **Integrated Lithium Adsorption/Regeneration Tests**

The object of the process integration task was to demonstrate recovery of lithium from a geothermal brine using SRI's newly developed sorbent and provide system performance data.

Initial experiments were conducted by performing adsorption/regeneration cycles on two different sorbents in 1-cm diameter columns. Synthetic and actual geothermal brines were used for these tests. The composition of the synthetic geothermal brine is listed in Table 4.

**Table 4: Composition of Synthetic Brine Tested**

<b>Cation</b>	<b>mg/L</b>
Li	397
Na	66700
K	15400
Ca	23500
Sr	129
Ba	718

Source: SRI International

The pH of the synthetic geothermal brine was buffered at 5.5 by addition of acetic acid/sodium acetate.

The actual geothermal brine was pre-treated to remove iron-silicates and other heavy metals known to be present in these brines. The as-received geothermal brine sample had a pH of approximately 2. The brine was acidified to ensure that no precipitate would separate from the liquid phase at room temperature during shipment. For the pre-treatment, the team added sodium hydroxide [NaOH(aq)] to the brine and raised the pH to about 8 – 9 before filtering the solid formed. The filtrate fluid was clear and was found to contain Li (319 mg/L), Na (77,173 mg/L), K (27,409 mg/g), Ca (42,831 mg/g), and strontium (Sr) (694 mg/L) as indicated in Table 5. Figure 3 shows a sample of the geothermal brines as received and after the pre-treatment

An X-ray fluorescence analysis of the precipitate showed it contained aluminum, manganese, iron, and zinc, along with small quantities of magnesium and calcium.

**Table 5: Composition of Geothermal Brine After Pre-Treatment**

Cation	mg/L
Li	319
Na	77173
K	27409
Ca	42831
Sr	694

Source: SRI International

**Figure 3: Geothermal Brines as Received (left) and After Pre-treatment (right)**

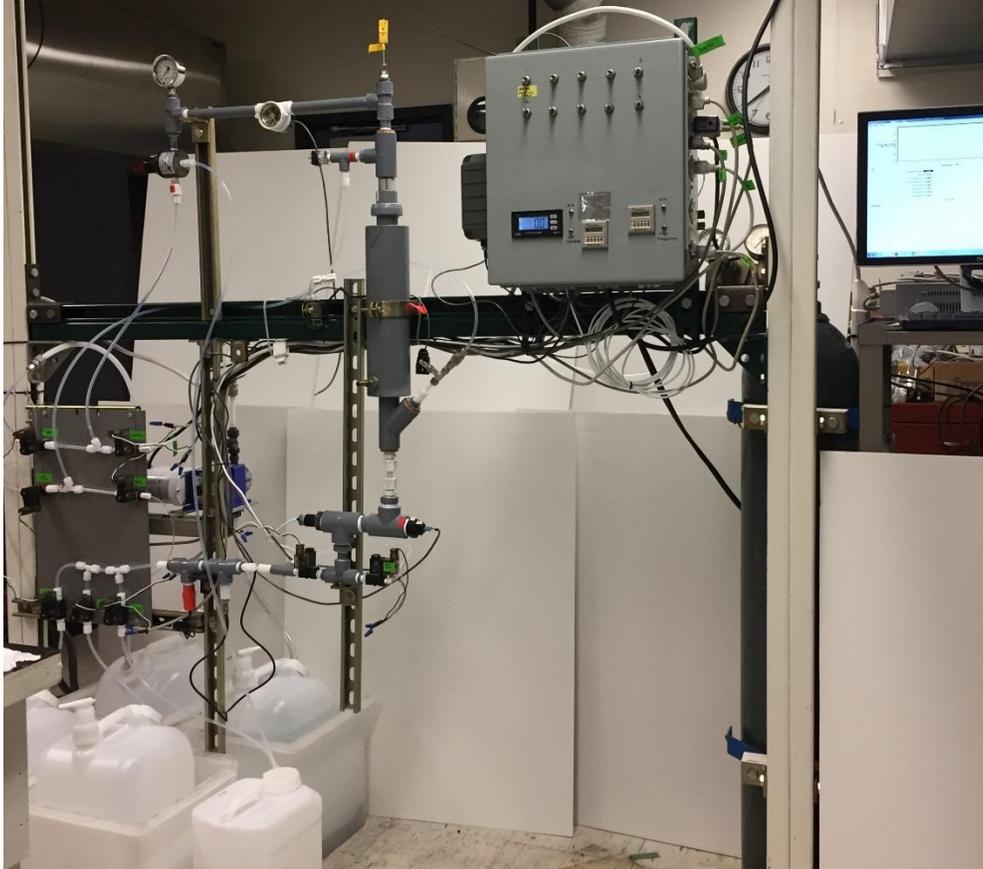


Source: SRI International

The two different sorbents were tested for their adsorption/desorption performance at 122°F (50°C) and 158°F (70°C) in a 1-cm diameter column. The sorbent with the highest working capacity and lithium extraction efficiency was selected to perform multiple cycles of adsorption and desorption in a 1-inch diameter column.

A computer-controlled integrated system (Figure 4) was designed and set up to perform automated multiple adsorption/desorption cycles to test sorbent capacity and performance and determine the stability of the sorbent. The main purpose of these experiments was to determine any loss in capacity for repeated adsorption/desorption steps.

**Figure 4: Computer-Controlled Automated System to Test Lithium Extraction From Brines**



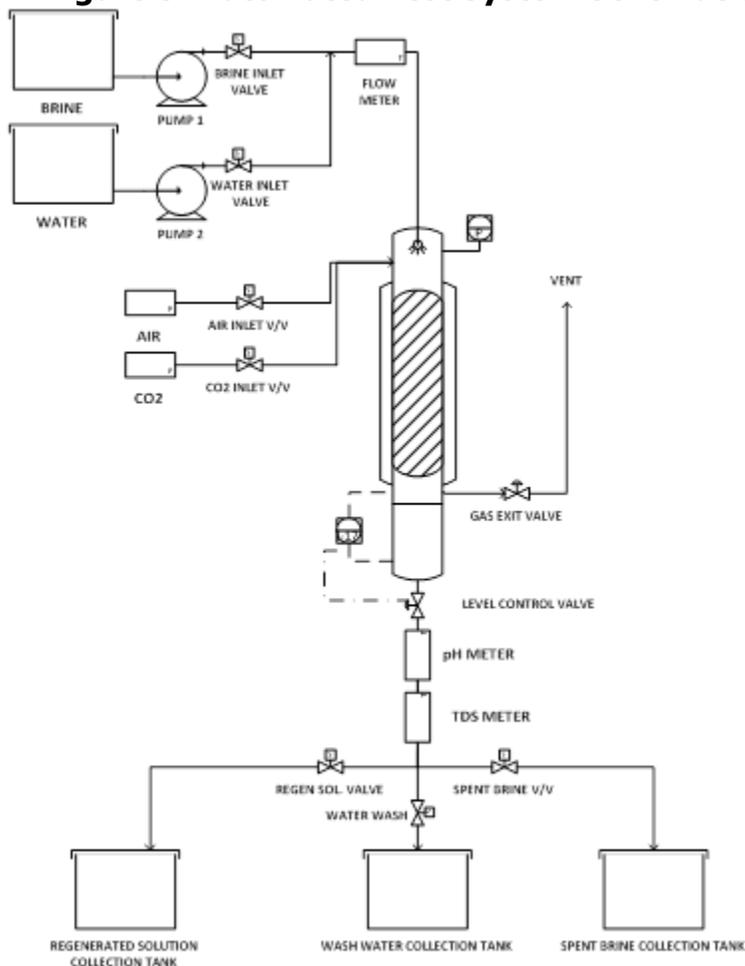
Source: SRI International

A synthetic geothermal brine and an actual geothermal brine received from EnergySource were used to test the integrated system.

Another filtration through a 20-micron filter was carried out before testing lithium adsorption. The automated integrated test setup (Figure 5) was comprised of a column with a 1-inch diameter and a jacket to maintain sorbent temperature by circulating hot and cold fluid. The jacketed sorbent column was designed to test the brine at a pre-set temperature. The test protocol involved passing the brine at 27 BV/hour through the column for 15 minutes (adsorption step), followed by a water wash for 10 minutes. The regeneration step involved passing deionized water through the column at 34 BV/hour.

Diaphragm pumps with compatible wetted materials were used to circulate fluids in the system. Spent brine, the water wash, and regenerated solutions were separately collected for measurement, analysis, and post-processing. Solenoid valves were used to control the flow streams during automated operation.

**Figure 5: Automated Test System Schematic**



Source: SRI International

A computer-based data acquisition and process control program was set up to operate the automated system. The following data were collected:

- Liquid flow rate
- Column pressure
- Inlet stream temperature
- Outlet stream temperature
- pH of exit stream
- Total dissolved solids (TDS) of exit stream

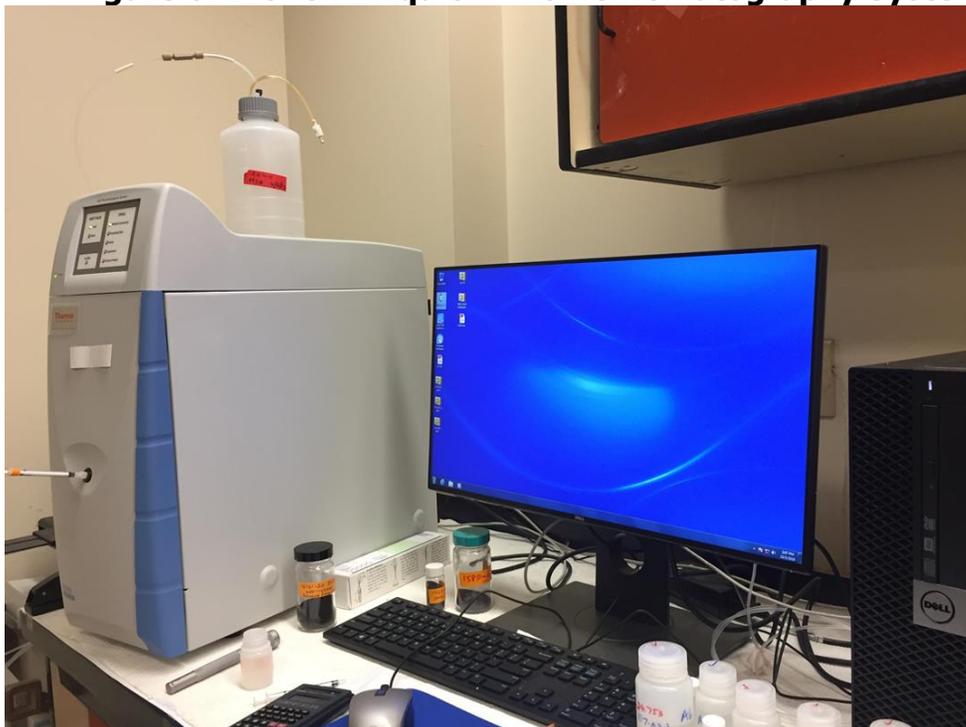
As noted earlier, brine was pumped to the reactor using a diaphragm pump with a set flow rate for 15 minutes. The solenoid valves were controlled such that a slight air pressure was applied during the adsorption step, and the spent brine was collected in the spent brine tank. The pH was recorded during the adsorption step to monitor change in pH as lithium was adsorbed onto the sorbent and H<sup>+</sup> was released.

A TDS meter was used in the exit stream during the water-wash step. Based on the data collected during testing, TDS is a good indicator for the completion of the wash step. The water-wash step removes contaminants from the surface of the sorbent before regeneration.

The regeneration of the sorbent was carried out using water and a positive pressure of CO<sub>2</sub>. The TDS of the exit stream indicates completion of the regeneration step as the amount of lithium desorbed from the sorbent progressively decreases.

Eluate samples were collected during adsorption and the wash and regeneration steps to monitor the actual lithium concentration, and those of other metals present in the exit stream. A Dionex™ Aquion™ ion chromatography system from Thermo Fisher (Figure 6) was used for the analysis of lithium and other metal cations with a concentration down to a few mg/L.

**Figure 6: Dionex™ Aquion™ Ion Chromatography System**



Source: SRI International

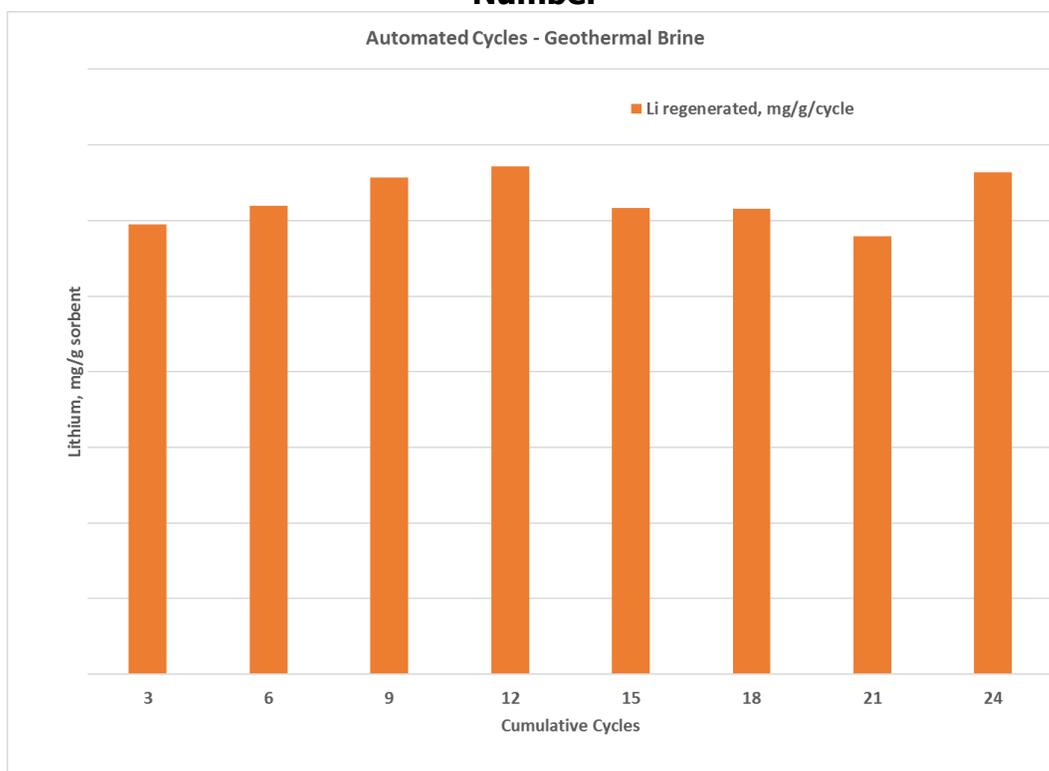
The instrument was periodically calibrated to maintain its accuracy and sensitivity.

Based on the metal ion analysis and the amount of fluid collected at each step, the team determined the amount of lithium captured and regenerated, along with any other metal ion species present in solution.

The sorbent was first cycled 25 times through a sequence of adsorption/wash/regeneration steps using the synthetic brine (Table 4). Then the pre-treated geothermal brine (Table 5) was cycled through the sorbent bed for an additional 24 cycles. The spent brine, wash water, and regenerated solution were collected over three cycles before analyzing the average ionic composition.

The adsorption and regeneration times for each test cycle were adjusted to a fixed value. Figure 7 shows the lithium working capacity after sorbent regeneration as an average over three consecutive cycles. Following the 24-cycle adsorption/desorption test using the pre-treated geothermal brine, the sorbent performance was stable and showed only minor capacity variation (less than +/- 10 percent), thus supporting its promising durability under repeated cycling.

**Figure 7: Lithium Working Capacity of the Sorbent as a Function of the Cycle Number**



Source: SRI International

Because the sorbent cost is expected to be a significant part of the operating cost in a commercial-scale plant, these initial cycling data support the commercial viability of the separation process.

Furthermore, lithium was collected as lithium bicarbonate at the end of the regeneration step. This solution can be further processed to isolate high purity lithium carbonate.

# **CHAPTER 4:**

## **Technology/Knowledge/Market Transfer**

### **Activities**

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#### **Process Benefits**

SRI's lithium-extraction technology will lower the cost of geothermal production by co-producing lithium carbonate from geothermal fluids. Revenue will be produced from the sale of the metal, and the scaling and re-injection issues associated with high-solid-content brines will be minimized. The efficient separation of metals from geothermal brines promises to make the production of geothermal power economically favorable, even from lower-temperature geothermal fluids. Demand for lithium is fueled by the growing market for lithium batteries used in electric vehicles and the current price of lithium carbonate, which is about \$12,000 per ton. The Salton Sea Known Geothermal Resource Area is thought to be capable of producing more than 600,000 tons per year of lithium carbonate (Besseling, E. 2018) corresponding to a value of \$7.2 billion.

Furthermore, developing additional geothermal energy sources is an important part of the Imperial Irrigation District's (IID) Salton Sea Restoration and Renewable Energy Initiative, which will provide environmental benefits to the region, including reduced greenhouse gas air emissions which may benefit the health of people in affected zones. In addition, projects sited on exposed lakebeds will produce renewable energy and provide groundcover that will also help mitigate harmful air emissions (<http://www.iid.com/energy/salton-sea-initiative>). Revenue from the land leases and mineral recovery is expected to support restoration projects, which some sources estimate may cost about \$3 to \$9 billion (California Energy Commission, Public Interest Energy Research 2014 Annual Report, March 2015, p.B4).

This technology enables new geothermal plants to be built and natural gas-fired power plants to be replaced, which will also reduce greenhouse gas emissions. The 2010 weighted average CO<sub>2</sub> emission of California geothermal power plants was 180 pounds per MWh, whereas according to the EPA, the average rate of CO<sub>2</sub> emissions for natural gas power plants was 1,135 pounds per MWh (Holm, A et al. 2012). In geothermal power plants, CO<sub>2</sub> is not a product of combustion but is a minor natural constituent of the geothermal reservoirs.

If lithium-recovery-enabled geothermal plants are built and displace electricity generated by natural gas, an average of 955 pounds of CO<sub>2</sub> emissions per MWh of power could be avoided or eliminated.

According to a 2008 feasibility study sponsored by the IID, developing geothermal resources could result in the creation of some 7,000 to 9,000 jobs, many of which would likely be higher paying than typical jobs in the county (Renewable Energy Feasibility Study Final Report, 2008). Many of these jobs are likely to be in communities to the north, east, and south of the Salton Sea, areas that meet the CalEnviroScreen designation as disadvantaged communities.

## Market Transfer Activities

SRI's lithium-extraction process is based on a patent pending, selective, low-cost, and reusable sorbent processed in the form of microporous beads that allows rapid and selective capture of lithium ions from brines. The sorbent is then regenerated to produce lithium carbonate.

SRI's technical and business development project staff worked closely to promote outreach of the newly developed process with the public and commercial entities. Public outreach was planned by online dissemination of project information and by presenting technical progress to geothermal stakeholders at appropriate scientific meetings.

The project was highlighted on SRI's webpage: <https://www.sri.com/work/projects/lithium-recovery-geothermal-operations>.

In 2018, SRI presented a paper on the technology developed under this contract at the 43rd Workshop on Geothermal Reservoir Engineering at Stanford University held on February 12 – 14. The paper, entitled "Selective Recovery of Lithium From Brines," was published online in the workshop proceedings shortly after the workshop ended.

SRI filed two pending patents that cover the lithium-extraction process technology.

1. "Metal ion extraction from brines," WO 2018035463, was filed on August 18, 2017. The disclosure describes hybrid sorbent beads for the selective extraction of lithium from brines prepared from nanostructured ion sieves and lithium-imprinted polymers. A process to regenerate the sorbent by direct treatment with CO<sub>2</sub>(gas) is also described.
2. "Concentrating lithium carbonate after regeneration of lithium sorbent" was filed on December 21, 2018. The disclosure describes systems and techniques for selectively extracting metal ions from metal-containing liquid media, such as geothermal brine. Methods to concentrate lithium bicarbonate solutions and enable the production of high-purity lithium carbonate are described.

For SRI's lithium-extraction process to be successful, it should be scalable to a commercial-scale plant and generate profit after accounting for all expenses and investments. ASPEN™ software was used to model the process based on data obtained from lab-scale adsorption/regeneration experiments and assumptions for polishing and concentrating lithium in subsystems. The process was scaled to produce 20,000 tons per year of lithium carbonate equivalent. Major equipment sizes were determined from the model, and the cost of equipment was estimated based on data available from various websites and literature. The Chemical Engineer's Plant Cost Index (CEPCI) was used to update the estimated equipment costs where applicable.

In addition to the capital expenditure (CAPEX) for acquiring the equipment, various other factors required for setting up a commercial scale production facility were taken in account based on accepted industry practices and included in the cost estimates. Factors like equipment installation costs, piping and interconnects, instrumentation and controls, electrical services, and others, are included in the cost estimates along with engineering design costs, supervision costs, and legal and contractual costs. Utilities like electricity, process water, steam, waste treatment, and consumables were estimated based on the process information, and costs were estimated based on industry practices for such utilities. In addition, operating labor costs were taken in account using published information on similar processes to estimate

the operating expenses (OPEX) for the large-scale production facilities. The cost of sorbent was estimated on the process successfully demonstrated at the lab-scale and based on production-scale efficiency.

Table 6 below summarizes the estimated CAPEX and OPEX of a 20,000-ton-per-year plant for a brine containing 400 mg/L of lithium.

**Table 6. Project Costs**

<b>Costs</b>	<b>20,000 MTA</b>
Bare equipment cost	\$8.5 M
CAPEX	\$52.3 M
OPEX	\$76.9 M
Revenue @ \$12,000/ton lithium carbonate equivalent (LCE)	\$240 M

Source: SRI International

SRI’s estimated cost of production of lithium carbonate is less than \$4,000 per ton and therefore competitive with that of traditional processes such as mining and evaporation. (Besseling E. 2018). The estimated payback of SRI’s process is less than one year, thus more favorable than mining or evaporation whose CAPEX is typically several hundred million dollars.

Based on available online information, ExSorbition, Inc. made an initial contact with the project’s principal investigator, and a collaboration between the two companies was established. SRI exclusively licensed the technology to ExSorbition, Inc., which is currently pursuing commercial development of the technology. The company intends to further develop this technology with the demonstration of a skid-mounted system for the extraction of lithium from various brine sources, including geothermal brines.

## **CHAPTER 5:**

# **Conclusions/Recommendations**

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SRI has demonstrated a new solid-phase extraction process to capture lithium from geothermal brines. This technology has the potential to lower the cost of geothermal production and expand the market for geothermal energy by co-producing lithium carbonate from geothermal fluids.

The process is based on (1) a new hybrid sorbent made from nanostructured inorganic ion sieves embedded into a lithium-imprinted polymer, and (2) a sorbent regeneration process that uses eco-friendly carbon dioxide to form lithium carbonate. The sorbent was prepared in the form of beads that were tested in a flow-through column to demonstrate their high lithium uptake capacity and good selectivity for lithium capture even in the presence of high concentrations of other metal ions, such as sodium, potassium, magnesium, and calcium. The sorbent beads loaded with lithium were regenerated with the use of CO<sub>2</sub> to produce an aqueous stream containing primarily lithium bicarbonate. The regenerated stream can be further polished and concentrated to produce high-purity lithium carbonate using a combination of industrially developed and commercially available technologies like ion-exchange, membrane-based separation, and crystallization.

SRI demonstrated multiple lithium adsorption-desorption cycles of the sorbent using a pre-treated geothermal brine in automated system. The working capacity of the sorbent was found to be stable, thus providing an initial validation of the sorbent durability.

Based on the process design, a commercial-scale plant with 20,000 ton/year production of lithium-carbonate equivalent (LCE) was designed to demonstrate process economics including CAPEX and OPEX. The estimated cost of production of lithium carbonate is less than \$4,000 per ton, with a projected CAPEX of \$52.3 M, OPEX of \$76.9 M and revenue of \$240 M for a price of \$12,000 per ton of lithium carbonate.

SRI technology is expected to lower the cost of geothermal production by co-producing lithium carbonate from geothermal fluids. Demand for lithium is fueled by the growing market of lithium batteries for electric vehicles and the current price of lithium carbonate, which is about \$12,000 per ton. It is estimated that the Salton Sea Known Geothermal Resource Area is capable of producing more than 600,000 tons per year of lithium carbonate, corresponding to a value of \$7.2 billion. To the extent this technology enables new geothermal plants to be built instead of, or to replace, natural-gas-fired power plants, greenhouse gas emissions will be avoided.

Furthermore, developing additional geothermal energy sources will bring additional jobs to the Imperial Irrigation District and provide needed revenues to enable environmental restoration projects of the dry lakebed.

## **CHAPTER 6:**

# **Benefits to Ratepayers**

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Geothermal energy is an important source of renewable energy in California. In 2018, geothermal energy in the state produced 11,528 gigawatt hours (GWh) of electricity, contributing to almost 6 percent of the state's total system power. Geothermal energy provides reliable baseload power and frequency-response features that stabilize the grid.

It is desirable to expand geothermal energy production in California to help the state achieve the goals of 60 percent renewable electricity and a 40 percent reduction in greenhouse gas emissions below 1990 levels by 2030. Combining geothermal power production with the production of lithium carbonate and other salable minerals extracted from the geothermal fluid is expected to bring down the cost of geothermal energy production and make it competitive with other renewable energy sources.

A 50-MW geothermal plant in the Salton Sea area can produce up to 20,000 metric tons of LCE per year. Considering that the geothermal fluid contains lithium in concentrations as high as 400 mg/L, transitioning at a volumetric flow rate of more than 6,000 gal/min, and assuming a recovery efficiency of 90 percent, more than 20,000 metric tons of LCE per year can be produced from the geothermal fluid for a value of about \$168M based on \$12,000 per LCE metric ton.

It is estimated the Salton Sea Known Geothermal Resource Area is capable of producing more than 600,000 tons per year of lithium carbonate, which corresponds to a potential value of \$7.2 billion.

Furthermore, geothermal power plants can contribute to reducing greenhouse gas emissions. The greenhouse gas emissions of geothermal power plants are on average 180 pounds of carbon dioxide per MWh of electricity, which is less than 8 percent of that produced by conventional coal-fired power plants. Geothermal power also helps stabilize the electric grid by providing reliable power and ancillary services.

Developing additional geothermal energy sources with mineral co-production is an important part of the IID's Salton Sea Restoration and Renewable Energy Initiative, which aims to provide environmental benefits to the region, including reduced air emissions. Projects sited on exposed lakebed will produce renewable energy and provide groundcover to mitigate air emissions. Revenue from the land leases and mineral recovery is expected to support restoration projects, which some sources estimate may cost about \$3 to \$9 billion.

According to a 2008 feasibility study sponsored by the IID, developing geothermal resources could result in creation of some 7,000 to 9,000 jobs, many of which would likely be higher paying than typical jobs in the county.

## LIST OF ACRONYMS

Term	Definition
BV	bed volume
CAPEX	capital expenditure
CEPCI	chemical engineer's plant cost index
DI	deionized
EPIC	electric program investment charge
GWh	gigawatt hour
HMO	hydrous manganese oxide
IID	Imperial Irrigation District
KGRA	known geothermal resource area
LCOE	levelized cost of energy
LCE	lithium carbonate equivalent
LMO	lithium manganese oxide
MWh	megawatt hour
OPEX	operating expense
PAM	polyacrylamide
PAN	polyacrylonitrile
PVC	polyvinylchloride
SEM	scanning electron microscope
SRI	SRI International
TDS	total dissolved solids

## REFERENCES

- California Energy Commission, Public Interest Energy Research 2014 Annual Report, March 2015, p. B4. <https://www.energy.ca.gov/2015publications/CEC-500-2015-009/CEC-500-2015-009-CMF.pdf>
- Chitrakar, R., Kanoh H., Miyai, Y., and Ooi, K., 2001, "Recovery of Lithium from Sea Water using Manganese Oxide Adsorbent ( $\text{H}_{1.6} \text{Mn}_{1.6} \text{O}_4$ ) Derived from  $\text{Li}_{1.6} \text{Mn}_{1.6} \text{O}_4$ ", Ind. Eng. Chem. Res., 40, 2054.
- Eric Besseling, "Lithium Recovery from Geothermal Brines", CEC Workshop, Nov 2018.
- Holm, A., Jennejohn, D. and Blodgett, L., "Geothermal Energy and Greenhouse Gas Emissions", [http://geo-energy.org/reports/GeothermalGreenhouseEmissionsNov2012GEA\\_web.pdf](http://geo-energy.org/reports/GeothermalGreenhouseEmissionsNov2012GEA_web.pdf)
- Neupane, G. and Wendt, D.S., 2017, "Assessment of Mineral Resources in Geothermal Brines in the US", Proceedings 42nd Workshop in Geothermal Resources Engineering, Stanford, CA.  
[https://www.researchgate.net/publication/313904235\\_Assessment\\_of\\_Mineral\\_Resources\\_in\\_Geothermal\\_Brines\\_in\\_the\\_US](https://www.researchgate.net/publication/313904235_Assessment_of_Mineral_Resources_in_Geothermal_Brines_in_the_US)
- Renewable Energy Feasibility Study Final Report, April 1, 2008, prepared by Summit Blue Consulting, LLC for the Imperial Irrigation District
- Salton Sea Revenue Potential Study, Final, December 10, 2013, prepared by EES Consulting for the Imperial Irrigation District, p. 10.  
<https://www.iid.com/home/showdocument?id=8464>
- Salton Sea Restoration and Renewable Energy Initiative. <http://www.iid.com/energy/salton-sea-initiative>
- Shi, X., Zhao, D., Zhang, Z., Yu, L., Xu, H., Chen, B., and Yang, X., 2011, "Synthesis and Properties of  $\text{Li}_{1.6} \text{Mn}_{1.6} \text{O}_4$  and its adsorption application", Hydrometallurgy, 110, 99-106.
- Sun, S.-Y., Xiao, J.-L., Wang, J. Song X., and Yu, J.-G., 2014, "Synthesis and Adsorption Properties of  $\text{Li}_{1.6} \text{Mn}_{1.6} \text{O}_4$  by a Combination of Redox precipitation and Solid-Phase", Ind. Eng. Chem. Res., 29, 15517-15521.
- Xiao, G., Tong, K., Zhao, L., Xiao, J., Sun, S., Li, P., and Yu J., 2012, "Adsorption and Desorption Behavior of Lithium Spherical PVC- $\text{MnO}_2$  Ion Sieve", Ind. Eng. Chem. Res., 51, 10921-10929.
- Xiao, J.-L., Sun, S.-Y., Zhao, L., Song, X., Li, P., and Yu J., 2015 "Lithium Ion Recovery from Brines using Granulated Polyacrylamide- $\text{MnO}_2$  sieve", Chem. Eng. J., 279, (2015), 659-666.

Zandevakili, S., Ranjibar, M., and Ehteshamzadeh, M., 2014, "Recovery of Lithium from Urmia Lake by Nanostructured MnO<sub>2</sub> Sieve", *Hydrometallurgy*, 149, 148-152.