Final Report

Federal Agency and Organization: DOE EERE – Geothermal Technologies Program

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***The Prime Recipient certifies that the information provided in this report is accurate and complete as of the date shown.**

Executive Summary

The purpose of this work was to complete a proof of concept study to apply and validate a novel method developed by Tusaar for the capture and recovery of rare earth elements (known as REEs) and other critical and valuable elements from geothermal waters produced from deep within the earth. Geothermal water provides heat for power production at many geothermal power plants in the western United States.

The target elements, the REEs, are vital to modern day electronics, batteries, motors, automobiles and many other consumer favorites and necessities. Currently there are no domestic sources of REEs while domestic and international demand for the products they are used in continues to rise. Many of the REEs are considered "strategically" important. A secure supply of REEs in the USA would benefit consumers and the country at large. A new method to recover these REEs from geothermal waters used at existing geothermal power plants around the country is a high priority and would benefit consumers and the USA.

The result of this project was the successful development and demonstration of an integrated process for removal and recovery of the REEs from synthetic geothermal brines on a small laboratory scale. The work included preparation of model geothermal brines to test, selection of the most effective proprietary sorbent media to capture the REEs and testing of the media under a variety of potential operating conditions.

Geothermal brines are generally very high in salt content and contain a wide range of elements and anions associated with the rock layers from which they are produced. Processing the geothermal water is difficult because it is corrosive and the dissolved minerals in the water precipitate easily once the temperature and pressure change. No commercial technologies have been shown to be effective or robust enough under these geothermal brine conditions to be commercially viable for removal of REEs. Technologies including ion exchange, traditional sorptive media and membrane concentration are too expensive, difficult or impossible to regenerate and easily rendered ineffective under these working conditions.

The work completed during this project has demonstrated that a selective media that is robust and durable under the conditions associated with geothermal brines is possible. The initial economic analysis indicates that the process would not be financially viable at current market prices for REEs. The world market price for REEs has been turbulent over the past several years and are currently near historical lows. Historical trends and market forces suggest that the world price is stabilizing and will rise. At the same time, further development has the potential to reduce the costs associated with the technology.

This work opened the door to the idea that a large scale process for removal and recovery of REEs from geothermal brines is possible. Upward price pressures coupled with technology improvements suggest that this process has the opportunity to be commercially successful at a point in the future.

Project Overview

Results

The purpose of this work was to complete a proof of concept study to apply and validate a novel sorptive media and new method proposed by Tusaar for the removal of rare earth elements (known as REEs) from geothermal waters produced for energy extraction at existing or future geothermal power plant locations.

The results of this project were the successful use of the Tusaar media and the demonstration of an integrated process for capture and recovery of the REEs from synthetic geothermal waters on a laboratory scale. The work included preparation of model geothermal brines to test, selection of the most effective proprietary sorbent media to use, exploration of the impact of critical variables on the ability of the media to sorb the target REEs, testing of the media under a variety of potential operating conditions designed to mimic a perceived commercial process and the successful recovery of the REEs from the media after sorption was complete.

The media proved to be effective and robust in the modeled geothermal environment. While loss of ligand from the media surface shortened life cycle in use, it was found that the column could be regenerated many times and reused with no measurable degradation of performance. The ligand recovered from the catch column could be used to reload the sorption column. The overall process that was conceived and experimentally explored was designed to accommodate a continuous flow of hot brine containing REEs. This was accomplished using two parallel process lines configured to allow for continuous operation and minimum down time. A commercial operation was conceived from the results and a techno economic analysis completed to assess the potential commercial opportunity.

The results of this work opened the door to the idea that a large scale process for removal and recovery of REEs from geothermal brines was possible. Further, upward price pressures coupled with technology improvements indicate that this process has the opportunity to be commercially successful at a point in the future. There are many obstacles to overcome and advancing any process to commercial scale has risks that cannot be anticipated. At this point in development, the media and associated process characterized by this project are ready for pilot scale development for further refinement and understanding.

Techno Economic Analysis

An integrated process utilizing an innovative sorbent to sequester and recover REEs from geothermal process water at commercial geothermal energy production sites was demonstrated at the bench level. The work included preparation of model geothermal brines and evaluation of three proprietary sorbent media under a variety of potential operating conditions which included temperature, pH, and brine contact time with the media. Conditions for optimal stripping or removal of the REE once sorbed on the media and media regeneration were also investigated. Additional bench-scale experiments were conducted to gather insights into the sorbent lifecycle and the sorbents effectiveness for individual REEs found in the geothermal brines.

Data from these experiments were used to validate conceptual commercial-scale processes that would be located at the water source within the geothermal energy production site. Results suggest that the greatest process cost variables are the REE concentration within the geothermal water, contact time between the media and the geothermal water, and the method for media stripping and regeneration.

The preliminary cost estimate predicts an operating cost for REE concentrate at $89.90/kg of REEs compared to a blended current market value of $15.90/kg. Operational efficiencies and market improvement are needed to close this gap. A more favorable mix of individual REEs in brine could easily overcome this variance. The cost to produce the REE concentrate is not dependent upon the specific REE found in the brine.

The preliminary capital estimate to construct a commercial plant is $2,815,000. With a 50% variance the projected cost could range upward to $4,272,500. Media startup costs of $4,637,145 must also be included. These numbers assume that the facility will be located within the foot print of an existing geothermal power

plant and take advantage of existing infrastructure and capabilities. Increased capital costs would help reduce operating costs as the process matures and is perfected.

Project Accomplishments Overview

The designed proof of concept study was completed. Tusaar Media 1 -50+100 was found to effectively remove the REEs from high salt content synthetic brine modeled after known geothermal brine associated with existing power production in California. The REEs sequestered by the media could be quantitatively removed and the media reused. A complete process was designed using the media that has the potential to be scaled to commercial levels. The estimated costs based upon the experimental data and reasonable assumptions proved to be high under current market conditions. However, the production cost estimates were low enough that projected market trends and expected process cost improvements warrant further investigation of the process at the pilot scale.

The accomplishments achieved by the research and development reported here are first measured by the SOPO Tasks and Milestones, the objectives. Secondarily, the accomplishments are measured by unanticipated learnings or results from the work and future implications.

The original hypotheses for this work was based upon the known and suspected sorptive properties of the Tusaar media over a wide range of conditions. Tusaar proposed that at least one of their media would be effective at selective removal of REEs from high salt content geothermal brines. Further, the sequestered REEs could be efficiently removed from the media and the media reused many times without significant degradation. A process could then be developed that had the potential to be scaled to the commercial level and ultimately be a cost effective domestic source for REEs

The experimental approach was based upon deploying a small scale microcosm shaker tests to rapidly examine a range of variables. The experimental design was iterative in nature as new findings opened new questions requiring additional experiments to find the ultimate answers. After the completion of the exploratory microcosm shaker experiments the research moved into column sorption studies focused initially on the identified key variables.

The initial round of column studies provided data that was incorporated into an initial experimental design for a continuous process for sorption and stripping of REEs from the synthetic brines. Ultimately a third step, media regeneration, was added. The load/strip/regenerate process model helped identify a number of key variables and explore their impacts on the complete process. Following the iterative approach of exploring key variables in a full process setting an optimized process was designed and tested.

Ultimately the complete process was sequentially repeated to explore the capacity of the media and its ability to be regenerated and reused. Finally, the complete process was completed to model the process under assumed commercial conditions.

The following simplified outline details the Objectives as the Tasks and Milestones taken from the SOPO. These guide a more detailed discussion which follows the outline.

Goals and Objectives - Abbreviated SOPO Outline

Task 1.0: Initiation
Task Summary: Conduct literature survey, choose and formulate two distinct but representative synthetic analogs (models) of geothermal brine (GB) compositions and develop an initial experimental design.

- Milestone 1.2.1 Successful selection & formulation of two GB models (solution stability≥48, ±10%)
- Milestone 1.2.2 Establish definitions for sorption and recovery capacity goals (%wt./wt.)
- Milestone 1.3.1 Complete the initial experimental design

Task 2.0: Exploration of Process Requirements (M3-M9)
Task Summary: Ascertain the best ranges of temperature, pH, concentration, media/ligand type, and media loading rates to optimize for adsorption capacity, selectivity, and recovery efficiency;

- Milestone for Task 2: GO/NO-GO Decision Point (M10), The Go decision will be based on Tusaar's successful demonstration of media capacity and recovery for at least one metal of value in the model brine.

Task 3.0: Process Optimization (M11-M13)
Task Summary: Continue work initiated in Phase 1A, optimize variables and begin the preliminary techno-economic estimates

- Milestone for Task 3: Completion of the preliminary economic analysis

Task 4.0: Verification (M14-M17)
Task Summary: Verify process optimization results at volume ~12 mL and larger ~ volume 150 mL and complete/conclude the techno-economic analysis

- Milestone for Task 4: Completion of the Techno-Economic Analysis, include conceptualized commercial process diagrams, include characterization of unit operations and size including a design for a pilot facility.

Task 5.0: Reporting (M17-M18)
Task Summary: Completed reporting in accordance with the Federal Assistance Reporting Requirements document.

Project Accomplishments detail

Specific accomplishments that highlight the complete development effort of this project are addressed specifically toward the SOPO requirements and the overall objectives of the work. This discussion is followed by a general discussion of unanticipated findings that impacted the development process and the actual research accomplished against the plan.

Task 1.0: Initiation
Task Summary: Conduct literature survey, choose and formulate two distinct but representative synthetic analogs (models) of geothermal brine (GB) compositions and develop an initial experimental design matrix.

- Milestone 1.2.1 Successful selection & formulation of two GB models (solution stability≥48, ±10%)

Tusaar conducted a literature survey of known and investigated geothermal waters. Tusaar formulated two distinct representative synthetic brine models that underwent chemical analysis for verification of composition and stability. Over a period of months the stability and nature of the original formula were re-investigated and new brine formulas created. Eventually a final, single brine, was selected for the final development work leading to the proof of concept sorptive column work and the techno economic analysis. This brine, Brine 1CF was compared to one natural brine and one comparative DOE provided brine and proved to be the most complex of the three and most similar to what the literature data suggested.

The following charts shows the comparison of the brine composition as the work progressed.

TABLE 1 - Synthetic brine #1				
Elements	Original Brine 1 Calc values ppm*	Brine 1M Experimental ppm*	Brine 1C Experimental ppm*	Brine 1CF Experimental ppm*
Na	45700	43300	45700	51100
K	17400	17400	20300	17800
Ca	14300	14300	14500	14600
Mn	720	0	760	710
Ba	180	0	190	180
Sr	410	0	400	410
Zn	280	0	320	290
Li	160	0	140	150
Mg	160	0	160	150
Fe	470	0	660	0
B	180	0	180	0
Pb	50	0	0	0
Si	270	0	0	0
La	2	2	2	2
Ce	2	2	2	2
Pr	2	2	2	2
Nd	2	2	2	2
Eu	2	2	2	2
Tb	2	2	2	2
Dy	2	2	2	2
* Formula prepared to original specification as described; values reported as experimentally determined.				

- Milestone 1.2.2 Establish definitions for sorption and recovery capacity goals (%wt./wt.)

The first work performed confirmed that the media candidates were effective for the sorption of single elements and mixtures of REEs from the model brines. This lead to development of standard microcosm tests to examine sorption properties under a large variety of conditions and materials. Moving from single REEs to mixtures the apparent sorption capacity within the microcosm shaker test environment was established. These values established our goal for what might be accomplished within the more complex column sorption format. Values above 1.5 % by wt. were observed and an apparent capacity of 1.0% by wt. was targeted.

The original work established a capacity for europium (Eu) on Media derived from the 90 minute microcosm shaker test at 22ºC. This became the qualifying test for the media throughout the project.

Media Eu Capacity - 90 Minute Kinetic Shaker Test		
	Solution:Media Ratio 75:1	
	500 ppm Eu	
	Total Capacity (wt/wt)	Average Kd (ml/g)
Media 1	1.760%	58.7
Media 2	1.360%	49.4

Later work established a similar capacity for our complete REE7 mix at 22ºC as determined by REE breakthrough as measured in the effluent from a column loading experiment. This confirmed the expected capacity range.

Flow Rate Breakthrough Sorption Study			
		Media -50+100	
		Brine 1CF	
		Load 200 ppm REE7	
		~22°C	
	Contact time minutes	**10g Column Equivalent Flow Rates in ml/min**	**Capacity**
Run 1	3.8	4.4	1.57%
Run 2	6.1	2.75	1.84%
Run 3	7.1	2.36	1.64%
Average			**1.68%**

As the test environment advanced toward the simulated commercial operating conditions, the media capacity was also determined. Two experiments in sequence were performed under the following conditions.

- 8.9g Media 1 -50+100
- Brine 1CF
- 1000 ml load 100ppm REE7
- 90°C
- 1 ml/min flow rate, 14.8 min contact time

In both experiments the loaded capacity was 100% of the REE offered to the media, 1.1 % wt./wt. It was concluded that an expected commercial capacity for planning purposed would be >1.0 % wt./wt.

The REEs sequestered by the media were quantitatively removed from the media. This was confirmed based stripping the media to recover the REEs in the shaker test environment and the column environment.

The amount of acid used and the contact time (or flow rate) were important variables. For the in-column (in situ) stripping technique, the molarity of the acid was a key variable and a significant research target during the column optimization work. At the same time, temperature during the stripping operation was important. Under sorption conditions at 90°C there was a potential to produce NOx gas as oxidation of the nitric acid was observed. Ultimately the stripping temperature was reduced to 40°C for safety reasons.

- Milestone 1.3.1 Complete the initial experimental design

REE concentration, solution pH and solution temperature were selected as the three key variables to be explored in a matrix experimental design. Secondary outcomes to be part of the screening process were selected; sorbent loading and brine composition. The final experimental design selected was a 34 component experimental grid. Completion of the grid was the design trigger to move to the next phase in the development plan. In essence, the grid approach allowed for an iterative approach to evaluate which experiments were positioned to advance the plan most efficiently.

The following chart depicts the complete matrix describing the initial microcosm shaker test targets and its completion.

Milestone 1.3.1 Master Matrix - Status Update			
	REE Conentration	Brine pH	Sorption Temperature
Media 1	Complete	Complete	Complete
Media 2	*NA	*NA	Washed out

Milestone 1.3.1 REE Concentration			
REE Conc. Ppm	Media 1 (+50 mesh)	Media 1 (-50 +100 mesh)**	Media 2
0.2	Complete	Complete	NA*
2	Complete	Complete	NA*
20	Complete	Complete	NA*

Milestone 1.3.1 Brine pH		
pH	Media 1	Media 2
5.5	Complete	NA*
4.5	Complete	NA*
3.5	Complete	Complete

Milestone 1.3.1 Sorption Temperature		
	Media 1	Media 2
Ambient	Complete	Complete
70oC	Complete	Washed out

* NA = not applicable because Media 2 was not acceptable at 70oC

** New Media based upon particle size substituted for Media 2

Task 2.0: Exploration of Process Requirements

Task Summary: Ascertain the best ranges of: temperature, pH, concentration, media/ligand type, and media loading rates to optimize for adsorption capacity, selectivity, and recovery efficiency;

- Milestone for Task 2: GO/NO-GO Decision Point (M10), The Go decision will be based on Tusaar's successful demonstration of media capacity and recovery for at least one metal of value in the model brine.

The results from the completed work demonstrate that the Tusaar Media 1 was able to sequester a series of valuable REEs from simulated geothermal brines. The media demonstrated the ability to remove over 50% of the available REEs in the microcosm shaker test environment, well over the SOPO requirement. The Media was robust as supported by laboratory data from several repeat sorption and strip cycles. These results exceeded the requirements of the SOPO at the GO/NO-GO decision point.

Data supporting the key findings from the GO/NO-GO report were taken from experimental finding at the time and primarily represent microcosm shaker test data. Many of the early tests were performed under conditions that preceded later validation work at projected commercial operation conditions. In this frame work, the data demonstrating sorption of all the REEs in our REE7 standard, data supporting sorption over a range of pH values, data demonstrating the ability to reuse the media and data demonstrating that the media could be stripped of the sorbed REEs were foundational for advancing the project to the column sorption studies and geothermal brine environmental conditions.

Sorption by Media 1 (-50 +100 Mesh) from Brine 1M									
Shaker test @ 70°C, 2 ppm REE7 mix, 150 ml, 2 g media, 90 minutes									
	pH 3.5			pH 4.5			pH 5.5		
	Available mg	mg picked up	% of available	Available mg	mg picked up	% of available	Available mg	mg picked up	% of available
La	0.324	0.080	24.8%	0.358	0.095	26.6%	0.335	0.090	26.9%
Ce	0.321	0.099	31.0%	0.356	0.117	32.7%	0.333	0.116	34.8%
Pr	0.346	0.110	31.8%	0.345	0.115	33.4%	0.336	0.134	40.0%
Nd	0.348	0.117	33.5%	0.350	0.122	34.9%	0.336	0.138	41.0%
Eu	0.326	0.129	39.5%	0.331	0.138	41.7%	0.318	0.153	47.9%
Tb	0.316	0.127	40.1%	0.327	0.140	42.7%	0.313	0.151	48.3%
Dy	0.343	0.143	41.5%	0.354	0.154	43.5%	0.339	0.167	49.3%
Total REE	2.325	0.805	34.6%	2.421	0.881	36.4%	2.310	0.949	41.1%

Regeneration Study GG2-90 (ave. duplicute runs)					
Shaker test with strip and wash					
Brine 1M, 14 ppm REE7, 150 ml, 2 g Media 1, 90 minutes at 70°C					
	Run 1	Run 2	Run 3	Run 4	Run 5
REE removed					
% wt/wt of available REE	25.0%	58.5%	51.1%	50.2%	50.6%
% wt/wt media	0.028%	0.065%	0.057%	0.056%	0.056%
REE Recovered					
% wt/wt removed	113.1%	94.0%	89.2%	97.2%	93.9%

Task 3.0: Process Optimization

Task Summary: Continue work initiated in Phase 1A, optimize variables and begin the preliminary techno-economic estimates

- Milestone for Task 3: Completion of the preliminary economic analysis

The process for sorption of REEs using the Tusaar media in a column sorption format advanced. The early column sorption work helped to complete the preliminary economic analysis. It was completed and submitted as part of the quarterly report. In the absence of capacity data supporting the "true" capacity under projected operating conditions and in the absence of a complete strip/regenerate in situ process, the preliminary report primarily dealt with market dynamics that would/could impact the financial viability of the proposed process.

Representative, sequential load/strip/equilibration (regeneration) column runs confirmed that the process could be repeated in series, REE sorption was complete when the theoretical load was well below the expected apparent capacity and the REE recovery during the strip process was at or near quantitative.

Integration of the laboratory findings into a potential commercial process and the configuration of such a process was conceptualized as part of this task. Estimates for the economics of a commercial process are based upon what the actual process might look like in practice.

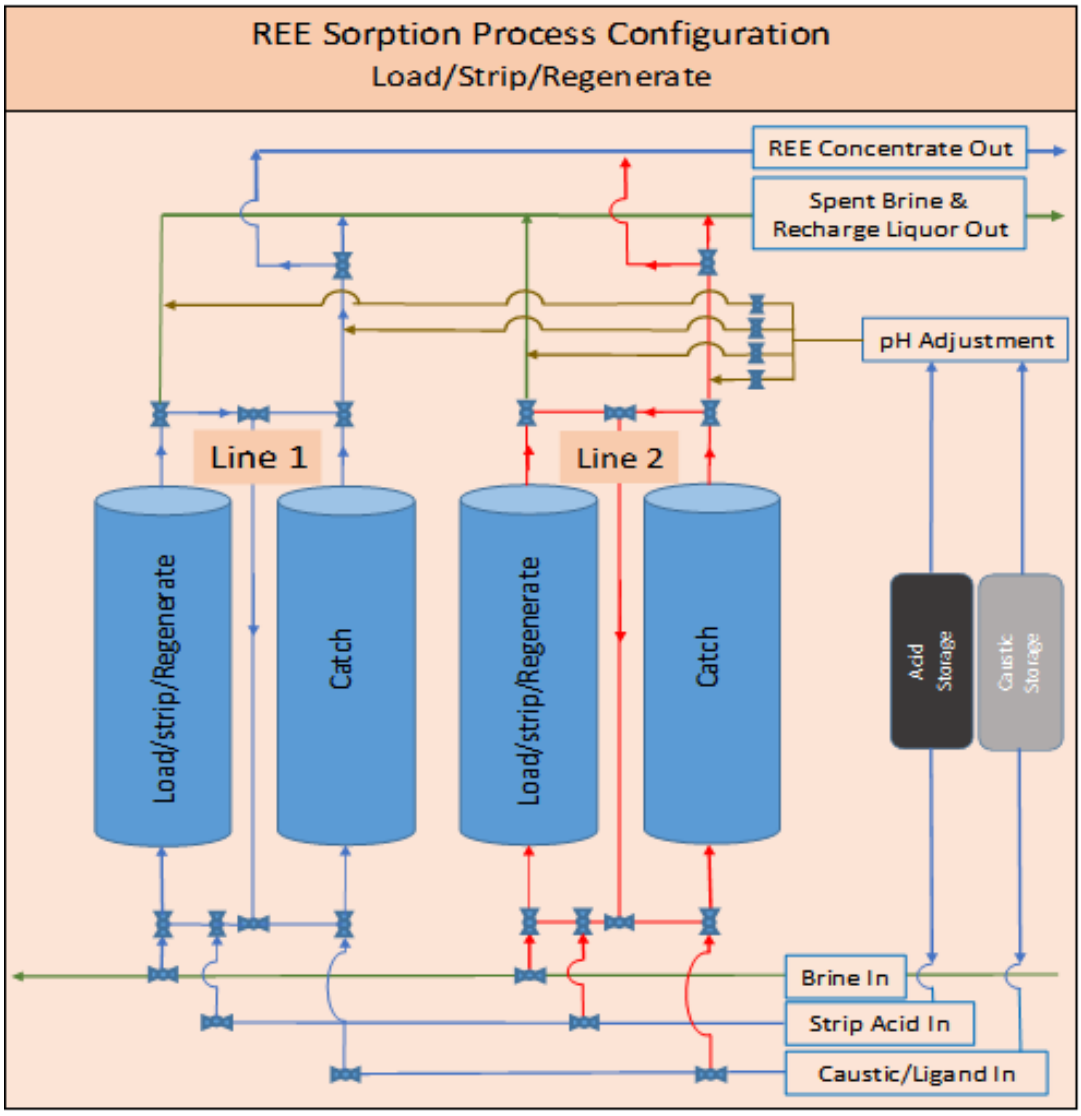
The process model that evolved was as simple as flowing the geothermal water through a fixed bed column of select media until it was saturated with REEs (loaded) followed by replacement of the media with new media. The loaded REEs could then be removed (stripped) from the loaded media, the media regenerated and put back into service.

Observations that the media experienced measurable bleed when longer sorption studies were performed at 90°C necessitated an addition to the simple process model. First, the amount of bleed lost from the media had to be replaced during the regeneration step. Second, over very long sorption runs equivalent to very low REE concentrations in the brine, some replenishment of ligand during the run could be required. Strategies to introduce options to account for both situations were developed and the process adjusted. Most significantly a "catch" column was added following in series the load

column to capture potential ligand bleed from the media. In addition, ligand replenishment was added to the regeneration process after the strip.

For continuous operation, parallel process lines are required with one line operating while the alternate line is being stripped and regenerated. The complete load/strip/regeneration cycle now is represented by a complete process sequence. Operationally, once the operational media in the load column in line #1 is fully loaded the column pair is taken "off" line and replaced with line #2, the alternate column line. Line #2 which is now operational was previously regenerated after a load/strip cycle. The line #1 and #2 continuously alternate in this way to continuously perform their function to remove the REEs from the continuous brine stream.

The following schematic depicts the perceived commercial process with two parallel process lines.



The loading/stripping/regenerating sequence is described in a simple outline as follows. It was a guide in our preliminary techno economic analysis. Specific variables seen in the outline were explored during the next phase of this work.

- Load – Media sorption of REEs from brine
  - REE concentration
  - Temperature
  - Flow rate and contact time
  - Load capacity
  - Ligand bleed
- Strip – Media unloading, REE removal
  - Acid strength
  - Acid volume
  - Strip temperature
  - Flow rate and contact time
- Regeneration
  - pH adjustment
  - Ligand addition
  - Equipment design
  - Sorption characteristics

Task 4.0: Verification

Task Summary: Verify process optimization results at volume ~12 mL and larger ~ volume 150 mL and complete/conclude the techno-economic analysis

- Milestone for Task 4: Completion of the Techno-Economic Analysis, include conceptualized commercial process diagrams, include characterization of unit operations and size including a design for a pilot facility.

The column sorption experiments were advanced and repeated in series to establish the shape and form of the final process to be verified. Variables were optimized and duplicate experimental runs completed for consideration in the final techno economic analysis. The final techno economic analysis was competed and included with the Q6 report.

A description of the in situ process selected for final verification follows.

In Situ Regeneration Load/strip/regenerate Process 10 g Media 1 -50+100 Brine 1CF Load at 90°C - Strip at 40°C In situ regenerate at 40°C 1 ml/min flow			
	Process Steps	Volume ml	Time Minutes
1	Prepare media	0	60
	pH adjust		
	brine equilibrate		
2	Pack column	0	1
	slurry load		
	tap down		
3	Wash column	50	50
	50 ml brine		
	equlibrate temperature 90°C		
4	Load column	1000	1000
	pump REE loaded brine		
	1000 ml containing 100 ppm REE7		
5	Wash column	50	50
	25 ml brine at 90°C		
	25 ml brine @ 40°C to equilibrate		
6	Strip column	30	30
	30 ml		
	1.5M HNO3		
7	Wash column	50	50
	50 ml brine		
8	Wash column		
	50 ml DI water		
9	Regenerate column	16	16
	adjust to pH 5.5		
	16 ml of 1.56M NaOH,		
	4.1% ligand in DI water		
10	Wash column	50	50
	50 ml DI water at 40°C		
	Equlibrate temperature 90°C		
11	Wash column	50	50
	50 ml brine equilibrate		
	Equlibrate temperature 90°C		
12	Repeat steps 4-7		
Total		1296	1357

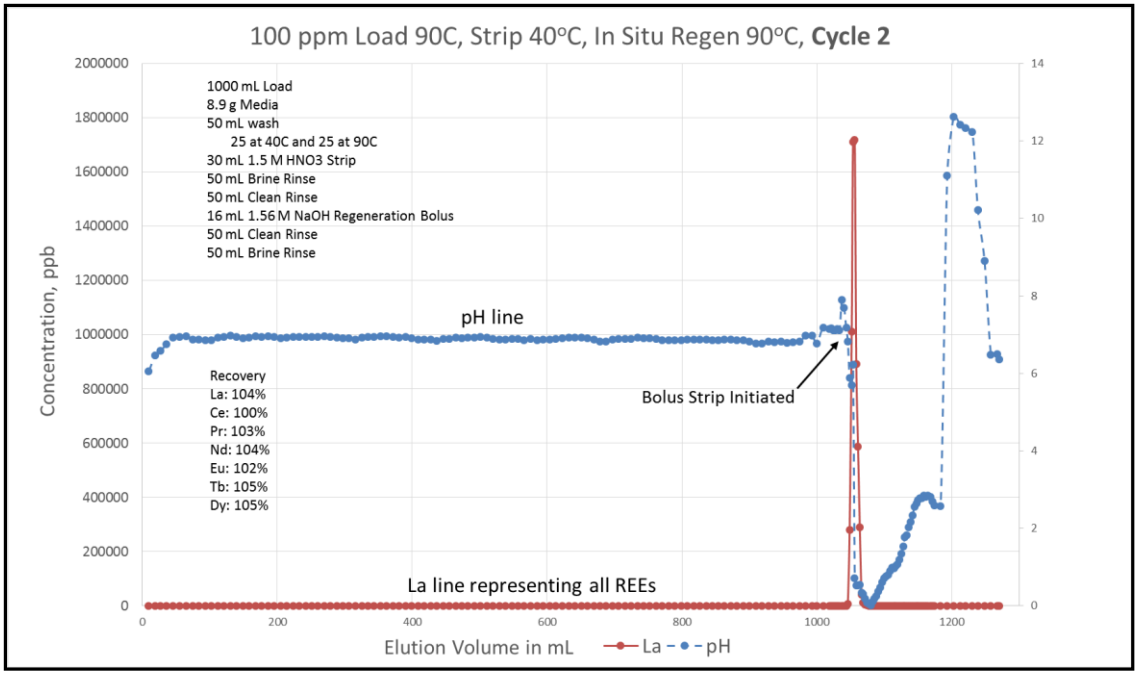
The verification run was completed in duplicate, simulating the “in series” use of duplicate, two column process lines. The following graph depicts the entire process flow for a single pass on one process line as observed by monitoring the REE content of the effluent and simultaneous monitoring of the effluent pH.

In this experiment the load REEs in the brine solution was continued until approximately 1.0% wt/wt REE was introduced to the media in the column. The total volume was 1050 mL and is represented on the graph at the point that the La line (representing all REEs in red) sharply spiked up. Until that point in time, no REEs were detected in the effluent which means that all of the REEs introduced were sorbed on the media. The second run following strip/regeneration of the initial loaded media produced the same results.

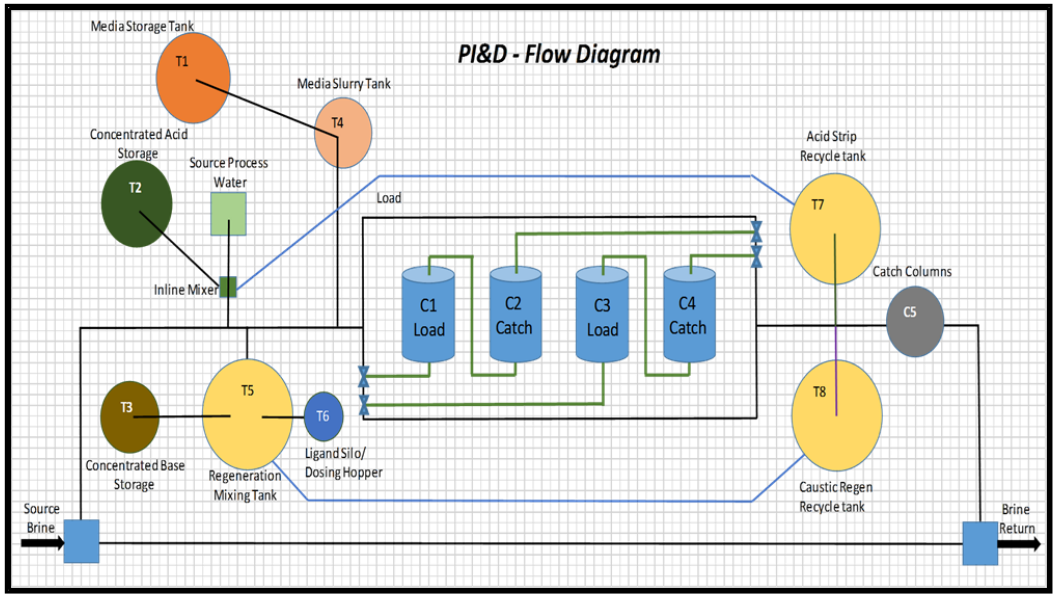
The pH line (dashed line in blue) represents the pH of the effluent. The perturbation of the line moving left to right at the point marked with the arrow and labeled "Bolus Strip Initiated" represents the introduction of the strip acid to the column. At one column volume of effluent after that point the pH drops to 0 rapidly as the REEs are stripped. Essentially, all of the sorbed REEs are desorbed and eluted from the column for collection and later recovery. The pH line after the REE elution represents the normal drift toward higher pH as the neutral water follows the acid strip bolus. The sharp inflection in pH from 2.2 to 12+ reflects a bolus of caustic introduced to the column to bring the pH back to operating pH of 5.0 to 6.0.

Lower REE concentrations were used and influent volumes reached over 10x this value. Loading and stripping of the media was quantitative as seen above when optimal contact time was achieved. Unfortunately, operating issues prevented repetition of the long run time experiments.

Another important finding represented by this graph is the potential for pH tracking. The pH in the effluent directly tracts what is happening on the column and in the effluent. As a result, pH appears to be a good tool to deploy in commercial operation to monitor and control the process and associated acid/base streams in real time.



The work was incorporated into the commercial process model by adding the ligand adjustment component to the regeneration step. The "catch column" was also added to collect potential ligand bleed. The full PI&D for a commercial design and plant foot print was completed yielding the following diagram. This diagram shows the overall flow of materials and the use of two equivalent column sets and associated process tanks to allow for liquid storage and handling to accommodate the two lines. This allows continuous operation.



Based upon the process flow described above and improvements to the original PI&D, a final techno economic analysis was completed. The final estimates for the capital cost and the operating costs are seen in the following table.

CAPEX & OPEX		
$	512,500	Regeneration Ligand inventory
$	4,637,145	Media Inventory
$	2,865,000	CAPEX For plant build
		OPEX, per work cycle
$	5,274	Nitric total Cost - reuse 3X before released
$	520	Caustic Total Cost - reuse continually assuming 10% equilient loss as dilution
$	15,375	Ligand Cost, assuming 3% loss of regen Ligand
	1,000	Labor annualized to 20% FTE
$	8,014,645	Total CAPEX
$	22,169	OPEX per Cycle
$	809,178	OPEX per Year

Task 5.0: Reporting

Task Summary: Completed reporting in accordance with the Federal Assistance Reporting Requirements document.

All quarterly reports were submitted on time and according to the contract requirements.

Unanticipated findings and their impact

Research and development activities involve risk. Risks vary from complete failure when the proposed hypothesis is wrong or cannot be verified to small experimental setbacks associated with poor experimental design and/or unexpected experimental results, equipment failure or human failure.

Details of the most significant problems and their impact on the project follow. In summary, collectively the problems that were encountered cost the project materially in labor utilization, time to completion and overall performance as originally projected. Most importantly, the problems resulted in setbacks that prevented the research team from completing all the work originally planned. At the end of the project as funds were used up and completion time was drawing to a close the final experiments were modified and shorter in duration than originally anticipated.

Geothermal brine formulation challenges

Early in the project we experienced challenges in formulation of a Simulated Geothermal Brine. The inherent complexity of the brine was more difficult to understand and mimic in the synthetic formulas than expected. In addition, the scope of this program did not anticipate the apparent variability and instability associated with producing the targeted brine models including the REE components at required concentrations.

The research plan was advanced through the microcosm testing and early column work using a simplified version of the desired brine, Brine 1 which was labeled Brine 1M. When new data supporting a more complex brine formula was available, Brine 1C, it was substituted for Brine 1M. This proved to be premature as precipitate appeared over time and some studies using the brine had to be redone. Upon further consideration better solutions were considered which lead to the selection of the final brine, Brine 1CF. The final selection of Brine 1CF required that several experiments be repeated comparing the results from Brine 1M, 1C and ICF. This work provided confidence that the early work could be used and compared directly as we advanced the project with the new brine.

In re-examination of some early work it became clear that adding SiO_2 in all forms to our synthetic brine formulas was the most significant problem. Brine instability was also observed with the addition of Pb, Fe and B. pH shifts that were encountered when adding the REE elements to brines also contributed to the formation of insoluble complexes. Through minor formula changes Brine 1CF was considered acceptable.

Difficulty in preparing a stable complex brine that was modeled after our target brine resulted in several program adjustments and strategies. First, the time spent to obtain the target brine was more than anticipated and took more man power and analytical resources. The time to obtain the final brine also delayed some of the longer term column experiments and ultimately contributed to final experimental design changes that impacted our final verification runs.

Equipment failure

The equipment required for the microcosm shaker test phase of this project performed as expected and the experimental plan advanced well. As the experimental plan advanced to higher temperature column sorption studies equipment failures of two types were observed; unexpected chemical incompatibly and over use.

At higher temperatures the frit within the cap of several of our columns failed during the strip procedure. The purpose of the frit is to hold the granular media in place while allowing the sorbent liquid to pass through. During the procedure to strip the REE from the load column we used up to 3 M nitric acid. While the contact time with the frit was short leakage at the frit shortly after the strip was observed. The failure resulted in lost work time and a complete stoppage of column experiments until the problem could be identified and appropriate corrective action taken. In this case a replacement endcap/frit assembly was not readily available and a replacement had to be fabricated. Valuable time and manpower was lost and several experiments had to be repeated. A final solution required that the complete column assembly be replaced.

A second significant equipment failure involved the ICP-MS used for elemental analysis. While this equipment worked as expected and planned most of the time, three unanticipated major components failed. Each failure cost the program time and manpower. Of most significance was that one component related to cooling the instrument failed twice in a row un-expectantly. Generally, this component operates for years without failing or needing to be replaced. The failure we experienced caused us to lose weeks of analytical time.

Surprising experimental results

Two significant experimental findings that materially impacted the research project were observed. First, during one of our first 90^{o}C load/strip/regenerate experiments a reddish brown discoloration was observed within a column. The color appeared at the solvent front during the strip. The experiment was completed without incident. The second time the experiment was performed to see if the observation was repeatable, gas was seen exiting the column and the eluent flow rate dramatically increased and was followed by red gas. The experiment was stopped and an investigation completed. It was determined that the nitric acid was decomposing under the specific conditions producing NOx.

This observation was not expected and no precedent was observed in the literature. Steps were taken to prevent the event to happen again. Ultimately, the entire strip procedure was modified to prevent this situation. The resulting

procedural changes were material to the overall process and had an impact on the final economic analysis. Fortunately, the research team was able to overcome the problem and continue to advance the project.

The second unexpected result was related to the durability of the media. The research team expected to adjust pH after the strip process to regenerate the media for the next run. After several experiments at lower temperatures the final target temperature of 90°C was achieved. Meaningful ligand bleed from the media was observed in the effluent. This was not considered a concern as the experimental plan moved from room temperature to 70°C. The final 20°C increment was significant.

The research team immediately examined options to control the bleed and explore ways to regenerate the lost ligand onto the media. The team was able to modify the regeneration procedure to replace the lost ligand and they devised a strategy to capture the lost ligand from the effluent in real time during the load procedure. After several strategies and conditions were explored a suitable revised load/strip/regenerate procedure was devised, confirmed and implemented as the prototype commercial process.

This unanticipated result was a significant setback for the project when it happened. The solution took considerable manpower time and instrument time to overcome. Other work was stopped until a solution was in hand. At the conclusion of the project over coming this problem impacted the availability of manpower and resources to complete the project. At the same time, the changes implemented early in the trouble shooting phase, allowed the team to drop one of the backup routes that were under investigation by the end of the 5th quarter freeing up resources for this final solution. The solution added meaningful costs to the projected commercial process that was validated in the final experimental runs.

Incomplete tasks

A minor component of the project was to establish a strategic partnerships with the geothermal technologies groups and/or with other commercial partners would might benefit from this project. Efforts were made to establish such relationships to no avail. While some interest was voiced, the project was deemed premature to establish their interests or the prospective partner was too risk averse at this point.

The description of work indicated that process demonstration would include some work with larger columns. Due to scope changes and unanticipated experimental results this was not attempted. Given the long run times and associated equipment failures, the project did not have the band width to advance to the larger scale.

The project scope speculated that validation of the process using authentic geothermal brines was a worthwhile goal. While no partners were secured, efforts to obtain authentic brines continued. One authentic brine was obtained from a geothermal sources. This brine proved to contain no measurable REEs and was a low salt brine. As a result no additional work was performed with it.

The DOE was able to provide two brines with the potential to be reference points for authentic brines. One sample was an authentic brine for above ground origin and one was a DOE synthetic brine. The samples can be described as seen in the following charts. These brine samples were used to compare results with Tusaar Brine 1CF

REE Sorption from Brine Matrices - Shaker test @ 70oC - 14ppm REE7 - 90 minute contact time	
Brine Identification	**REE Removed %by wt.**
Idaho National Laboratory Synthetic Brine	81%
Great Salt Lake Brine CSR-7	67%
Tusaar Brine 1CF	57%

Brine Composition *			
	Idaho National Laboratory Synthetic Brine	**Great Salt lake Brine CRS-7**	**Tusaar Brine 1CF**
	mg/L		
Na	19,000	51,330	43,184
Ca	200	323	14,297
Mg	100	5,169	155
K	700	4,101	17,424
Ba	20	-	184
Si (Sio_2)	**	29	**
Mn	**	**	732
Ba	**	**	184
Sr	**	**	407
Zn	**	**	284
Li	**	**	156
Mg	**	**	155
$SO_4^=$	**	10,358	**
Cl^-	30,600	30,600	108,400
TDS	50,600	101,910	185,562

* composition data supplied with samples ** below 1 mg/L

The sorption of the available REEs from all three brines was over 50% during the 90 minute microcosm shaker test at 70ºC. There appears to be a trend toward lower sorption as the complexity and/or the total solids content increases. From this comparison, it appears that the Tusaar Brine 1CF is the most challenging for the selected media. No further effort was made to compare the brines or the sorption from the brine.