Technologies for Extracting Valuable Metals and Compounds from Geothermal Fluids

---

Final Report for Department of Energy Geothermal Technologies Program
Grant DE-EE0002790

April, 2014

Principal Investigator: Dr. Stephen Harrison, Simbol Materials

6920 Koll Center Parkway, Suite 216

Pleasanton, CA 94510

Acknowledgements

Simbol Materials would like to acknowledge funding for this research from Mohr Davidow, Firelake Capital Management and Itochu Corporation, and the Dept. of Energy Geothermal Technologies Program under Grant DE-EE0002790. Simbol would also like to thank its many team members in Simbol’s Calipatria, Brawley and Pleasanton, CA facilities.

Simbol Materials would like specifically to acknowledge Dr. Carol Bruton, Dr. Brian Viani, Sue Martin M. Scott Conley and Luka Erceg both as founders of the company and for their contributions to the research, development and project management.

Simbol Materials would also like to specifically recognize the work of the development teams that developed the sorbent technologies without which lithium extraction would not be possible in these brines.

Dr. Khalil Amine, Huiming Wu and Mark Ziffer of Argonne National Laboratory conducted the research that formed the basis of the section titled “Geothermal Lithium Carbonate as Precursor in the Manufacture of Lithium-ion Cathode Materials” under a Work for Others agreement with Simbol Materials.

Dr. Jacqueline R. Houston of California State University Sacramento conducted the research that formed the basis of the section titled “Potassium Extraction from Geothermal Brines” under a Research Agreement between Simbol Materials and University Enterprises Inc. on behalf of California State University Sacramento.

Simbol also wishes to thank CalEnergy and EnergySource geothermal power producers for giving SIMBOL Materials access to their operating plant sites and their geothermal brines.

Contents

Executive Summary

Simbol Materials studied various methods of extracting valuable minerals from geothermal brines in the Imperial Valley of California, focusing on the extraction of lithium, manganese, zinc and potassium. New methods were explored for managing the potential impact of silica fouling on mineral extraction equipment, and for converting silica management by-products into commercial products.

Studies at the laboratory and bench scale focused on manganese, zinc and potassium extraction and the conversion of silica management by-products into valuable commercial products. The processes for extracting lithium and producing lithium carbonate and lithium hydroxide products were developed at the laboratory scale and scaled up to pilot-scale. Several sorbents designed to extract lithium as lithium chloride from geothermal brine were developed at the laboratory scale and subsequently scaled-up for testing in the lithium extraction pilot plant.

Lithium

The results of the lithium studies generated the confidence for Simbol to scale its process to commercial operation. The key steps of the process were demonstrated during its development at pilot scale:

1. Silica management.
2. Lithium extraction.
3. Purification.
4. Concentration.
5. Conversion into lithium hydroxide and lithium carbonate products.

Results show that greater than 95% of the lithium can be extracted from geothermal brine as lithium chloride, and that the chemical yield in converting lithium chloride to lithium hydroxide and lithium carbonate products is greater than 90%. The product purity produced from the process is consistent with battery grade lithium carbonate and lithium hydroxide. [redacted]

Manganese and zinc

Processes for the extraction of zinc and manganese from geothermal brine were developed. It was shown that they could be converted into zinc metal and electrolytic manganese dioxide after purification. These processes were evaluated for their economic potential, and at the present time Simbol Materials is evaluating other products with greater commercial value.

Potassium

Silicotitanates, zeolites and other sorbents were evaluated as potential reagents for the extraction of potassium from geothermal brines and production of potassium chloride (potash). It was found that zeolites were effective at removing potassium but the capacity of the zeolites and the form that the potassium is in does not have economic potential.

Iron-silica by-product

The conversion of iron-silica by-product produced during silica management operations into more valuable materials was studied at the laboratory scale. Results indicate that it is technically feasible to convert the iron-silica by-product into ferric chloride and ferric sulfate solutions which are precursors to a ferric phosphate product. However, additional work to purify the solutions is required to determine the commercial viability of this process.

Conclusion

Simbol Materials is in the process of designing its first commercial plant based on the technology developed to the pilot scale during this project. The investment in the commercial plant is hundreds of millions of dollars, and construction of the commercial plant will generate hundreds of jobs. Plant construction will be completed in 2016 and the first lithium products will be shipped in 2017. The plant will have a lithium carbonate equivalent production capacity of 15,000 tonnes per year. The gross revenues from the project are expected to be approximately $ 80 to 100 million annually. During this development program Simbol grew from a company of about 10 people to over 60 people today. Simbol is expected to employ more than 100 people once the plant is constructed.

Simbol Materials' business is scalable in the Imperial Valley region because there are eleven geothermal power plants already in operation, which allows Simbol to expand its business from one plant to multiple plants. Additionally, the scope of the resource is vast in terms of potential products such as lithium, manganese and zinc and potentially potassium.

Introduction

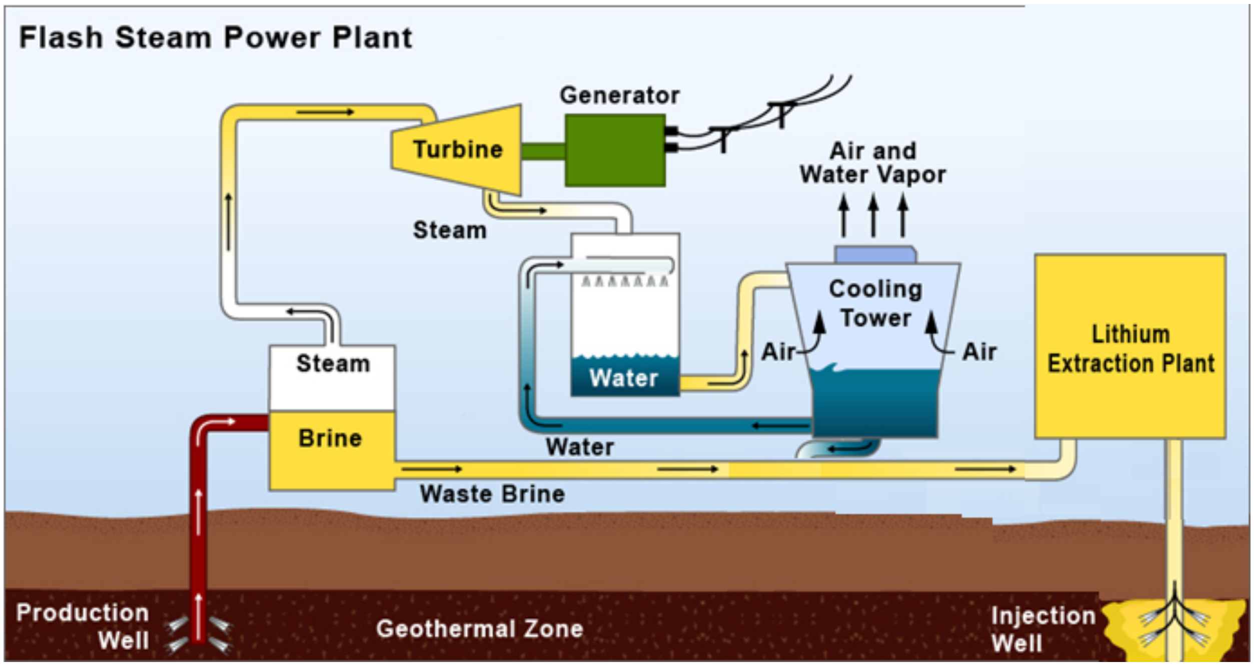
Many of the brines used by geothermal power plants to generate electricity contain an abundance of valuable dissolved minerals. This is especially true of geothermal plants located in California. Simbol Materials (Simbol) develops technologies to profitably extract these minerals and will build and operate mineral extraction plants alongside geothermal power plants (Figure 1). These mineral extraction plants will transform raw materials extracted from geothermal fluids into marketable by-products. Simbol is particularly focused on lithium, zinc and manganese for applications in batteries, especially lithium-ion batteries. The sale of lithium and other products will create new revenue streams for the geothermal operator through royalties, and improve significantly the economics of conventional and enhanced geothermal systems.

The hypersaline brines located in the Imperial Valley of California are particularly rich in metals. Sufficient brines are produced today to generate 377 MW of electricity, yet none of the post-power production brine is utilized to produce mineral by-products. Typical lithium, manganese, zinc and potassium concentrations in these geothermal brines are about 250, 1,500, 500 and 29,000 ppm, respectively. It is estimated that a single 50 MW plant could annually produce about 15,000 tonnes of lithium carbonate, 24,000 tonnes of electrolytic manganese dioxide, 8,000 tonnes of zinc metal and 410,000 tonnes of potash (KCl).

The high metal content of the brine occurs in part because of the high salinity of the brine, which can exceed 30 wt% in the post-power production brine. The high salinity of the brine and its tendency to foul equipment pose special challenges to brine management. Economic processes must be developed to selectively extract metals from the challenging brine chemistry and produce marketable by-products with sufficient purity from the post-power production brines.

Simbol conducted a multi-year project to develop and pilot-test technologies to extract lithium and other metals from the hypersaline brines typical of geothermal systems in the Imperial Valley, and then convert these metals to marketable products. Technologies were first developed in Simbol's laboratory facilities in Pleasanton, CA using surrogate brines. If promising, the technologies were upscaled to laboratory pilot scale and operated at Simbol's facilities at either Pleasanton or Brawley, CA using surrogate and geothermal brines. Technologies then proceeded to testing at Simbol's pilot plant sited in Calipatria, CA adjacent to an operating geothermal plant to obtain access to live geothermal brine. The first pilot plant was located adjacent to CalEnergy's Elmore geothermal plant, and later moved to EnergySource's John L. Featherstone geothermal plant. Pilot testing was conducted to test and optimize the processing technologies first as standalone operations and then as part of a multiple-step process. Testing was used to evaluate process economics and gather sufficient engineering data for scale-up to commercial operations.

Figure 1: Simbol concept of mineral extraction plant utilizing post-power production, pre-injection geothermal brine.



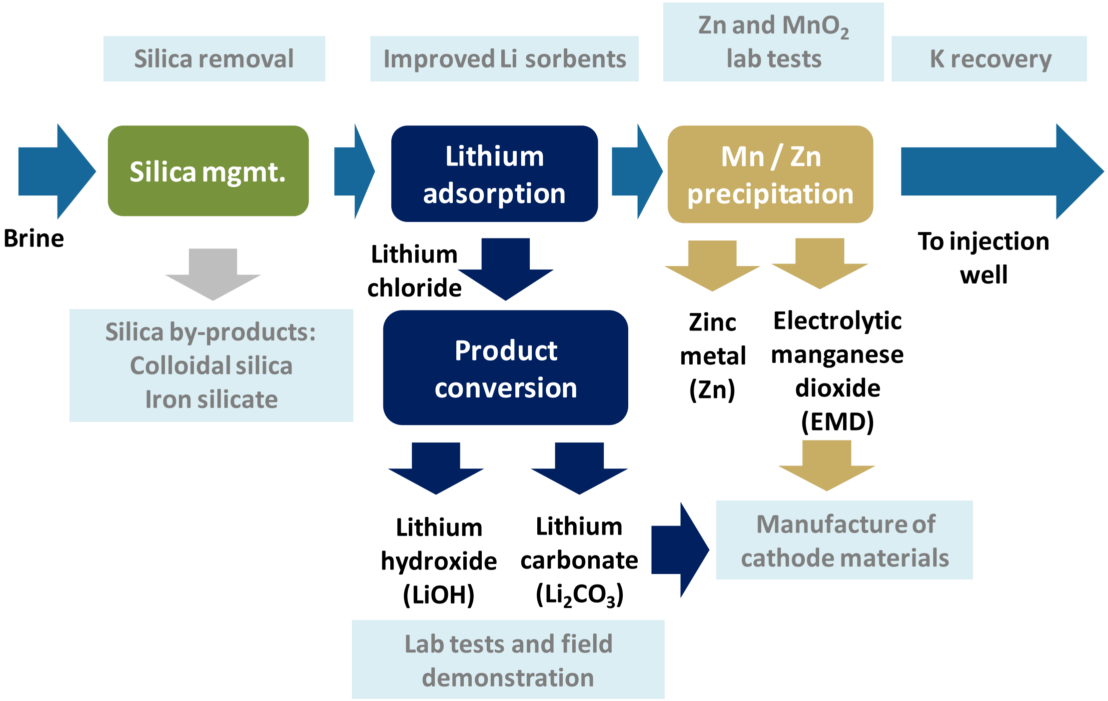
Organization of the report

Simbol carried out research on the following technical tasks (illustrated in Figure 2):

- Extraction of silica from geothermal brines and creation of a commercial product.
- Conversion of silica precipitate to value-added product.
- Development of new high capacity sorbents for lithium extraction from geothermal brines.
- Laboratory piloting of production of lithium hydroxide and high purity lithium carbonate from geothermal brines.
- Lithium extraction field pilot.
- Zinc and manganese extraction from geothermal brines.
- Geothermal lithium carbonate as precursor in the manufacture of lithium-ion cathode materials.
- Zinc and manganese extraction from geothermal brines.
- Potassium extraction from geothermal brines.

The following chapters summarize Simbol's research and development in these areas.

Figure 2: Schematic illustration of research tasks.



Extraction of Silica from Geothermal Brines and Creation of a Commercial Product

To prevent silica scaling during mineral extraction processes, dissolved silica in geothermal brines must be either removed or the brine stream must be chemically altered to prevent silica from precipitating and scaling downstream unit operations. Silica is a potentially valuable product in colloidal or precipitated forms, hence operations that remove silica also have the potential create a valuable product. Simbol Materials (Simbol) is currently employing its first generation technology for silica management in the field, and is seeking next generation technologies.

Simbol tested two next-generation silica removal processes at laboratory bench scale, one based on adsorption onto a commercially available sorbent which had a strong adsorptive affinity for dissolved silica (SiO_2), and the other for precipitating silica by addition of a precipitant. The feasibility of producing a colloidal silica product from the extracted silica was assessed.

Testing of sorbent ability to remove dissolved silica from geothermal brines

A series of commercially available forms of a sorbent with differing porosities, surface areas, and particle sizes were selected for testing of their ability to extract silica from a surrogate geothermal brine with chemistry typical of hypersaline geothermal fields in the Imperial Valley, CA. In addition to silica, other brine components were monitored for uptake during loading and release during stripping. Extraction was conducted at temperatures near 100ºC which is representative of the geothermal injection brine used as the feedstock for mineral extraction.

Bench-scale kinetics batch tests were conducted on five of the sorbents by placing 0.75 g of sorbent in 25 mL of brine solution containing nominally 100 mg/L SiO_2. The mixture was incubated at 100°C in a heating block and stirred. The tests were run in duplicate and 0.6 mL analytical samples were removed at intervals of 10, 20, 30, 40, and 60 minutes.

Adsorption isotherm tests were employed to determine silica uptake by sorbent at varying silica concentrations. 0.5 g of sorbent was added to 200 ml of brine containing silica at 10, 20, 40, 60, 80 and nominally 100 mg/L. This provided a solid to solution ratio of 2.5 g:L. Reaction time was ~16 hours (overnight) to ensure that the silica in contact with the sorbent had reached equilibrium. All tests were conducted at 95°C.

Flow-through testing was conducted to determine loading characteristics for each material.

The new sorbent proved very effective at removing silica from solution to below non-detect concentrations with a large capacity for capturing silica. Three of the sorbent materials were more efficient at adsorbing silica than the others. Flow-through testing identified a kinetic limitation to loading which limits the flow rate.

Results indicated that other components in the brine will likely be partly removed by the media, which must be monitored. For example, two of the tested materials exhibited lithium uptake in the batch tests.

Based on these results, three of the sorbents were selected for further testing of silica stripping and sorbent regeneration.

Testing of silica stripping from sorbent and regeneration of the sorbent

Bench scale tests were conducted to determine means of stripping silica from the sorbent while minimizing dissolution of the sorbent during stripping. Flow rates, strip chemistry, and strip volume were varied to optimize silica removal.

Adsorbed silica was stripped from the sorbent using alkaline strips, such as NaOH, followed by acid regeneration. These steps were performed at ambient temperature because such strip and regeneration solutions may result in significant dissolution of the sorbent at geothermal fluid temperatures which would reduce the lifetime of the sorbent and increase operating costs.

Flow-through tests, both single and multi-pass, were conducted on three of the sorbents determined to be most promising based on the results of the prior batch tests and particle size considerations. The tests were designed to both conserve strip chemicals, and produce a higher SiO_2 concentration in the strip solution, and hence, enhance the production of a marketable SiO_2 colloid product.

Sorbents with different size ranges were selected because particle size can have an impact on adsorption kinetics. Testing was conducted at 95°C either in an oven or in a heated water circulation system. After the sorbent was loaded with silica, it was stripped with caustic soda (NaOH), washed again, regenerated with acid (HCl), and washed until the pH increased to 4. At this point, loading could resume.

The caustic soda volume needed to strip the silica was not known *a priori* but the intent was to strip until ≥80% of the adsorbed silica was eluted. Quick, efficient stripping is desired for synthesis of a colloid product. Parameters varied during loading, strip and regeneration included feed and wash flow rates and concentration of the caustic strip. Lithium concentrations were monitored in the post-loading wash and strip solutions to determine if lithium was absorbed onto the sorbent. Lithium adsorption was not desired because product is lost to the sorbent and difficult to recover.

Single pass and multi-pass stripping of the sorbent were optimized. Results indicated wide variation in the ease of silica removal for the different forms of sorbent. One material proved recalcitrant to stripping and was eliminated from further consideration. Of the other two materials, one stripped more quickly, and the other had a silica load >50% greater than the other. Under conditions tested, silica proved difficult to strip.

Two methods to improve stripping were tested: higher concentration of caustic soda, and multi-pass stripping. Multi-pass stripping would reduce the volumes of strip solution needed by recirculating the strip solution through the sorbent and concentrating silica in solution. Higher caustic soda concentration resulted in faster silica stripping but with additional loss of the sorbent. Multi-pass stripping was not effective for silica removal because stripped silica was subsequently re-absorbed by the sorbent.

Two issues were identified that impact the feasibility of generating a commercial silica product from the strip solution. First, silica removal from the sorbent required large volumes of stripping fluids. Ideally, long loading times with very short stripping cycles are desired. Second, loss of sorbent during stripping with NaOH was significant in some of the materials that were tested. Two of the test materials showed losses greater than 13 wt% during a single cycle. This would result in replacing lost sorbent every 1-2 cycles. Reducing the concentration of the base helps to mitigate sorbent loss but requires larger volumes of strip solution to remove the silica.

Precipitation of silica

Additional tests for silica removal via a precipitation technique were performed. Two types of commercially available precipitants were tested. The precipitant was added to the brine and then neutralized with a base to form an amorphous aluminosilicate precipitate, thus lowering the concentration of dissolved silica in solution. Aluminosilicate 'seed' was added to provide a nucleation point for the reaction. When the brine was seeded with previously precipitated aluminosilicate, the silica preferentially attached to the seed material, after which both silica and aluminum can then be removed from solution using conventional filtration or clarification processes. Caustic soda was used to maintain pH. Tests were performed in triplicate.

In a typical test, seventy mL of hot (95°C) brine containing nominally 100 mg/L silica was added to 1.26 g of aluminosilicate seed (1.5 wt%) and stirred. Initially, 1.17 mL of the first precipitant solution was added to the mixture and 1N caustic soda was titrated into the solution until the pH was ~5. The bulk of the precipitation occurred immediately but was allowed to proceed for 10 min with stirring and heating to ensure that the reaction had reached completion. The mixture was removed from the heat and immediately filtered (0.45 μm) to separate the liquid and solid phases. The solid phase was washed with 15 mL of refrigerated water and air dried prior to digestion and analysis. Lithium loss from the brine was monitored by determining lithium content in the solid.

The two precipitants removed 67 % and 80% of the silica from the surrogate geothermal brine. A significant amount of caustic was necessary to maintain pH at 5 for one of the precipitants. One of the precipitants caused significant losses of lithium from solution. Based on the test conditions and results, one precipitant was more effective at removing silica from the geothermal brine with minimal lithium loss, but caustic costs will be higher. Analysis suggested that the sorbent technology had a cost advantage relative to the precipitants.

Concluding remarks

The sorbent effectively removes silica from solution but there is no economical method for stripping the silica from the sorbent for re-use. It is practical to use the sorbent for the removal of low concentrations of silica (<5 to 10 ppm). In this case the sorbent would not be regenerated but used as a single-use material and replaced on a regular basis once saturated. It is envisaged that this could be used as a polishing system to prevent down-stream contamination of extraction media.

Conversion of Silica Precipitate to Value-added Product

To prevent silica scaling during mineral extraction, dissolved silica in geothermal brines must be either removed or the brine stream must be chemically altered to prevent silica from precipitating and scaling downstream unit operations. Silica is a potentially valuable product, hence operations that remove silica also have the potential create a valuable product. Simbol Materials (Simbol) is currently employing its proprietary technology for silica management in the field. Silica removal is achieved by altering the properties of the brine which causes silica to precipitate as an iron silicate. The iron silicate is removed from the brine to form a filter cake. An undesired result of this process was the adsorption of arsenic (As) to the iron-silicate filter cake. This may make the products generated from the filter cake undesirable for some applications.

The objective of this work was to develop processes for removing arsenic from geothermal brine prior to silica management, and to convert the iron-silica precipitate into commercially viable products.

Removal of arsenic from geothermal brine prior to silica management

Two methods were tested for removing arsenic from geothermal brine prior to silica management:

[redacted]

[redacted]

[redacted]

[redacted]

[redacted]

[redacted]

[redacted]

[redacted]

[redacted]

- [redacted]
- [redacted]
- [redacted]
- [redacted]

[redacted]

[redacted]

[redacted]

[redacted]

Conversion of iron-silica filter cake to value-added product

Simbol investigated methods of producing iron phosphate ($FePO_4$) from iron-silicate filter cake precipitated from geothermal brine during silica management. Iron phosphate is used to make lithium-ion battery cathodes and to make pesticides and snail pellets.

[redacted]

[redacted]

[redacted]

[redacted]

Tests of making ferric phosphate from both ferric chloride and sulfate solutions were made by reacting each solution with phosphoric acid and then neutralizing the solution with caustic soda. This precipitated iron phosphate with greater than 95 % yield. Once washed and dried, the iron phosphate meets commercial specifications for making lithium iron phosphate cathode powders.

Concluding remarks

The intent of these studies was to convert the iron-silica filter cake produced from silica management operations into marketable by-products. A key to achieving this goal is the minimization of impurities in the filter cake and in intermediate solutions used to produce downstream marketable products.

[redacted]

It was also proven that the filter cake could be digested and converted into ferric chloride and ferric sulfate solutions, but the purity required to make these solutions into marketable materials has not yet been demonstrated.

Although Simbol demonstrated the production of ferric phosphate from ferric sulfate solution, the ability to generate purified iron salt solutions from filter cake suitable for production of ferric phosphate must still be confirmed. Work accomplished to date suggests that it is technically feasible to convert the filter cake into products. However, it may be a challenge to do so economically.

Developing New High Capacity Sorbents for Lithium Extraction from Geothermal Brines

A patented sorbent technology currently used to extract lithium from salt lakes in South America uses polycrystalline pellets of hydrated alumina intercalated with lithium salt to create active lithium-specific sites within the crystal layers. The lithium in these sites can be washed out (unloaded) and then loaded when in contact with a lithium-containing brine. Repeated loading and unloading of the active sites yields a lithium chloride solution which can then be converted to commercial products such as lithium carbonate and lithium hydroxide.

Simbol developed a new, first generation proprietary sorbent which also contains lithium-specific sites which can be loaded and unloaded to extract lithium from geothermal brines such as those in the hypersaline geothermal fields in the Imperial Valley of California. The goal of this work was to develop new and improved lithium sorbents with higher capacity (amount of lithium loaded onto the sorbent), longer lifetimes and lower manufacturing costs in order to lower the costs of lithium extraction. Minimization of impurities in the lithium chloride extracted from the brine is also a critical parameter because impurities require further purification at additional cost.

Sorbent-P (2nd generation material)

Simbol conducted laboratory-scale and pilot-scale trials of processes to increase the capacity of Simbol's proprietary sorbent and to manufacture the sorbent in commercial quantities while maintaining sorbent properties. Multiple bench scale tests were conducted to assess the physical and chemical parameters controlling synthesis and the properties of the sorbent. Formation of the lithium-specific sites was discovered to be a very robust process that can be carried out over a wide range of conditions, however the number of these sites created was strongly temperature dependent. A laboratory pilot with a lithium extraction system employing the sorbent was operated with synthetic geothermal brine. The sorbent exhibited about twice the lithium extraction capacity as the first generation sorbent and fewer impurities.

Four types of equipment were used initially for the first four steps in manufacturing sorbent, but eventually the multi-step process was consolidated to the use of a single mixer/reactor. The next seven manufacturing steps were carried out in multiple pieces of equipment. Multiple processes, procedures and equipment were tested. Procedures for each step of the manufacturing process were defined that include specification of raw materials, masses, equipment, and reaction times. Production quality control tests were developed and specifications set for sorbent acceptance.

Sorbent-S (3rd generation material)

This material was a precipitated form of the active ingredient in Sorbent-P. The sorbent was precipitated on an inert inorganic substrate. The precipitation reaction worked well in the laboratory and generated a sorbent that had good capacity and produced lithium chloride with low impurities, and behaved similarly to Sorbent-P in laboratory testing using synthetic geothermal brine. The two-step production process of Sorbent-S was far simpler than that of Sorbent-P and therefore was very attractive as an alternative.

This production process was scaled-up to produce 200 to 400 kg of sorbent for pilot scale trials. The scale-up successfully produced a sorbent with high capacity similar to the sorbent produced in the laboratory. However, the sorbent had significant affinity for impurities, so this approach was abandoned in favor of Sorbent-P and Sorbent-A (see below), neither of which had the impurity problem when scaled-up.

Sorbent-A (4th generation material)

Simbol developed a new method of synthesizing lithium sorbent which significantly increased the sorbent's capacity for lithium. Multiple screening tests were run to determine optimal conditions for synthesis (e.g. temperature, concentrations of starting materials, reaction time). Sorbent characteristics of loading capacity, physical robustness, particle size and presence of impurities were measured. A laboratory-based process for synthesizing the sorbent was defined and the sorbent was synthesized for further lab testing in configurations to be utilized in its commercial applications.

Lab testing evaluated loading capacity of the sorbent to confirm that sorbent performance was substantially improved relative to commercial lithium sorbents. Other physical and chemical characteristics of the sorbent and operational conditions for optimal lithium extraction were measured.

Given the positive results of laboratory-scale synthesis and performance tests, methods of scaling up production of the sorbent to quantities needed for commercial scale applications (hundreds of kilograms per year) were evaluated. The first goal was to synthesize 50 kilogram batches of sorbent. Difficulties in reproducing laboratory-scale procedures on a much larger scale necessitated identification of alternate processing methods and equipment for synthesis. One system was found to offer several processing and scale-up advantages. Laboratory-scale synthesis of 4-5 kilogram batches was conducted before testing this system. These tests revealed a new approach to the final synthesis step that worked consistently, was readily scalable, improved lithium loading capacity, and lowered impurities in the product.

The new, larger scale system for sorbent manufacturing was used successfully to produce more than 300 kilograms of sorbent in 50 kilogram batches. The sorbent was tested for its physical and chemical properties. The sorbent ultimately was used in Simbol's lithium extraction demonstration plant in Calipatria, CA. Experimental protocols and process flow diagrams were produced.

Concluding remarks

Simbol developed new sorbents for lithium extraction from geothermal brines that had improved loading capacity relative to currently known lithium sorbents and that had appropriate physical and chemical properties for field use. Sorbent-A is the preferred sorbent because it has both high capacity and low affinity for impurities and can be produced in a simple two-step process. Processing methods for scaling up sorbent synthesis to multiple ton quantities were developed and a preliminary design for a commercial production unit was completed.

Laboratory Piloting of Production of Lithium Hydroxide and High Purity Lithium Carbonate

Simbol Materials has developed a process for extraction of lithium chloride (LiCl) from geothermal brines. This process generates a product stream of concentrated LiCl which although a valuable product, has a limited market. On the other hand, lithium carbonate (Li_2CO_3) and lithium hydroxide monohydrate ($LiOH{\cdot}H_2O$) are used in a variety of industrial processes and are therefore more desirable products.

Simbol investigated two methods for the conversion of LiCl to $LiOH{\cdot}H_2O$ and Li_2CO_3:

- Reaction of soda ash (Na_2CO_3) with LiCl to produce Li_2CO_3, followed by reaction between Li_2CO_3 and lime CaO to produce LiOH solutions which are evaporated to give $LiOH{\cdot}H_2O$.
- Conversion of LiCl to LiOH via Simbol's patent pending process, followed either by concentration to give $LiOH{\cdot}H_2O$, or direct carbonation of the LiOH using carbon dioxide (CO_2) to give Li_2CO_3.

The soda ash method is essentially the conventional approach for making Li_2CO_3 and $LiOH{\cdot}H_2O$ products. However, it requires an additional input to the overall process, Na_2CO_3, and while high purity LiCl is available from Simbol's upstream process to feed the carbonation unit, impurities added with the Na_2CO_3 result in a lower purity Li_2CO_3 product. The Li_2CO_3 must be washed to remove sodium chloride (NaCl), which produces an additional NaCl stream with a small amount of entrained Li_2CO_3 which needs to be recycled. The second reaction step to produce $LiOH{\cdot}H_2O$ requires mixing two slurries, $Ca(OH)_2$ and Li_2CO_3, which both have limited solubility in water, producing a third slurry, $CaCO_3$ suspended in LiOH solution. The maximum LiOH concentration that can be achieved by this method is ~3.5 wt% LiOH. This solution must be evaporated and the product washed and purified to produce $LiOH{\cdot}H_2O$. [redacted]

[redacted]

The purpose of this work was to design, build and operate two laboratory scale pilot plants for converting LiCl to $LiOH{\cdot}H_2O$ and Li_2CO_3. The plants used synthetic LiCl solutions for their feed stock. Operation of the pilot plants allowed identification of optimal operating conditions and key metrics needed for scale-up to commercial scale. One pilot plant converted LiCl to LiOH using Simbol's patented process (the lithium hydroxide plant), and the second plant converted LiCl to Li_2CO_3 ia reaction with soda ash and included downstream processes of filtering, washing and drying the Li_2CO_3 product (the soda ash plant).

Lithium hydroxide plant

The primary objectives of this work were to:

- [redacted] Design, build and operate a laboratory scale lithium hydroxide production pilot plant [redacted]
- Establish the best operating conditions for technology.
- Determine the key metrics needed for scale-up.

Simbol designed and built a laboratory scale pilot plant for the production of LiOH [redacted] The plant was designed to be a single pass system, with separate tanks for the feed and exit [redacted] and LiOH streams. This provided better accounting for the [redacted] consumed and LiOH made. The pilot plant was instrumented with various temperature, pH, flow and pressure sensors and the data from these sensors recorded by computer or by operator's logs.

[redacted]

[redacted]

Depending on operating conditions, the plant could convert 0.12-0.19 kg LiCl per hour, producing 0.10-0.14 kg Li_2CO_3 equivalents per hour.

[redacted]

Based on the operation of the lithium hydroxide pilot plant, various recommendations for improvements to this and future lithium hydroxide plants were made. Improvements include addition of a purification system to eliminate trace impurities in [redacted] and changes in plant equipment. Different feed concentrations or flow rates of LiOH into the pilot plant should be explored to determine under what conditions the process can be operated to achieve higher concentrations of LiOH in the product.

Soda ash plant

The main objective of this work was to build and operate a laboratory scale pilot plant that would convert LiCl to Li_2CO_3 via reaction with soda ash and then filter, wash and dry the Li_2CO_3 solids produced in order to:

- Produce Li_2CO_3 of 99.0-99.9% purity from LiCl and Na_2CO_3 feed stock.
- Determine the amount and composition of wash water consumed.
- Determine chemical yield and reagent composition.
- Determine the key parameters which affect particle sizes/morphologies, and provide a tool to produce a range of these.
- Determine any fouling problems in the system.

A pilot plant was built comprising three major pieces of equipment (Figure 3):

- A 100 liter precipitator, where the LiCl and Na_2CO_3 reactants were mixed together at 95°C.
- A 0.1 m^2 belt filter to capture the solid Li_2CO_3 formed in the precipitator. This filter was equipped with a counter-current wash system to wash the product.
- A rotary tray dryer, with five plates, to dry the Li_2CO_3 product.

Equipment was chosen which could be scaled to commercial scale equipment.

Dosing of reactants into the precipitator was designed as a continuous process, and this part of the pilot was operated for a total of 14 experiments of 3-21 hours duration. The filter and dryer required a feed rate an order of magnitude larger than the precipitator, so these were operated in batch mode once sufficient Li_2CO_3 had been produced in the reactor.

Samples of all liquids and solids were collected from the precipitation loop every 2-4 hours, and from the filter and dryer once or twice per run. These were analyzed for composition and physical properties such as particle size. The pilot plant was instrumented with various temperature, pH, flow and pressure sensors and the data from these sensors recorded by computer or by operator's logs.

The laboratory production pilot plant succeeded in its primary goal of producing Li_2CO_3 of 99.9% purity on a dry materials basis from technical grade LiCl and Na_2CO_3 feed stocks. The material produced exceeded technical grade and was close to meeting battery grade specification. The largest impurity was Na at ~250-350 mg/kg. The other major impurities, Ca and Mg, were both ~100 mg/kg. These entered the system as impurities in the feed chemicals. Other minor metal impurities (Ba, Ni, Zn, Fe and Mn) in the feed chemicals also reported to the dry Li_2CO_3 product. In Simbol's overall process, these elements are removed in the purification stages downstream of Li_2CO_3 production, so the result achieved with the surrogate LiCl should be able to be reproduced with LiCl from the geothermal brine.

[redacted] Li_2CO_3 of wash water was required, which is higher than ideal. However, the high purity of the product shows that washing was very efficient, so room exists to reduce the amount of wash water used. The final composition of the wash water discharged from filter contained ~1600 mg/L Li and ~17000 mg/L Na. This indicates that a significant amount of the mother liquor was being captured with the wash water in the final stage of filtration, and further optimization of the filtrate take-offs from the filter was required.

Overall, yields of dry Li_2CO_3 as high as 92% were achieved, although typically the yield was in the low to mid-80% range. The main factors which reduce the yield are the amount of wash water used, the temperature of the wash water and the temperature of the reaction slurry fed to the filter. About 4-6% of Li remained in the wash water with a roughly equal amount remaining in the mother liquor. Neither of these represents a loss of Li from the system as a whole, as both streams are recycled elsewhere in Simbol's overall process.

The particle size distribution in the system was not strongly affected by any of the parameters under operator control in the system. Typically, the median diameter of the particle size distribution was in the range of [redacted], and the diameter of 90% of the particle mass was less than [redacted].

The pilot plant was operated fairly free of major fouling issues. The biggest exception was that dosing both LiCl and Na_2CO_3 directly into the return line from the heat exchanger to the precipitator caused the line to plug between the two dosing points. The severity of the plugging was enhanced if the reaction mixture was LiCl-rich. The issue was resolved by dosing LiCl directly into the reservoir, although an alternative solution would be to greatly increase the flow rate through the heat exchanger.

Guided by the test results described above, the following testing and process improvements were implemented at the pilot plant:

- Operation of the plant in semi-continuous mode (continuous precipitation, batch wise filtration and drying).
- Optimization of filter cake washing to reduce water usage and the amount of Na captured in the wash filtrate.
- Improvement in sampling and analysis methods to better account for the inventory of Li remaining in the system to provide a better overall mass balance.
- Operation with LiCl produced from geothermal brine to determine product purity (see section "Lithium Extraction Field Pilot").

Figure 3. Lithium carbonate (soda ash) pilot plant (left) at Simbol's facilities in Pleasanton, CA and production of lithium carbonate powder (right) from surrogate geothermal brine.

Lithium Extraction Field Pilot

Simbol Materials (Simbol) designed a process to recover lithium from geothermal brines in areas such as the Imperial Valley, CA and produce high value products such as lithium chloride (LiCl), lithium carbonate (Li_2CO_3) and lithium hydroxide monohydrate ($LiOH \cdot H_2O$ or LiOH). The steps in this process are as follows:

- Silica Management to control silica and iron fouling on extraction equipment.
- Lithium Extraction to capture lithium from the brine and recover it as lithium chloride (LiCl) product solution.
- Purification of the LiCl product solution to remove impurities that might be incorporated into the final products.
- Concentration of purified LiCl solution to 35-40 wt.% LiCl solution before it is converted into Li_2CO_3 and LiOH products.
- Conversion of concentrated, purified LiCl into Li_2CO_3 and LiOH products.

Simbol's strategy in developing this technology was to deploy a six gallon per minute (gpm) pilot plant at the site of an operating geothermal power plant in the Imperial Valley region, specifically the Elmore plant operated by CalEnergy, and later the John L. Featherstone Plant operated by EnergySource, in order to have a live post-power production brine source.

Prior to field deployment, the silica management and lithium extraction units of the 6 gpm pilot were installed at an indoor piloting facility in Alameda, California, and operated using surrogate brine as feed. This enabled the pilot to be operated under controlled conditions so that the process units could be tested and modified as needed.

After completing the objectives of the indoor piloting, the pilot was moved to CalEnergy's Elmore power plant in Calipatria, CA for operation using 6 gpm brine piped directly from the injection brine return line. The silica management and lithium extraction units were operated using live brine. Two different lithium sorbents were tested in the lithium extraction unit. This part of the process was operated for more than 3,000 hours at the Elmore site.

The pilot was moved to EnergySource's John L. Featherstone plant after its commissioning. The Featherstone plant will be the site of Simbol's first commercial plant. A new generation lithium sorbent was tested. Purification and concentration unit operations were added to the pilot plant downstream of lithium extraction. Purification of LiCl from lithium extraction is necessary to assure the quality of lithium carbonate and lithium hydroxide products. This process purifies the LiCl product by removing divalent and trivalent cations and boron from the LiCl feedstock. Concentration of the purified LiCl stream was conducted to produce about 35 wt% LiCl solution which is optimal for conversion to lithium carbonate and lithium hydroxide products.

The product conversion pilots were built in Simbol's indoor facility in Brawley, CA. The LiCl product solution was shipped to Simbol's facility in Brawley, CA for processing into Li_2CO_3 and LiOH.

The following sections describe each of these activities in more detail.

Silica management and lithium extraction pilot plant at Alameda, CA using surrogate brine

The pilot plant for silica management and lithium extraction was designed and built and then installed at an indoor facility in Alameda, CA. The primary objective of the pilot tests was to operate silica management and lithium extraction for an extended continuous run, both as stand-alone units and coupled together for at least 100 hours of continuous operation of the two systems together. Secondary objectives were to enable operators and the technical team to gain experience in operating the system and to develop operating procedures to use after deployment of the plant to an operational geothermal plant.

Silica management: The silica management system successfully removed silica and iron to below detection limits once operation had stabilized. Optimal operating conditions (temperature, pH, chemical feed rates and residence time) were defined. The need for improved procedures and data acquisition for the pilot when moved to the field were defined.

Lithium extraction: The lithium extraction unit performed similarly to smaller scale units operated in Simbol's laboratory, showing that this part of the process scaled well. Simbol's first generation sorbent was used to extract lithium as LiCl solution from the surrogate brine. Although the sorbent performed adequately, new sorbents being developed at Simbol provide increased capacity as soon as they are manufactured in sufficient quantity. Operation of the unit helped clarify process steps necessary to maximize product cut and minimize impurities.

Simbol operated silica management continuously for a total of ~230 hours and lithium extraction continuously for ~238 hours; the two units were operated together for a total of 136 hours. Operators and technical staff gained experience operating the system, and changes in the design necessary to improve the process and operability of the plant were identified.

Silica management and lithium extraction pilot plant in Calipatria, CA using live geothermal brine

Simbol moved its pilot plant adjacent to CalEnergy's Elmore power plant in Calipatria, CA (Figure 4) and installed ancillary equipment and connections to the Elmore injection brine line as the brine feed. The average flow rate and temperature of the brine were 5 gpm and 105°C, respectively. Data acquisition systems were installed to continuously monitor operational data. An analytical lab was installed on-site to provide routine chemical and physical analysis of fluids and solids and to provide CalEnergy with a complete analysis of the brine and iron silica filter cake recovered from the brine. The analytical capabilities of this lab were supplemented by Simbol's analytical facilities in Pleasanton, CA. The Pleasanton laboratory is equipped to analyze a greater range of materials and deal with any unknown substances generated during operation.

A series of campaigns were conducted to optimize the silica management and lithium extraction operations. A typical campaign lasted about two weeks. The equipment was operated continuously by a team of operators, and an engineering and scientific team provided support in designing the methodology of operation. Equipment was modified, replaced or added as necessary to improve performance or test new approaches.

The performance of two lithium sorbents developed by Simbol were tested at the Elmore plant site. [redacted]

Sorbent[redacted] also represented a significant improvement because it produced LiCl solution with lower impurity content, which will significantly reduce the costs of purifying and concentrating the solution. It was possible to extract >95 % of the lithium chloride from the geothermal brine under certain operating conditions. The pilot plant was ultimately operated for about 3,500 hours at Elmore.

The pilot plant was moved to the EnergySource John L. Featherstone plant after its commissioning because it will be the site of Simbol's first commercial plant. The performance of Simbol's fourth generation lithium sorbent "Sorbent-A" was tested at the plant and found to have higher capacity than Sorbent-P.

Unit operations for purification and concentration were added at the EnergySource site and additional campaigns were conducted. The purification skid receives the LiCl feed stream from lithium extraction and removes metal impurities. The purified solution was then sent to the concentration skid where it was concentrated to a 35 to 40 wt.% LiCl solution. The concentrated LiCl was then processed by Simbol's proprietary technology to produce Li_2CO_3 product at a pilot scale.

Parameters tracked during the campaigns to monitor system performance include efficiency of lithium extraction and iron-silica removal, wt.% of LiCl in the product solution, impurities in the LiCl product solution, masses of process chemicals and water consumption. This data was used to identify key operating costs and areas for system improvements for scale-up to a commercial plant.

Simbol operated lithium extraction at EnergySource for well over 9000 hours from November 2012 through December 2013 and produced a purified 36 to 40 wt.% lithium chloride product in the process.

Silica management demonstrated efficient removal of both silica and iron after adjusting operating parameters from those identified during operation at Alameda, CA using surrogate brine. Greater than 93% of silica and 98% of Fe(II) were removed. The filter cake generated by this process is considered to be non-hazardous under EPA regulations. The lithium extraction process has been further enhanced by the use of a fourth generation sorbent material [redacted] with a higher capacity than [redacted] yet similar impurity content. This enables an increased concentration of lithium chloride to be produced while still removing 95 % of the lithium chloride from the geothermal brine. [redacted]

Testing showed that the original three step purification process could be reduced to two steps in order to reduce capital and operating costs. The purification skid produced 23 batches of LiCl solution, or 6,754 gallons (25,192 liters). The average yield was 86%. Initial yields averaged 75%. Through plant and process modifications yields in later batches increased to as high as 94%. After purification of the LiCl solution, Ca averaged < 3.0 ppm, and Mn averaged < 0.3 ppm.

[redacted]

Pilot plant for converting lithium chloride to lithium carbonate

The pilot plant for converting product LiCl product to lithium carbonate via addition of soda ash, originally constructed and operated at Simbol's Pleasanton facility, was relocated to Simbol's Brawley facility for testing with LiCl sourced from geothermal brine (Figure 5). The LiCl was collected in totes at the pilot plant and shipped to the Brawley facility. The pilot converted the LiCl to Li_2CO_3 by addition of soda ash (Na_2CO_3) in a precipitator, along with downstream processes of filtering, washing and drying the Li_2CO_3 solids produced. A filter captured the solid Li_2CO_3 and was equipped with a counter-current wash system. A rotary tray dryer with five plates dried the Li_2CO_3 product. The filter and dryer required a feed rate an order of magnitude larger than the precipitator, so these were operated in semi-batch mode once sufficient Li_2CO_3 had been produced in the reactor.

The pilot plant succeeded in its goal of producing battery grade Li_2CO_3 of a 99.9% purity on a dry materials basis from geothermal LiCl and Na_2CO_3 feed stocks. The material produced exceeded technical grade and met battery grade specifications with the exception of a specific particle size. The material was subsequently ground in a laboratory scale jet mill at the Pleasanton facility and the battery grade specification was met.

Pilot plant [redacted] to produce lithium hydroxide

A production pilot was built in Simbol's Brawley facility (Figure 6) to convert purified and concentrated 36% LiCl solution into LiOH and Li_2CO_3 using Simbol's proprietary technology. [redacted] Conversion of LiCl to product is the critical link between the extraction of lithium from geothermal brine and the production of marketable lithium carbonate, (Li_2CO_3) and lithium hydroxide monohydrate ($LiOH \cdot H_2O$). Following the development of operating procedures, the pilot plant was operated for in excess of 1000 hours over three campaigns using both surrogate and geothermal sourced LiCl as the feed.

[redacted]

[redacted]

[redacted] The filter cake was counter current washed with fresh hot deionized water to remove impurities such as sodium and potassium from the filter cake. The lithium carbonate wet cake (> 25% water content) was fed to a dryer where it was dried to give a 99.99% pure product (Table 1). [redacted] successfully produced 26.3 kg of dried 99.99% pure Li_2CO_3 product. This exceeded the technical grade specifications specified as the target for the campaign, and achieved battery grade specifications once jet milled for sampling purposes.

The campaign demonstrated the technical viability of producing Li_2CO_3 from geothermal brine while producing a 99.99% pure Li_2CO_3 product. The plant produced the first samples of Li_2CO_3 from LiCl extracted from geothermal brine.

Figure 4. Simbol's lithium extraction pilot plant Calipatria, CA adjacent to CalEnergy's Elmore geothermal power plant.

Figure 5. Lithium carbonate pilot plant at Simbol's Brawley, CA facility.

Figure 6. Control system of lithium hydroxide pilot at Simbol's Brawley, CA facility.

Table 1. Chemical analysis of 99.99% pure Li_2CO_3 produced from LiCl extracted from geothermal brine.

Element	Concentration	Unit
Purity	99.99	wt%
Impurities		
Fe	0.3	ppm
Cr	0.1	ppm
Mn	0.1 >	ppm
Ni	1 >	ppm
Cu	0.1	ppm
Zn	1	ppm
Pb	0.5 >	ppm
Na	13	ppm
Mg	1 >	ppm
Al	3	ppm
K	22	ppm
Ca	18	ppm
Si	5	ppm
Cl	11	ppm
SO4	10 >	ppm
H2O	0.03	wt%

Zinc and Manganese Extraction from Geothermal Brines

The objective of this work was to prove technologies at the laboratory scale for extracting zinc and manganese from geothermal brines and converting the zinc and manganese to zinc metal and electrolytic manganese dioxide products.

Zinc and manganese extraction from geothermal brines

Laboratory testing with surrogate and geothermal brine demonstrated that manganese (Mn) and zinc (Zn) can be recovered by precipitation as hydroxides from geothermal brine at pH values around 8 to 9. At least 95% of both metals can be extracted from the brine.

A process to wash and re-dissolve manganese oxides/hydroxide and zinc hydroxides in sulfuric acid was developed which recovered 99 % of the precipitated metals as a manganese and zinc sulfate solution. Zinc was then removed from the manganese and zinc sulfate solution by solvent extraction. Solvent extraction produced a solution of zinc sulfate suitable for electrolysis to zinc metal after the zinc sulfate solution had been purified by classic techniques such as cementation with zinc dust.

Purification of the remaining manganese sulfate solution was then studied, and it was proven that impurities could be removed to concentrations typical of those required for electrolysis to produce electrolytic manganese dioxide (EMD).

Zinc electrowinning

A test protocol for zinc (Zn) electrowinning using a Hull cell was developed. Hull cell tests allow different current densities to be explored during a single experiment. A synthetic 1M zinc sulfate solution with pH about 1 was used as the starting solution. The quality of the plated Zn was examined under an optical microscope, with a good quality plate being defined as a compact, dendrite free surface, free of inclusion of impurities (Figure 7). From these tests, the optimum current density to produce good quality Zn plate was determined with and without impurities in the electrolyte. As anticipated, the presence of impurities reduced the quality of the Zn plate for the range of current densities tested.

Electrolytic manganese dioxide electrowinning

The test protocol for electrolytic manganese dioxide (EMD; MnO_2) electrowinning was developed. An electrochemical plating bath and flow circuit was designed, assembled and commissioned. Testing focused on plating EMD from synthetic Mn sulfate solutions using the small flow-through plating cell and then optimizing operating conditions. The objective of these tests was to produce a dense layer of EMD of the correct phase and structure for use in battery electrodes at a high plating current efficiency.

Short duration experiments of up to 3 days length using a variety of current densities and electrode preparation techniques to achieve good plating were conducted to optimize the plating conditions. Tests produced increasingly better plated material. Tests of about a week in duration succeeded in producing the requisite dense EMD layer (Figure 7) that had an X-ray diffraction pattern typical of EMD used in battery electrodes. The current density for these tests was 60-80 A/m^2, typical of those used in industry.

EMD samples from several of the plating tests were characterized using X-ray diffraction in order to confirm that the plating method produced consistent material in the different trials. The X-ray diffraction patterns for all of the samples showed peaks which could be attributed to γ-MnO_2 and ε-MnO_2 phases, which are typically present in EMD materials used in batteries.

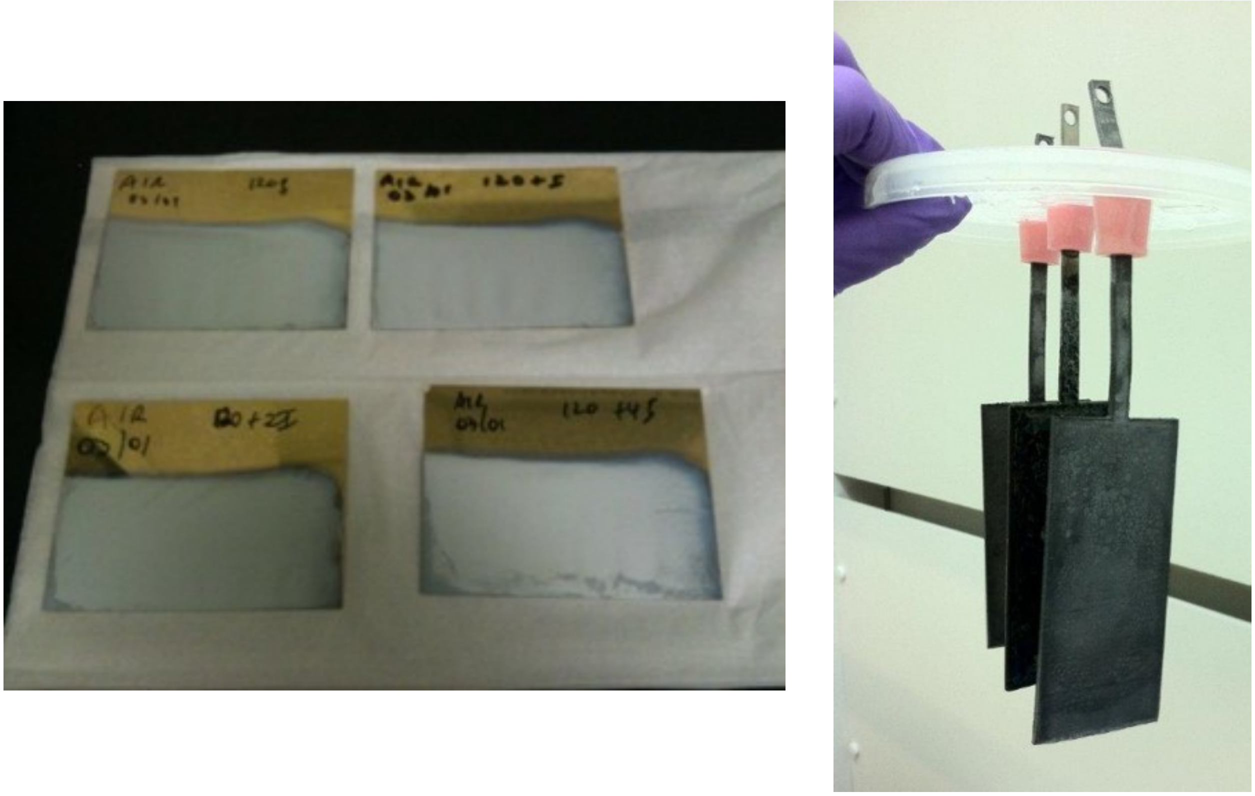
Combined electrolysis of EMD and zinc metal

Simbol evaluated an alternative approach to electrolysis involving electrowinning when both metals were present in significant quantities. However, it was discovered that the electrolysis conditions of EMD and zinc metal were too dissimilar for combined electrolysis to be feasible. The current densities typical of manganese electrolysis are vastly lower than those for zinc.

Economic analysis

An economic evaluation found that generation of zinc metal and EMD products using these processes was attractive economically and potentially competitive with commercial operations. Simbol is currently evaluating alternative products to zinc and EMD from its production facilities because they may have greater economic value and market potential.

Figure 7. Zinc plates (left) and EMD plates (right) produced during electrowinning tests.



Geothermal Lithium Carbonate as Precursor in the Manufacture of Lithium-ion Cathode Materials

The objective of this work was to use lithium carbonate (Li_2CO_3) from Simbol Materials to synthesize lithium manganese spinels ($LiMn_2O_4$) and to evaluate the electrochemical performance of the spinels relative to commercially available cathode materials. Lithium manganese spinels are used as cathode materials for lithium-ion batteries in high power and high energy applications such as the Chevy Volt and Nissan Leaf electric vehicles. The work was performed by Argonne National Laboratory (Dr. Khalil Amine, P.I.) under a Work for Others agreement with Simbol.

Researchers at Argonne National Laboratory conducted physical and chemical characterization tests (surface area, morphology, crystal structure and chemical analysis) of lithium carbonate obtained from Simbol Materials and four commercially available lithium carbonates as reference. Some morphology differences were observed, such as larger particle size which resulted in smaller surface area and higher tap density than the reference lithium carbonates. The impurity content of Simbol's lithium carbonate was significantly lower than the reference samples.

Argonne then synthesized lithium manganese spinels from the lithium carbonate samples to compare their electrochemical performance. Synthesis was performed by combining lab grade manganese oxide with four commercially available battery grade lithium carbonates and a lithium carbonate from Simbol. The actual target spinel composition was $Li_{1.06}Mn_{1.94}O_4$ because it has been shown that lithium doping can improve the performance of spinel materials as cathodes for lithium ion batteries.

Analysis showed that the thermal response of the spinel created with Simbol's lithium carbonate was similar to the other spinels, which indicates that the same heat procedure for $LiMn_2O_4$ preparation could be used. X-ray diffraction analysis showed that all five samples were pure, highly crystallized spinel of the correct phase. No impurity peaks were observed. The spinel made with Simbol's lithium carbonate exhibited higher tap density and lower surface area than the others. This is a good characteristic because it could lead to more loading in the electrode and thus more energy compared to the other materials.

Electrochemical testing showed that the initial charge and discharge capacities of all five spinels were similar. The spinel made with Simbol's lithium carbonate showed superior cycling performance, which was hypothesized to result from the higher purity of the lithium carbonate starting material.

Potassium Extraction from Geothermal Brines

Laboratory testing of ion exchange materials for selectively extracting potassium from hypersaline geothermal brines typical of the Salton Sea region of California were tested with the goal of producing potassium compounds such as potash for commercial sale. Potash is highly valued because it has no substitute in the market for fertilizers. The work was performed by Dr. Jacqueline R. Houston of California State University Sacramento under a Research Agreement between Simbol Materials and University Enterprises Inc. on behalf of California State University Sacramento.

Multiple inorganic materials exhibit the ability to selectively remove potassium by cation exchange. The cation-exchange reaction is represented by the following equation:

$$\bar{Z}Na^{+} + K^{+} \rightleftarrows \bar{Z}K^{+} + Na^{+}$$

The exchange material $\bar{Z}$ in the sodium form is able to exchange for potassium from geothermal brine with an equivalent quantity of sodium. Subsequently, the potassium loaded exchanger material may be treated with a sodium chloride solution, regenerating it back to the sodium form. However, the salinity of geothermal brines in the Salton Sea region is very high and numerous monovalent cations, such as sodium, and divalent cations, such as calcium, may compete with potassium and influence selectivity and capacity for potassium. Temperature can also affect ion exchange. There is a need to evaluate the uptake capacity, kinetic properties, and selectivity for potassium over a range of relevant temperatures using synthetic and naturally occurring cation exchangers.

The objectives of this research were:

- Conduct batch uptake tests to assess material capacity for potassium, the selectivity of the material, the kinetics of the uptake process, and the affinity of the material for potassium.
- Conduct batch strip tests at room temperature to evaluate the rate, completeness, and selectivity of potassium removal from the extractants.
- Conduct bench-scale column tests on the most promising subset of cation exchangers in which geothermal brine will be used to load the extractants with potassium, and various strip solutions that were identified in batch tests will be used to strip potassium from the material.

Lab testing of exchangers to capture potassium

Selection and synthesis of cation exchangers

Fourteen candidate cation exchange materials, listed in Table 2, were obtained and/or synthesized. Modified natural zeolites were prepared by converting natural zeolites into sodium-rich forms which are then receptive to potassium uptake. The synthetic sodium form of clinoptilolite was synthesized using chemical reagents and natural clinoptilolite as a seed under hydrothermal conditions. Synthetic zeolite W, synthetic crystalline silicotitanate (CST), and antimonate (SnSb) were synthesized using chemical reagents under hydrothermal conditions. Cation exchange materials were characterized by X-ray diffraction, scanning electron microscopy, and inductively coupled plasma optical emission spectroscopy based on analysis of acid digests of the washed solid phase.

Table 2: Theoretical Properties of Candidate Exchangers

Material	Structural formula	Theoretical CEC* (meq/g)	Major phase	Vendor, Country
As-received CH zeolite	$(Ca,Na,K)_6Al_6Si_{30}O_{72}$• $24H_2O$ (K >> Na, Ca)	1.8	clinoptilolite	Teague mineral products, USA
Modified CH zeolite	$(Ca,Na,K)_6Al_6Si_{30}O_{72}$• $24H_2O$ (Na >> K, Ca)	1.8	clinoptilolite	Teague mineral products, USA
As-received XY zeolite, 20x50	$(Ca,Na,K)_6Al_6Si_{30}O_{72}$• $24H_2O$ (Ca >> Na, K)	1.8	clinoptilolite	Teague mineral products, USA
Modified XY zeolite, 20x50	$(Ca,Na,K)_6Al_6Si_{30}O_{72}$• $24H_2O$ (Na >> Ca, K)	1.8	clinoptilolite	Teague mineral products, USA
As-received XY zeolite, 5x20	$(Ca,Na,K)_6Al_6Si_{30}O_{72}$• $24H_2O$ (Ca >> Na, K)	1.8	clinoptilolite	Teague mineral products, USA
Modified XY zeolite, 5x20	$(Ca,Na,K)_6Al_6Si_{30}O_{72}$• $24H_2O$ (Na >> Ca, K)	1.8	clinoptilolite	Teague mineral products, USA
Synthetic clinoptilolite	$(Ca,Na,K)_6Al_6Si_{30}O_{72}$• $24H_2O$ (Na >> Ca, K)	2.2	clinoptilolite	Teague mineral products, USA
CST	$HNa_3Ti_4Si_2O_{14}$ •$4H_2O$	6.5	sitinakite	-
Nb-CST	$HNa_2Ti_3NbSi_2O_{14}$ •$4H_2O$	4.7	sitinakite	-
Zeolite W	$(Na,K)_{10.3}Si_{21.7}Al_{10.3}O_{64}$ •$20H_2O$	3.9	merlinoite	-
SnSb	$(Sn,Sb)_3O_6$	5.1	pyrochlore	-
IE-911	$HNa_3Ti_4Si_2O_{14}$ •$4H_2O$	4.6	sitinakite	UOP LLC, USA
NHT mica	$Na_{0.33}Mg_{2.67}Li_{0.33}Si_4O_{10}F_2$	0.78	hectorite	Topy Industries, Japan
NTS mica	$NaMg_{2.5}Si_4O_{10}F_2$	2.33	tetrasilicic mica	Topy Industries, Japan

* *CEC: cation ion exchange capacity*

Studies of uptake capacity

The uptake capacity of each cation exchanger was calculated based on the results of batch equilibrium adsorption tests. Batch adsorption tests were carried out by using synthetic geothermal at 75°C, 85°C and 95°C. A predetermined amount of exchanger was added to synthetic geothermal brine at the target temperature and stirred for 24 hours. The suspension was filtered and the solids washed with refrigerated deionized water, dried at 80°C, digested in 6N HCl, and the digests analyzed for potassium and other constituents. The uptake capacity was calculated using the following equation.

$$Q = c_e^s - c_0^s \qquad unit: \frac{mg}{g}$$

where Q is the uptake capacity, that is, the amount of potassium adsorbed per unit mass of exchanger (*mg/g*). c_e^s and c_0^s are the equilibrium and initial concentrations of the potassium on the exchanger (mg/g). Selectivity coefficients, the preference of the exchanger to select one of two ions in the same solution, were calculated to examine the selectivity of potassium uptake. The selectivity for an exchanger to uptake ion B (i.e., K), vs. ion A, $S_{B/A}$, is defined as follows:

$$S_{B/A,uptake} = \frac{C_{B,s}C_{A,brine}}{C_{A,s}C_{B,brine}}$$

where $C_{A,s}$ and $C_{A,brine}$ are the equilibrium concentration of ion A in the solid phase and initial concentration in the brine, respectively and $C_{B,s}$ and $C_{B,brine}$ are the equilibrium concentration of ion B in the solid phase and initial concentration in the brine, respectively. The uptake capacity and selectivity are not a property of the extractant alone, but are defined only for a specific solid to solution ratio, temperature, and solution composition.

The uptake capacity of as-received XY zeolites was as high as 34.4 mg/g at 85°C in synthetic geothermal brine. The particle size did not play an important role on uptake capacity. The effect of temperature was significant on as-received CH zeolite. The uptake capacity of as-received CH zeolite decreased from 9.5 mg/g at 85°C to 0.2 mg/g at 95°C. After NaCl modification, the uptake capacity of natural zeolites was enhanced. The uptake capacity of modified natural XY zeolite reached around 36 mg/g and 34 mg/g at 85°C and 95°C, respectively. The selectivity for potassium versus calcium was also enhanced after NaCl modification.

The uptake capacity of zeolite W was about 33 mg/g at 95 °C which is lower than expected. The lower uptake capacity might have resulted from the higher potassium content of the as-synthesized zeolite W, or from the fact that the XRD pattern indicated that zeolite W sample contained vishnevite, a chabazite structure which is not selective for potassium exchange.

Synthetic clinoptilolite has 44 mg/g of uptake capacity at 95 °C. The selectivity for potassium versus calcium was as high as 43 at 75 °C. It shows a good capability for uptake of potassium from geothermal brine.

The uptake capacity of tin antimonate was poor. The uptake capacity of the two swelling micas was not as high as zeolites and silicotitanates.

CST has highest uptake capacity among all candidate exchangers: about 52 mg/g at 95°C in synthetic geothermal brine. However, the uptake capacity decreased to about 40 mg/g for Nb-CST when substituting the larger Nb^{5+} ion for Ti^{4+} in the CST framework. The selectivity for potassium versus calcium also decreased for the CST vs. the Nb-CST samples. There is no significant change on selectivity for potassium versus sodium. The commercial CST product, IE-911, has uptake capacity of 31 mg/g and 29 mg/g at 75°C and 95°C, respectively.

Tests of uptake capacity in actual Salton Sea geothermal brine post-mineral extraction showed a dramatic reduction in uptake capacity for CST. No changes in uptake capacity were observed for Na-XY zeolite and synthetic clinoptilolite.

Studies of kinetics for potassium uptake

Kinetic tests designed to obtain the rate of potassium uptake of each exchanger were performed by contacting a certain amount of exchanger with synthetic geothermal brine at target temperatures, and then sampling the reaction mixture as a function of uptake time. Potassium content in the exchanger was determined similarly to the batch equilibrium capacity test.

The top four exchangers from the uptake capacity tests were chosen for further tests: Na- XY zeolite 20x50, synthetic clinoptilolite, CST and Nb-CST. The kinetic properties of commercial ion exchange materials IE-911, NTS mica and NHT mica were also examined. Na-XY zeolite, synthetic clinoptilolite, CST, Nb-CST and IE-911 demonstrated a rapid uptake of potassium at 75°C and 95°C. Approximately 10 minutes of contact time is sufficient for these exchangers to extract potassium from synthetic geothermal brine. However, NTS mica and NHT mica showed a relatively slow uptake of potassium at 75°C.

Kinetic tests were also conducted for Na-XY zeolite, synthetic clinoptilolite and CST using actual post-mineral extraction Salton Sea geothermal brine at 95°C. All demonstrated a rapid uptake of potassium during the first 5 minutes. However, the uptake amount of potassium decreased with increasing time. An increase in magnesium and calcium uptake was also observed for Na-XY zeolite and synthetic clinoptilolite. CST also showed an increase of calcium uptake after 5 minutes.

Results showed that there are different uptake behaviors between synthetic geothermal brine and post-mineral extraction Salton Sea geothermal brine. The pH of these two brines might play an important role on uptake properties. Further studies are needed to examine the pH effect on potassium uptake.

Studies of adsorption isotherms

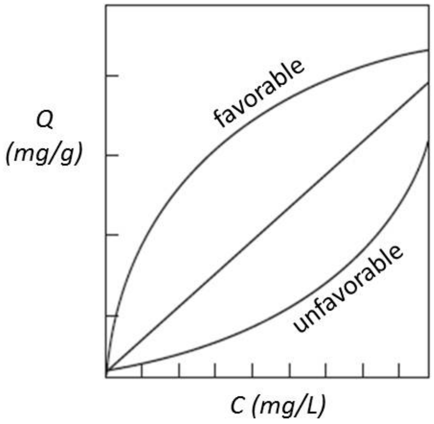
Adsorption isotherms provide useful information for estimating performance in a full-scale process. They can be used to determine the required ion exchanger dosage by plotting the amount of target ion remaining in the liquid phase versus the amount of target ion uptake in the solid phase. From the isotherm plot, the distribution coefficient can be determined as the tangent to the uptake isotherm according to the following equation:

$$K_d = \frac{Q}{c_e^l} \quad unit: mL/g$$

where Q is the adsorption capacity, that is, the amount of potassium adsorbed per unit mass of exchanger (*mg/g*) and c_e^l is the equilibrium concentration of potassium remaining in the geothermal brine (*mg/mL*). The distribution coefficient changes with the composition of the solution. The greater the distribution coefficient, the greater the preference for the ion.

The shape of the isotherm indicates the adsorption feasibility of the exchanger and factors heavily into design of bench column tests. As seen in Figure 8 below, the *favorable* curve means that it permits higher loadings at lower solution concentrations. The *unfavorable* curve only works well at high concentrations of targeted ion. The isotherm is not a property of the extractant alone, but is defined only for a specific solid to solution ratio, temperature, and solution composition.

Figure 8: Typical adsorption isotherms



Adsorption isotherms were measured by contacting the exchangers with synthetic geothermal brine with varying potassium levels at 75°C and 85°C for a few hours. The amounts of potassium in both liquid and solid phases were analyzed by inductively coupled plasma spectroscopy and the results plotted to show the adsorption isotherm for each exchanger at various temperatures.

The K_d for CST and Nb-CST increased slightly with increasing temperature. The isotherm at 95°C suggests that potassium is relatively strongly adsorbed up to 42-48 mg/g for the CST phases; thereafter there is a relatively slow increase in capacity as K increases in the brine to concentrations greater than 20,000 mg/L. This suggests that potassium may occupy multiple sites with different affinities for potassium.

In contrast to the CST phases, the zeolites show a small, but measureable decrease in K_d with increasing temperature, although the ultimate uptake capacity at high solution potassium concentrations is not significantly different.

Lab testing to strip potassium

Batch stripping tests

A batch strip test is a preliminary test for bench column operation. It is useful to screen the optimum test conditions; e.g., concentration of stripping solution, temperature, and strip time.

The batch strip tests were carried out by using potassium loaded exchangers contacted with different stripping solutions: ammonium chloride, sodium chloride and hydrochloric acid at target temperatures. Samples were taken periodically for analyzing the composition of both liquid and solid phases. The percentage of potassium stripped was calculated to examine the rate of potassium exchange for each exchanger/strip solution combination. Stripping selectivity was also calculated to obtain the overall selectivity of the K extraction process for each exchanger.

Stripping selectivity was calculated based on the following equation:

$$S_{B/A,strip} = \frac{C_{B,ex} C_{A,l}}{C_{A,ex} C_{B,l}}$$

where $C_{A,ex}$ and $C_{A,l}$ are the equilibrium concentrations of ion *A* in the exchanger and the initial concentration in the stripping solution, respectively and $C_{B,ex}$ and $C_{B,l}$ are the equilibrium concentration of ion *B* in the exchanger and the initial concentration in the stripping solution, respectively.

Batch strip tests were carried out by contacting potassium-loaded Na-XY zeolite, synthetic clinoptilolite and CST with various concentrations of ammonium chloride, sodium chloride and hydrochloric acid at target temperatures for varying time periods. Batch strip tests were initiated using saturated and 3M ammonium chloride and saturated sodium chloride solutions at room temperature for Na-XY zeolite and synthetic clinoptilolite. Potassium-loaded CST was stripped with 2.0 N and 0.5 N HCl solutions at room temperature. Results included strip efficiency and selectivity of each exchanger under various conditions.

Generally, potassium was rapidly and completely removed in under 20 min when contacted with saturated sodium chloride and ammonium chloride solutions at room temperature. Approximately 97% and 96% of potassium was leached from Na-XY zeolite and synthetic clinoptilolite, respectively. We also noticed that calcium was stripped relatively slower than potassium and sodium when using ammonium chloride as stripping solution, which suggests that K/Ca selectivity varies with time.

Graphs of selectivity versus time show that stripping selectivity for potassium versus calcium is relatively high in the first 30 minutes but significantly decreases with increasing stripping time. Because the total amount of K removed is relatively complete within the first 20 minutes, these data imply that Ca continues to be exchanged by NH_4^+ during the strip test, resulting in a lowered K/Ca selectivity. For the NaCl strip solution, the K/Ca selectivity shows a maximum at about 30 minutes of contact. These data imply that Ca is stripped more rapidly than K initially, and then K comes out more rapidly than Ca until about 30 minutes, and which point, Ca continues to exchange for Na. In addition, both zeolites show an increase in K/Ca selectivity for NaCl strip solutions with increasing strip time. The selectivity changes during stripping are consistent with the nature of the exchange sites in clinoptilolite. Clinoptilolite has at least two, and possibly 3 distinct sites where exchange cations reside. One of these sites has a higher affinity for large low-hydration cations such as Cs and K; the other site favors highly hydrated cations such as Ca and Na. It is the interplay between the incoming cation with these sites that controls the details of the stripping process. NH_4^+ behaves similarly to K, hence it is most likely to immediately exchange K from the sites that prefer low-hydration cations. In contrast, when NaCl is used as the stripping agent, it would immediately tend to exchange cations from the other site (i.e., Na, Ca), and the K/Ca selectivity would tend to increase early on in the stripping process, and then decrease as Na continues to exchange for Ca.

Potassium can be leached from CST using hydrochloric acid at room temperature. Based on the analysis of the CST solids, 98% of potassium was stripped from CST using either 2.0 N or 0.5 N of HCl solutions. The stripping selectivity for potassium versus sodium was constant at all times in both cases. However, the stripping selectivity for potassium versus calcium decreased with increasing of time when using 2.0 N HCl as stripping solution. This behavior is not as pronounced, or may not occur, when using 0.5 N HCl as stripping solution. In order to identify dissolution of the CST solid, the percentage of Ti released to the stripping solution was analyzed by ICP. Significant percentages of the Ti were leached when using 2.0 N and 0.5 N HCl stripping solutions.

Bench scale column tests

Process description

Bench scale column tests were performed to evaluate engineering parameters as well as economic viability for potassium extraction. Two ion exchangers, as-received XY zeolite and Na-XY zeolite, were selected for conducting bench scale column tests using geothermal brine at 95°C. The tests were performed using exchangers packed inside jacketed columns with 1.0 cm inside diameter and exchanger bed volumes around 10 mL at 95°C to extract potassium from hot geothermal brine feed. Once the capacity of exchangers was reached, excess geothermal brine was drained by water to wash off other ions from exchangers. The potassium was recovered from exchangers by various concentration of strip NH_4Cl solution. The exchangers were regenerated using saturated NaCl or performed next cycle without regeneration. Experimental parameters included flow rate, fluid temperature, column temperature, concentration of strip solution, and an additional regeneration cycle step.

Na-XY zeolite

A total of 20 cycles were completed using granular Na-XY zeolites with geothermal brine feeds. The dynamic capacity for potassium varied between 20 and 50 mg/mL. The average capacity for potassium was 32 mg/ml which well matched the result of batch tests discussed above. The differential pressure drop was below 3 psi which indicated no fine particles plugged the flow path. At the 4th cycle, exchangers were regenerated using saturated NaCl solution before loading geothermal brine feeds. The regeneration step resulted in an increase in the potassium capacity. The potassium capacity was able to remain in the average region without the optional regeneration step.

The potassium was recovered from exchangers using various concentration of NH_4Cl strip solution. The elution curves indicated that potassium could be recovered by using 0.5 M and1M of NH_4Cl solution at either room temperature or 95 °C. The elution time was shortened and the amount of strip solution was less when using 1M of NH_4Cl solution to recover potassium from the exchangers. The elution kinetics of impurities was different from potassium when using 0.5M of NH_4Cl as strip solution. The results indicated that the impurities could be reduced by using low concentration of strip solution. However, it took a relatively long time and large amount of strip solution to complete the strip process.

XY zeolite

A total of 10 cycles were completed using as-received XY zeolites with geothermal brine feeds. During the first 5 cycles, the dynamic capacity for potassium varied between 18 and 22 mg/ml. The average capacity for potassium was 20 mg/ml. The differential pressure drop was below 3 psi which indicated no fine particles plugged the flow path. However, due to the low capacity, the as-received XY zeolites were modified by feeding saturated NaCl solution into the column at the 6th cycle. This one-time modification process was done in the column followed by feeding geothermal brine, washing, elution and regeneration processes. The loading capacity for potassium was 50 mg/ml of cycle 6 and cycle 7. The results indicated that the as-received XY zeolites were able to be modified in the column. Once converted into Na form, the capacity increased from 20 mg/ml to 50 mg/ml. The pressure drop was below 3 psi during modification process as well as loading and elution processes.

Potassium was recovered from exchangers using various concentrations of NH_4Cl strip solution. The results were similar to the granular Na-XY zeolites.

Economic evaluation

The cost analysis for the commercial production of potassium was estimated based on the column performance of Na-XY zeolites. The target percentage of potassium recovery was 50%. The amount of zeolite needed to extract 50% of the KCl in geothermal brine with a potassium concentration 20 g/kg was calculated using the capacity of the zeolite. Process steps included loading, wash and strip cycles. The energy cost to heat and evaporate the potassium product cut to dryness was calculated. The cost of heating and evaporation proved to be prohibitive. Further optimization of the loading and elution steps to obtain a higher concentration of potassium in the product cut is required to develop a cost-effective technology.

Conclusions

The ion exchange properties of natural zeolite, modified natural zeolite, synthetic clinoptilolite, synthetic zeolite W, synthetic crystalline silicotitanate, niobium-substituted silicotitanate, and synthetic tin antimonates have been measured. Uptake capacity, uptake selectivity, stripping efficiency, stripping selectivity and overall selectivity of the exchangers were measured.

Bench column tests using two zeolites showed that we were able to selectively extract and recover potassium from geothermal brine at 95°C. However, the overall process was not cost effective which limits further scale-up. Using an ion exchange column to recover potassium from geothermal brine is applicable if one can optimize the loading and elution processes in a cost effective manner.

Conclusion

Simbol Materials is in the process of designing its first commercial plant based on the technology developed to the pilot scale during this project. The investment in the commercial plant is hundreds of millions of dollars, and construction of the commercial plant will generate hundreds of jobs. Plant construction will be completed in 2016 and the first lithium products will be shipped in 2017. The plant will have a lithium carbonate equivalent production capacity of 15,000 tonnes per year. During this development program Simbol grew from a company of about 10 people to over 60 people today. Simbol is expected to employ more than 100 people once the plant is constructed. The gross revenues from the project are expected to be approximately $ 80 to 100 million annually.

Simbol Materials' business is scaleable in the Imperial Valley region because there are eleven geothermal power plants already in operation, which allows Simbol to expand its business from one plant to multiple plants. Additionally, the scope of the resource is vast in terms of potential products such as lithium, manganese and zinc and potentially potassium.