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SOUTHERN RESEARCH

NOVUS ENERGY TECHNOLOGIES

Thermoelectric Generation System Development

CARUS®

Sorbent Development

AMT

Membrane Distillation Development

Cyrq energy

Geothermal Power Consulting

Geothermal Thermoelectric Generation (G-TEG) with Integrated Temperature Driven Membrane Distillation and Novel Manganese Oxide Lithium Extraction

Project Officer: Tim Reinhardt
Total Project Funding: $500,000 (with 10% cost share)
May 12, 2015

Principal Investigators:
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Southern Research

Track Name - Low Temp: Mineral Recovery

Relevance/Impact of Research

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Challenges being addressed by this project:

1) Conventional steam or organic Rankine power cycles achieve very ***low conversion efficiencies*** below T_{hot}=150C

2) Power ***specific capital costs*** of steam or organic Rankine power cycle systems increase dramatically below T_{hot}=150C

3) Power specific capital costs increase, and conversion efficiencies decrease, when using ***turbo-machinery based systems at distributed scales***

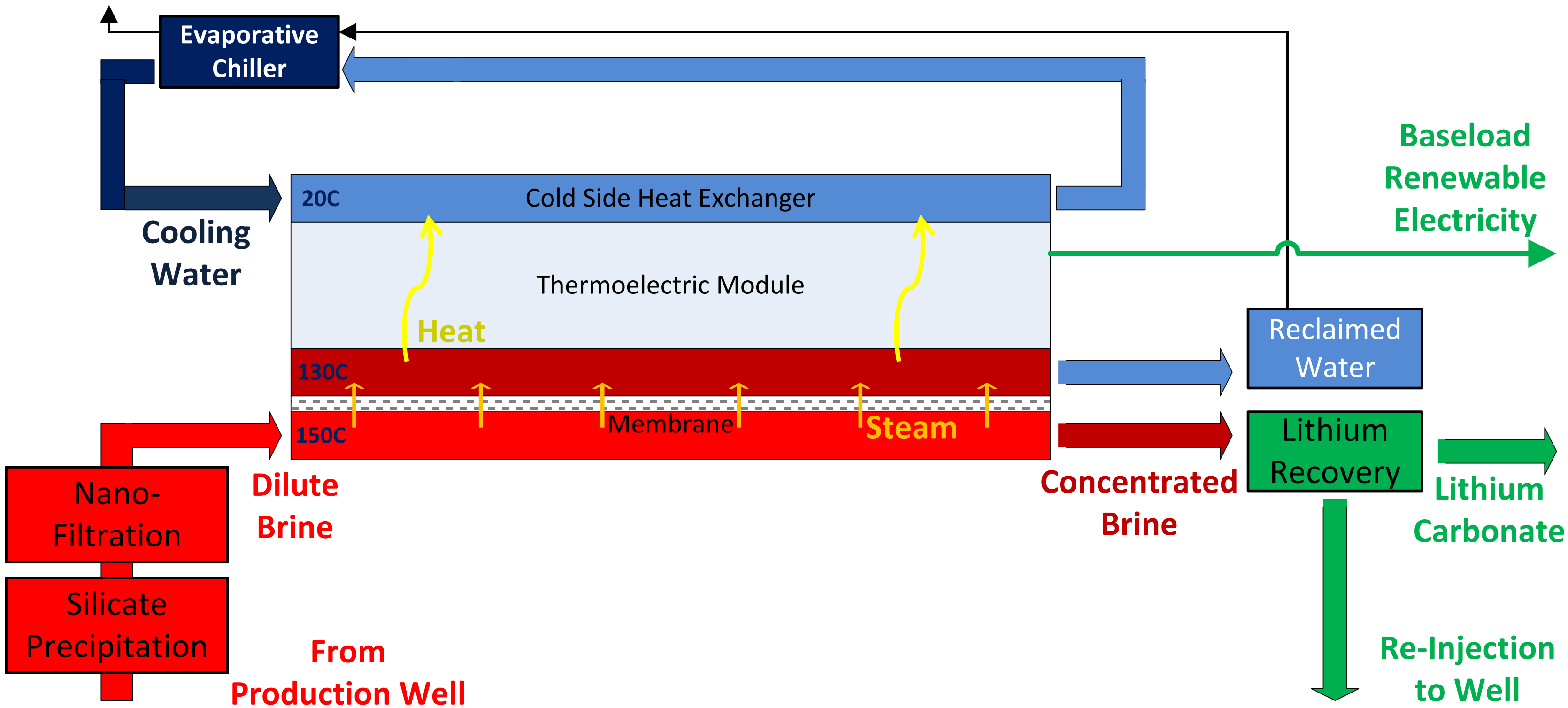
4) Economics of high-value mineral extraction from geothermal brines are ***not attractive when the mineral concentrations are low***

5) Scales of high-value mineral extraction operations ***do not always align well*** with scales of power generation systems

6) Large amounts of ***contaminants need to be removed*** from brines, and ***extraction processes optimized***, to allow for economic high-value mineral recovery

Project Objectives

1) Develop and validate a thermoelectric based power generation system that can achieve disruptively high conversion efficiencies from low-temperature resources (η>5.50% @ ΔT=100C), to economically produce baseload renewable electricity
2) Extract lithium from the filtered and concentrated brine to provide additional system revenue and to increase supply for this critical mineral



Project Design & Approach:

1) Rigorous system-wide thermodynamic and process flow modeling to simulate component interactions and quantify system metrics (Q1)
2) Individual component refinement and testing to achieve component level metrics (Q1-Q2)
3) Simultaneous testing of two integrated subsystems (Q3-4)
    1) Integrated testing of silica precipitation, nanofiltration, membrane distillation, and lithium extraction subsystem using synthetic geothermal brine
    2) Integrated testing of membrane distillation and thermoelectric power generation subsystem using pressurized hot water
4) Integration of empirically collected data into system-wide thermodynamic and process flow model, updated calculation of system metrics (Q4)
5) Development of techno-economic analysis, feasibility study, and business plan for evolution of system to integrated field testing (Q4)

Scientific/Technical Approach

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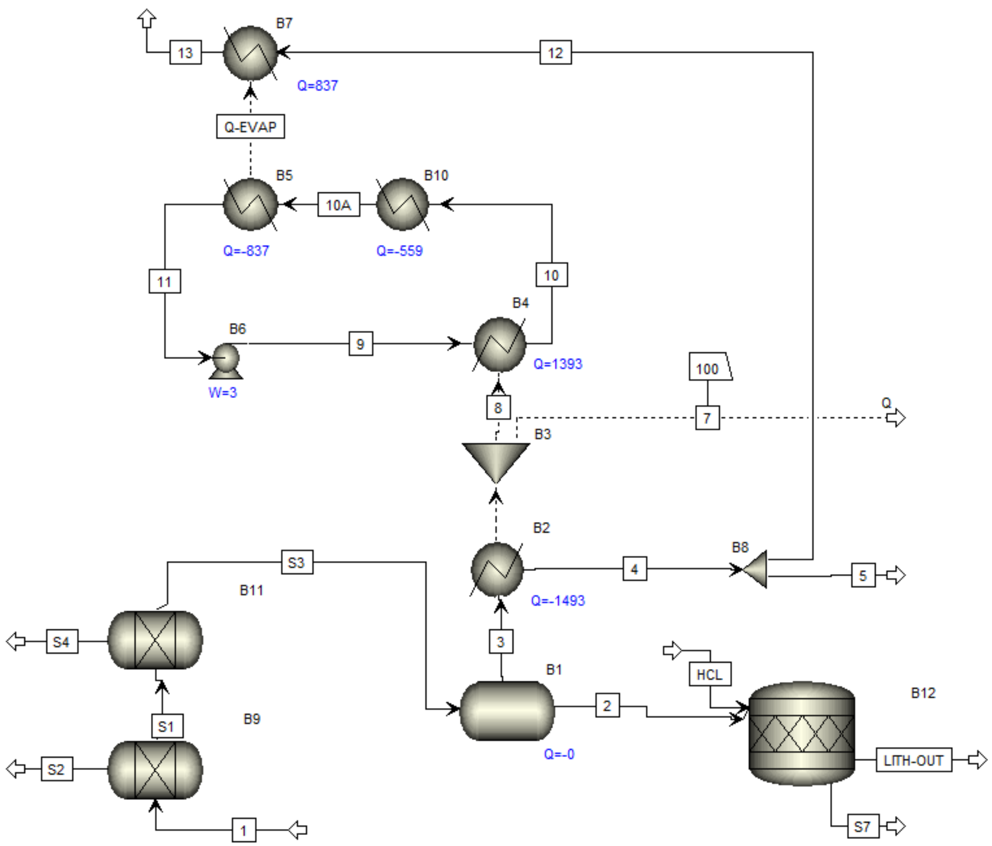
Thermodynamic and Process Flow Modeling *(Q1)*



Component Level Testing Metrics *(Q1-Q2)*

- Silica Precipitation
  - Silica removal > 80%
- Nanofiltration
  - Ca and Mg removal > 85%
- Membrane Distillation
  - Total dissolved solids > 30%
- Lithium Absorption
  - Lithium sorbent capacity > 50 mg/g
- Thermoelectric Conversion
  - $\eta > 5.50\%$ @ $\Delta T = 100C$

Silica Precipitation Experimental Design

1. Simulated brine formulas were prepared based on review of existing literature
2. Precipitants (Al^{3+}, Fe^{3+}, and Mg^{2+}) were added in metal-to-silica atomic ratios of approximately 1:2, 1:1, and 2:1
3. Brine pH was adjusted to 10.25 ± 0.25 for optimal precipitation conditions
4. Solutions gently mixed for a 30 minute reaction duration
5. Immediately after 30 minutes, solutions were filtered and the filtrate was sent for analysis

Component	Brine Level 1 (mg/L)	Brine Level 2 (mg/L)	Brine Level 3 (mg/L)	Brine Level 4 (mg/L)
Mg^{2+}	20	95	170	245
Na^{+}	1700	3622	5544	7466
Cl^{-}	2856	6284	9713	13141
SO_4^{2-}	75	200	324	448
Si^{4+}	10	36	63	89
Li^{+}	2	11	20	29

Scientific/Technical Approach

Membrane Distillation Simulation

- Fluoropolymer coated polypropylene hollow fiber membrane
- Simulated brines as shown below were prepared
- Simulated brine temperature was maintained at 90 – 100ºC
- pH was adjusted to 6.5 for Brine A and B

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

Time (min)	Brine A Residual Volume (ml)	Observations *(w/ Si)*	Brine B Residual Volume (ml)	Observatio ns *(No Si)*
0.0	300.0	Flocculation at bottom	300.0	Clear
45.0	250.0	Almost clear	250.0	Clear
60.0	200.0	Almost clear	200.0	Clear
75.0	175.0	Misty	150.0	Clear
120.0	60.0	Misty Flocculants settling	30.0	Clear
150.0	30.0	Misty, Flocculants Settling	6.0,Stopped	Clear
180.0	7.5	Turbid w/ Floating Precipitates		Clear

Lithium Absorption

- **Develop an optimized manganese oxide sorbent for lithium by varying:**
  - Chemical structure
  - Surface structure
  - Isoelectric point
  - Particle size
  - Porous area

- **Baseline evaluation of lithium sorption utilizing the column filter method for delithiated $LiMn_2O_4$**
  - Optimize media loading, mass lithium / mass of media
  - Optimize liquid face velocity
  - Optimize liquid space velocity (empty bed contact time)

- **Prepare and evaluate MnO_x’s of various structures utilizing simulated geothermal brines**

Lithium Absorption

- Simulated brine recipes were designed based on a review of existing literature. In addition, the concentrations found in literature were multiplied to account for the removals of each process by the following factors: Si^{4+} by 0.1, divalent ions by 0.3, and all other ions by 10
- Simulated brine recipes assume that removal targets for Ca^{2+}, Mg^{2+}, and Si^{4+} are achieved in upstream processes
- Temperature and pH of simulated brines will be varied

Comp.	Brine Level 1 (mg/L)	Brine Level 2 (mg/L)	Brine Level 3 (mg/L)	Brine Level 4 (mg/L)
Mg^{2+}	60	285	510	735
Na^{+}	11,392	24,842	38,291	51,740
Cl^{-}	19,094	42,885	66,675	90,465
SO_4^{2-}	750	1,988	3,225	4,463
Si^{4+}	10	36	63	89
Li^{+}	20	108	196	284

Scientific/Technical Approach

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Low-Temperature Thermoelectric Generator

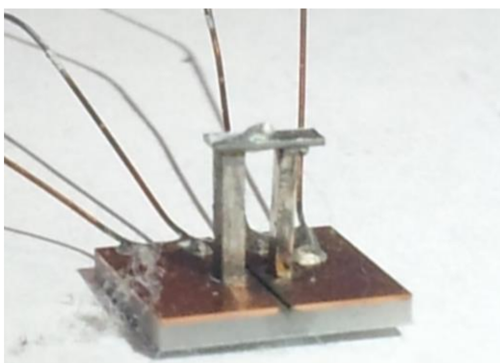
- Thermal efficiency of a TEG:

$$\eta\,(\Delta T) = \frac{P_{out}(\Delta T)}{Q_{TE}(\Delta T)}$$

- The average material ZT can be estimated as:

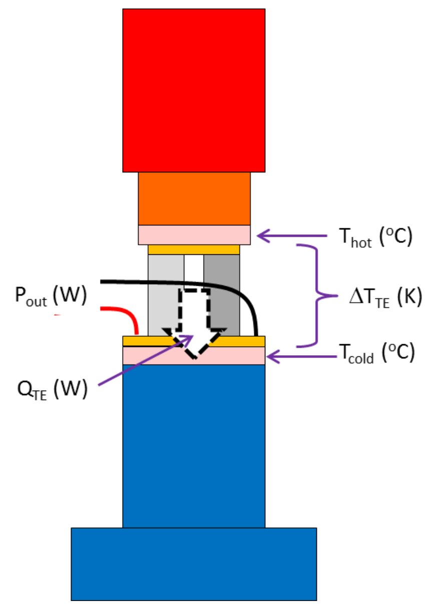
$$ZT_{ave} = \left[\frac{1 + \frac{\eta T_c}{\Delta T}}{1 - \frac{\eta T_H}{\Delta T}}\right]^2 - 1$$

Individual P-N Couple

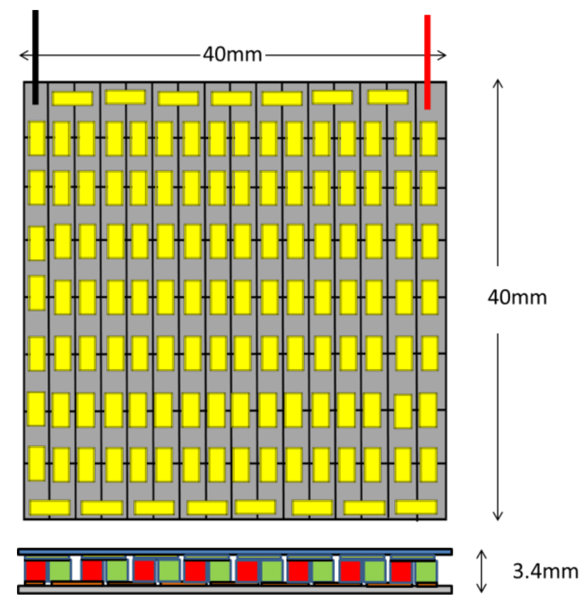


Dimensions	n-type	p-type
x (mm)	1.00	1.00
y (mm)	0.66	0.89
l (mm)	5.00	5.00
a (cm^2)	6.60E-03	8.90E-03
element l/a (cm^{-1})	75.8	56.2
couple l/a (cm^{-1})	32.3	

Couple Efficiency Testing



TEG Module – 127 Couples



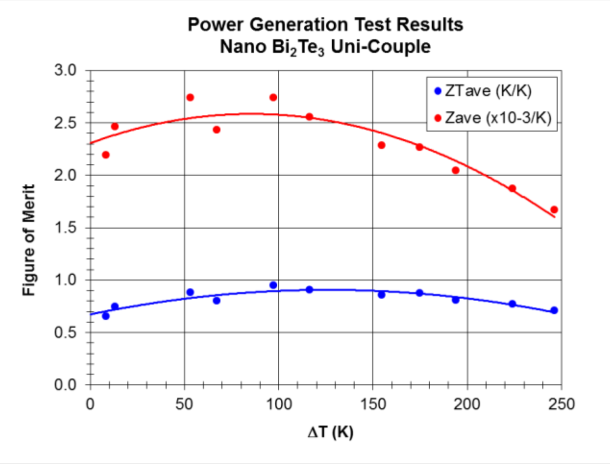
Low-Temperature Thermoelectric Generator

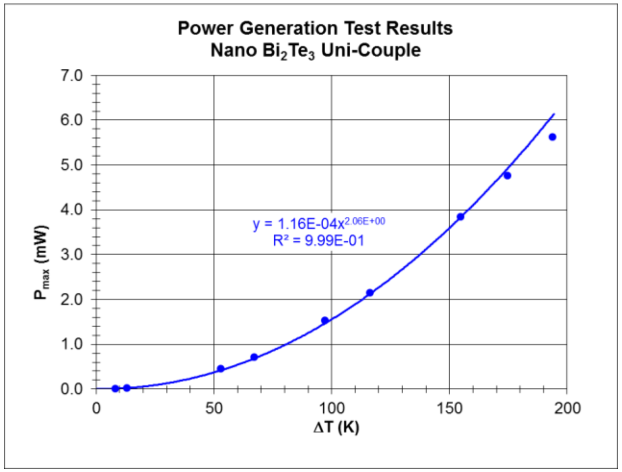
Individual Couple Testing Results

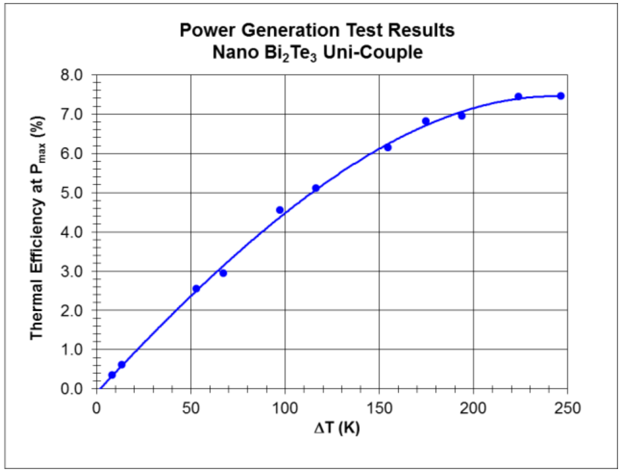
T_{hot} (°C)	T_{cold} (°C)	T_{hot} (K)	T_{cold} (K)	ΔT (K)	T_{mean} (K)	Q_{out} (mW)	Q_{rad} (mW)	V_{max} (mV)	I_{max} (mA)	R_{int} (Ω)	P_{max} (mW)	Q_{TE} (mW)	Eff. (%)	ZT_{ave} (K/K)
				0.0				0.00	0.00					
30.5	**22.3**	304	295	8.2	299.6	2.5	0.14	1.11	7.46	0.149	0.01	2.4	**0.34**	**0.66**
35.6	**22.4**	309	296	13.3	302.2	4.3	0.23	1.92	12.79	0.150	0.02	4.1	**0.60**	**0.74**
76.0	**22.9**	349	296	53.0	322.7	18	1.12	8.55	52.97	0.161	0.45	17.7	**2.55**	**0.89**
90.4	**23.1**	364	296	67.2	329.9	25	1.52	10.88	65.52	0.166	0.71	24.3	**2.94**	**0.80**
120.9	**23.6**	394	297	97.3	345.4	35	2.55	16.37	93.71	0.175	1.53	33.7	**4.55**	**0.95**
140.2	**24.0**	413	297	116.3	355.3	43	3.33	19.70	108.92	0.181	2.15	42.0	**5.11**	**0.91**
179.7	**24.9**	453	298	154.8	375.5	64	5.32	27.28	140.75	0.194	3.84	62.5	**6.14**	**0.86**
200.0	**25.3**	473	298	174.7	385.9	72	6.57	30.91	154.07	0.201	4.76	69.8	**6.82**	**0.88**
219.7	**25.8**	493	299	193.9	396.0	83	7.94	34.14	164.71	0.207	5.62	80.9	**6.95**	**0.81**
250.6	**26.7**	524	300	223.9	411.8	99	10.45	39.40	181.13	0.217	7.14	96.0	**7.44**	**0.77**
273.9	**27.5**	547	301	246.3	423.9	115	12.66	43.03	192.00	0.224	8.26	110.9	**7.45**	**0.71**
299.3	**28.3**	572	301	271.0	437.0	133	15.42	47.88	205.95	0.232	9.86	127.5	**7.73**	**0.68**
317.0	**29.6**	590	303	287.3	446.5	141	17.56	49.49	209.01	0.237	10.34	134.1	**7.71**	**0.65**
324.9	**29.9**	598	303	295.0	450.6	162	18.59	51.72	217.98	0.237	11.27	154.7	**7.29**	**0.59**
339.5	**30.6**	613	304	308.9	458.3	173	20.60	54.14	225.27	0.240	12.20	164.2	**7.43**	**0.58**

Low-Temperature Thermoelectric Generator

Individual Couple Testing Results







Improvements will be implemented to increase the conversion efficiency to the target value of 5.5% at ΔT=100C

- Material process refinement to:
  - Reduce metallic contamination
  - Improve doping level control and uniformity
  - Improve nano-structure density and uniformity of distribution
- Device process refinement to:
  - Control of parasitic losses due to ohmic contacts
  - Optimize relative aspect ratio of the p and n elements to improve couple performance

Accomplishments, Results and Progress

Technical Accomplishments/Progress at end of Q2:

- Rigorous thermodynamic and process flow modeling completed, using component level performance targets
- Silica precipitation and mineral nanofiltration simulations begun, synthetic brine composition finalized
- Membrane distillation system modified to include 2-stage process. High-temperature (>100C) ceramic membrane upstream, and low-temperature (<100C) polymer membrane distillation system downstream. Synthetic brine composition, after silica precipitation and mineral nanofiltration, entering membrane system finalized
- Lithium sorption simulations begun. Synthetic brine composition, after treatment and concentration, entering mineral extraction system finalized
- Nanostructured p- and n-type thermoelectric materials fabricated, p-n couples fabricated and tested, TEG module design finalized

Original Planned Milestone/ Technical Accomplishment	Actual Milestone/Technical Accomplishment	Date Completed
Silica precipitation > 80%		
Ca and Mg removal > 85%		
MD to > 30% total dissolved solids		
Lithium sorption > 50 mg/g		
TEG **η>5.50% @ ΔT=100C**		

Future Directions

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- Expected outcome
  - Validated testing of two integrated subsystems, and fully integrated thermodynamic and process flow modeling; TEA and business plan to document progress
- Deployment strategy
  - Extremely modular system can be deployed at virtually any scale; subsequent to successful bench scale testing, field testing of fully integrated system will be pursued
- Key activities for the rest of FY2015 and to project completion
  - Complete component testing of precipitation, nanofiltration, membrane distillation, lithium sorption, and TEG module
  - Assemble, test, and refine two integrated subsystems
  - Integrate subsystem empirical data into thermodynamic and process flow model
  - Finalize techno-economic analysis and business plan to evolve project to field demonstration

Milestone or Go/No-Go	Status & Expected Completion Date
Silica precipitation > 80%	Design complete, equipment being assembled, will complete in Q3
Ca and Mg removal > 85%	Design complete, equipment being assembled, will complete in Q3
MD to > 30% total dissolved solids	Low-temperature polymer being tested, high-temperature ceramic membrane design finalized, testing will be complete in Q3
Lithium sorption > 50 mg/g	Synthetic brine composition finalized, final sorbent being prepared, testing will be completed in Q3
TEG **η>5.50% @ ΔT=100C**	p- and n-type materials fabricated, couples being fabricated and tested, module will be fabricated and tested in Q3

Mandatory Summary Slide

- G-TEG system can cost-effectively produce baseload renewable electricity from low-temperature geothermal resources, in extremely modular fashion
  - Lithium-rich brine resources of any scale can be harvested
  - TEG system can provide all power for mineral harvesting, allowing for off-grid operation in remote locations
- Thermoelectric power generation and sorption based lithium extraction processes work synergistically, allowing hybrid system to perform economically under conditions where neither system could succeed on its own