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Modular Solid-State Thermoelectric Power Generation and High-Value Lithium Recovery From Low-Temperature Geothermal Brines

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ABSTRACT

Southern Research and its partners are developing an innovative modular solid-state thermoelectric based system designed to both generate electricity and extract high-value minerals from low-temperature geothermal brines. This system treats incoming low-temperature brine, uses a novel membrane separation process to extract water vapor from the brine, and utilizes this condensing vapor to provide a heat load to a thermoelectric generator. As water vapor is removed, the brine is concentrated, facilitating downstream extraction of high-value minerals, such as lithium, through a manganese oxide based extraction process.

The system provides both large quantities of previously inaccessible base-load renewable electricity to the grid, and high-value lithium to the critical minerals market. As all components in this system are highly modular, it can be deployed at a variety of scales dependent on quantity of thermal and mineral resources.

1. Introduction

Geothermal resources provide the opportunity for low-cost renewable baseload power generation, however only high-temperature (>150ºC) resources are currently able to be harvested economically. The thermal energy extracted from these geothermal reservoirs is converted to electricity through use of conventional steam or organic Rankine power cycles. Systems based on these power cycles are very mature and efficient under high-temperature thermal inputs, however conversion efficiency decreases substantially as resource temperature decreases. As volumetric power densities also decrease at low resource temperatures, the decreases in efficiency are accompanied by dramatic increases in power specific capital costs. Additionally, in small-scale distributed applications, these turbo-machinery based systems experience further decreases in efficiency and increases in power specific capital cost. The economics of high-value mineral extraction from geothermal brines are not attractive when the minerals are in low concentrations, as large volumes of brine are needed to be processed to extract minimal amounts of mineral. There is also a minimum total resource size that is needed to justify commercial extraction.

While neither the power generation nor mineral extraction systems are economically feasible on their own, a combined process that leverages the strengths of each can be implemented to synergistically create an economically competitive system. Southern Research has developed such a hybrid system that utilizes a thermoelectric based power generation system that can achieve disruptively high conversion efficiencies from low-temperature resources (η>5.50% at resource temperatures of ~150ºC), while extracting high-value lithium from the concentrated brine, to economically produce base-load renewable electricity from these previously inaccessible low-temperature geothermal reservoirs.

2. Overall System Design

The conceptual design for the process is shown in Figure 1. Figure 2 shows the thermodynamic and process flow model for the system. The approach consists of five critical stages: silica precipitation with a removal rate of greater than 80%, nanofiltration (NF) to remove calcium and magnesium (and other hardness) by greater than 85%, membrane distillation (MD) to increase the total dissolved solids (TDS) to greater than 30% of the overall brine composition, lithium absorption in which the sorbent capacity is greater than 50 mg lithium / g sorbent, and thermoelectric conversion with an efficiency greater than 5.5% at 100 ºC.

The system first precipitates silicates and nanofilters the brine upstream of a thermally driven direct contact membrane distillation (TD DCMD) system, as these minerals can foul the membrane and interfere with downstream lithium sorption. The hydrophobic membrane allows for water vapor to permeate, however no liquid water or dissolved solids will permeate. Water vapor permeating the membrane condenses on contact with the colder thermoelectric generator (TEG), which harnesses the latent heat given off by the water vapor to produce electricity and reject waste heat to an evaporative chilled cooling loop. As water vapor permeates the membrane, the remaining brine is concentrated allowing for high activity and selectivity of the lithium absorption process. In the mineral recovery system, a novel manganese oxide sorbent is utilized to extract lithium from the mineral rich concentrated geothermal brine effluent, which is then regenerated to produce stable lithium carbonate.

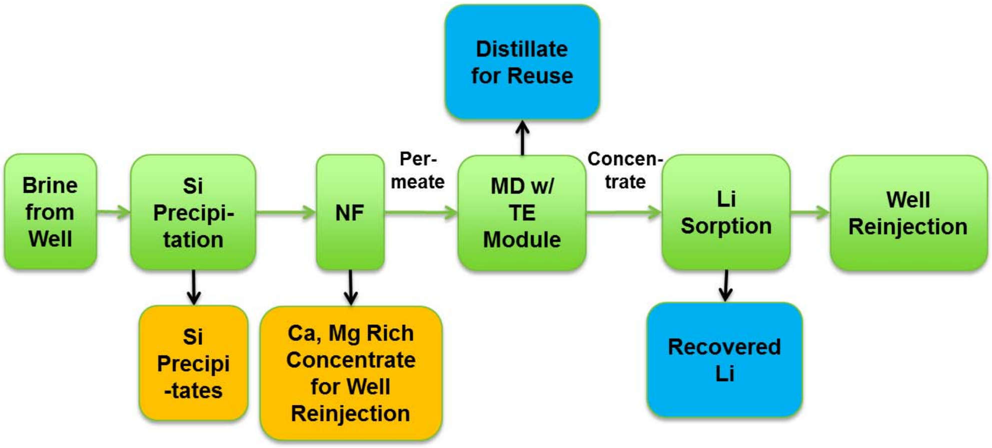

Figure 1. Single Membrane Distillation Stage Process Flow Chart.

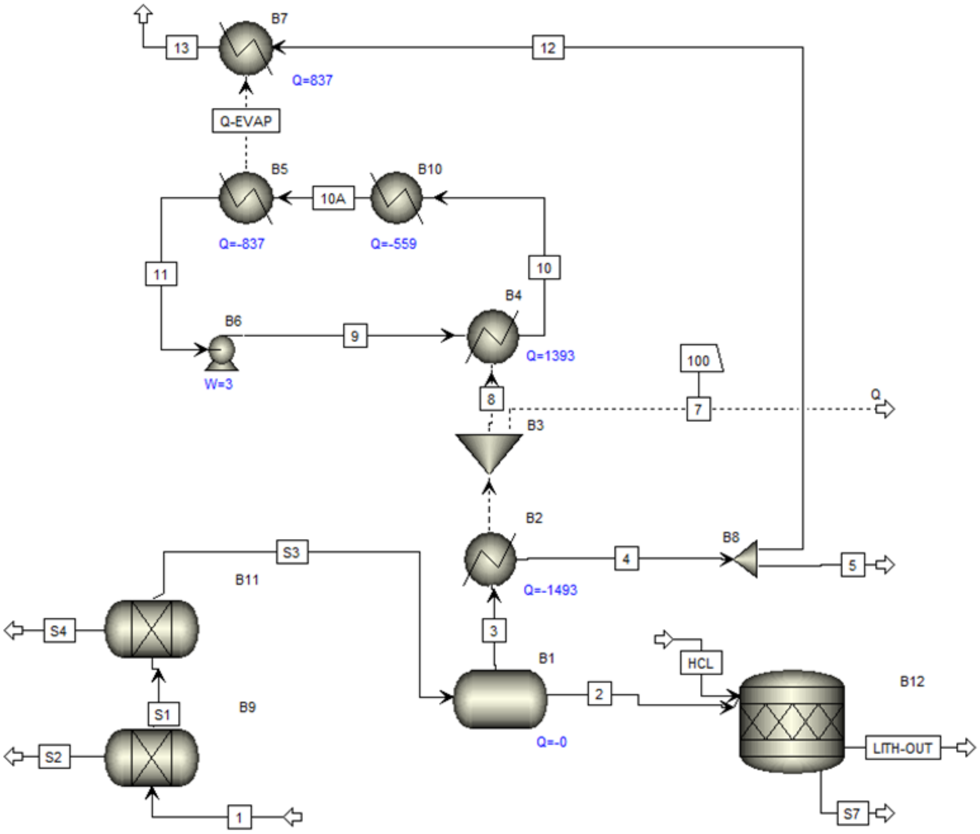

Figure 2. Thermodynamic and process flow model of integrated system

2.1 Silica Precipitation and Nanofiltration

Simulated brine formulas were prepared based on review available information. Brine pH was adjusted to 6.0 ± 0.25. The brine was adjusted to a higher pH with metal addition for optimum silica removal. Precipitants ferric and calcium were then added in varied metal-to-silica atomic ratios and allowed to react for 30 minute durations. Immediately after this duration, the solutions were filtered, and the filtrate was

Table 1. Initial Synthetic Brine Composition.

Component	Maximum Concentration (mg/L)
Mg^{2+}	245
Na^+	7466
Cl^-	11225
SO_4^{2-}	448
SiO_2	244
Li^+	29

Figure 3. Silica Removal Results.

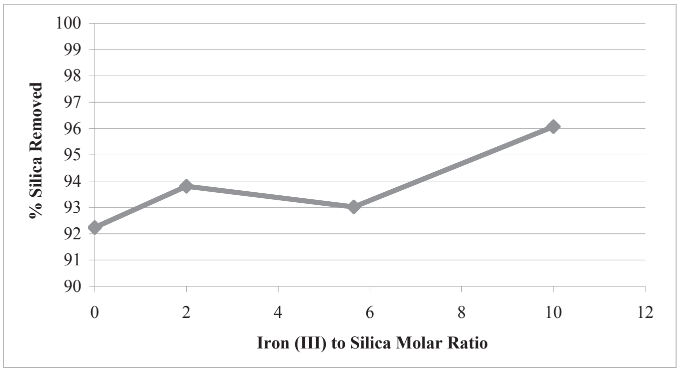

Table 2. Initial Synthetic Brine Compositions for Membrane Distillation Simulation.

Comp.	Brine A (mg/L)	Brine B (mg/L)
Ca^{2+}	20	20
Mg^{2+}	245	245
Na^+	1,700	1,684
Cl^-	3,265	3,265
Br^-	80	80
SO_4^{2-}	75	75
Si^{4+}	10	0
Li^+	2	2

Table 3. Observations and Data from Membrane Distillation Simulation

Time (min)	Brine A Residual Volume (ml)	Observations *(w/ Si)*	Brine B Residual Volume (ml)	Observations *(No Si)*
0	300	Flocculation at bottom	300	Clear
45	250	Almost clear	250	Clear
60	200	Almost clear	200	Clear
75	175	Misty	150	Clear
120	60	Misty, Flocculants settling	30	Clear
150	30	Misty, Flocculants Settling	6.0, Stopped	Clear
180	7.5	Turbid w/ Floating Precipitates		Clear

analyzed. Table 1 shows the initial brine composition for these experiments. Figure 3 show the initial silica removal results for the experiment.

2.2 Membrane Distillation

A simulation was conducted using a fluoropolymer coated polypropylene hollow fiber membrane. The brine temperatures were maintained at 90 to 100 °C, and the pH was adjusted to 6.5 for both brines. Table 2 shows the initial brine compositions used. Table 3 shows the collected and observed data.

2.3 Lithium Absorption

A spinel-lithiated manganese oxide sorbent for lithium is being optimized by the chemical and physical properties of the sorbent. The sorbent is being developed by utilizing the column filter method and the evaluation will optimize media loading (lithium mass per media mass), liquid face velocity, and liquid space velocity (empty bed contact time). Uptake capacities of competing sorbents have been benchmarked as shown in Figure 4 (Chitrakar 2001, Ryabtsev 2002).

2.4 Thermoelectric Power Generation

The design of the thermoelectric generator (TEG) module is based on the amount of heat that results from

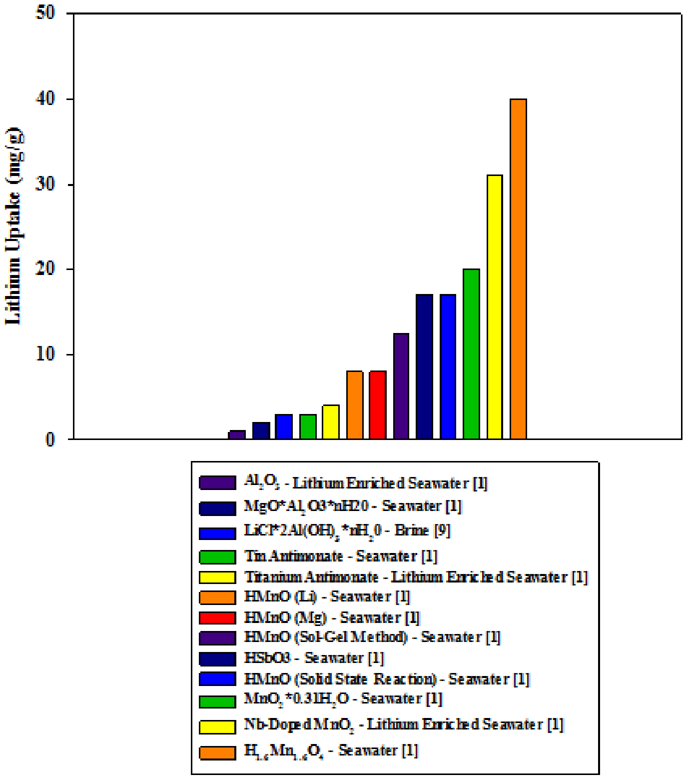

Figure 4. Lithium uptake capacities of various sorbents (Chitrakar 2001, Ryabtsev 2002).

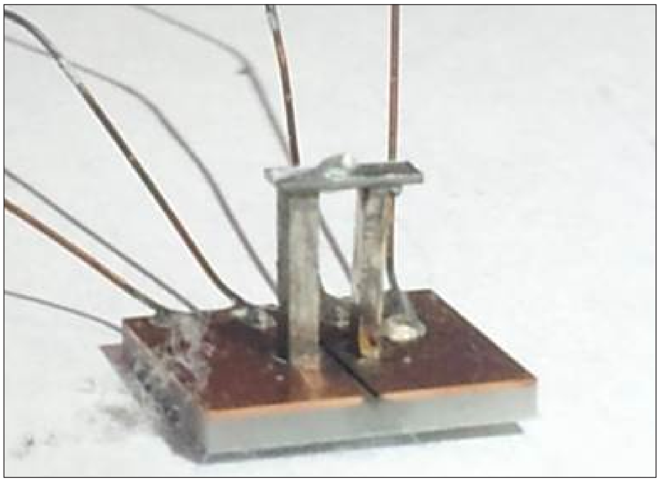

Figure 5. Individual thermoelectric p-n couple to be integrated in to TEG module.

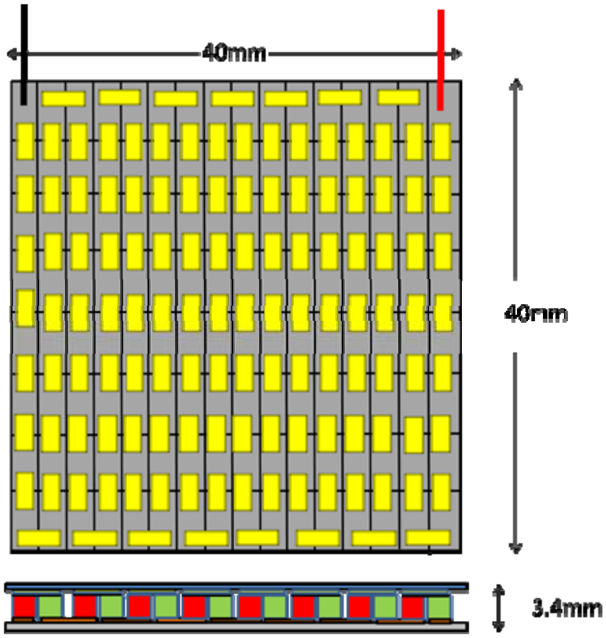

Figure 6. Schematic of single 4x4cm TEG module.

condensing the water vapor that permeates the membrane. The hot-side heat exchanger of the module is tailored to have a surface chemistry that encourages gravity removal of the condensate from the surface, thereby removing any thermal barrier to heat transfer from the water vapor and promote heat flow thorough the module. A preliminary estimate is that an electrical power density of about 4 W/cm^2 will be required for a standard TEG configuration at a ΔT of 110°C. The p- and n-type thermoelectric couples will be 1.4mm tall and 1.8mm square in the side dimension (Figure 6). Each TEG module will utilize a 49 couple configuration (Figure 6).

3. Progress/Results

Silica precipitation and mineral nanofiltration simulations have begun, and the synthetic brine composition has been finalized. Rigorous thermodynamic and process flow modeling has been completed using component level performance targets. The synthetic brine composition after the silica precipitation and nanofiltration and before the membrane system has been finalized to include the goal removal percentages. Lithium sorption simulations have begun, and the synthetic brine composition up to this stage has also been finalized. Nanostructured p- and n-type thermoelectric materials have been fabricated, p-n couples have been fabricated and tested, and the thermoelectric generation module design has been finalized.

4. Summary and Conclusion

Upon completion of the project, the resulting geothermal thermoelectric generation system will be able to cost-effectively produce base-load renewable electricity from low-temperature geothermal resources in an extremely modular fashion. Lithium concentrations in geothermal brines of any scale can be harvested. The thermoelectric generation system will be able to provide all power for mineral harvesting, allowing for off-grid operation in remote locations. The thermoelectric power generation and sorption based lithium extraction processes will work synergistically, allowing the hybrid system to perform economically under conditions where neither system could succeed on its own.

5. Acknowledgements

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6. References

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