

Critical and Strategic Materials and Potential Importance for Geothermal Projects

Holly P. Thomas¹, Timothy P. Reinhardt², Arlene Andersen², and Brittany Segneri²

US DOE EERE Geothermal Technology Office 1000 Independence Avenue S.W., Washington DC 20585 and US DOE Golden Filed Office, 15013 Denver West Parkway, Golden CO 80401¹

holly.thomas@ee.doe.gov; timothy.reinhart@ee.doe.gov, brittany.segneri@ee.doe.gov

Keywords: Geothermal, geothermal minerals, critical materials, rare earth elements, US Department of Energy, Geothermal Technology Office, material recovery

ABSTRACT

The need for secure supplies of high value, strategic, critical or near-critical materials are a consideration in the assessment of national business interests in the expanding clean energy economy. The definition of what is a strategic, critical or high value material varies over time and is driven by the current status of suppliers, technologies of national interest, the resulting commodity demands and the potential opportunities for substitutions. There is a clear need for a range of materials that may be available from elevated temperature fluids in the United States (U.S.). The Geothermal Technologies Office (GTO) in the U.S. Department of Energy (DOE) initiated a program in 2013 to evaluate the resource potential and methods for recovery, and is continuing that effort with an expanded Phase 2 initiated during 2015. This paper describes recent research progress in the program, planned additional work and the rationale for continued research.

1. INTRODUCTION

This paper discusses the United States Department of Energy (US DOE) Geothermal Technologies Office (GTO) critical materials recovery initiative from the rationale for program, initial research results and the next phase of planned work. Rationale for the project was first introduced at the Stanford Workshop in 2013 (Segneri, Reinhardt), and the Phase 1 research was described in 2015 (Thomas, Reinhardt, Segneri). Research results will be used to promote the advancement of technologies capable of providing additional revenue streams to geothermal operators.

In 2014 the GTO initiated R&D to identify methods to recover rare earth elements and other critical materials for m geothermal fluids. This work is identifying the new methods for recovering and concentrating very low concentrations of materials. During 2016, the GTO expanded its efforts to Phase 2, inviting R&D to evaluate current methods in other industries and the potential to transfer these approaches to recovery of materials form geothermal fluids. This paper reviews progress in Phase 1 and the plans for Phase 2 pf the Low Temperature Mineral Recovery Program. The US DOE actions in metals recovery options and opportunities in geothermal and elevated temperature fluids in the current economic context are also described.

2. MINERAL RECOVERY RATIONALE

The GTO plans focus on the metals often referred to ‘critical’ and ‘strategic’ in the literature. The goal is to demonstrate the technical and economic feasibility of material extraction and geothermal energy production. The research is being conducted to evaluate or develop new methods or through innovative approaches establish economic methods to recover dissolved, high value materials.

As recently as 2012, there was considerable U.S. Congressional interest in the availability of rare earth elements, many of which are important for emerging clean energy technologies. But times have changed. The commodity prices for virtually every metal group have declined, with many reaching new lows in early 2016. Commodities as a group have an historic variability, often punctuated by concerns over availability or general economic health of the nation or the world. As can be expected, this leads to a variable interest for research conducted on methodologies to identify and then recover particular materials.

Numerous papers and reports have been written about the need for secure supplies of high value, strategic and critical materials for national business and security interests (USGS 2013, DOD 2013, and MIT 2016). For example, the USGS Mineral Commodity Summaries 2015 reports that the U.S. reliance on imported materials continues to increase with the U.S. importing more than 50% of its apparent consumption of 43 mineral commodities. Of these, 100% of 19 commodities were imported (USGS 2015). Supplies of materials that are essential for clean energy technologies are of particular interest. It is possible that various materials can be recovered from elevated temperature fluids to not only improve the national supplies, but potentially enhance the economics of geothermal energy production operations, and expand the impact of geothermal energy as a renewable energy resource.

3. PHASE I CRITICAL MATERIALS RECOVERY

GTO initiated the Phase I Low Temperature Geothermal Mineral Recovery Program Funding Opportunity Announcement (FOA) in 2014 and selected eight R&D projects. The work can generally be grouped into two areas: assessment, and R&D. Six projects are currently evaluating methods to recover critical materials from geothermal fluids, one is working to model the presence of critical materials correlated with host rocks, and refine sampling methods, and one had to withdraw for business reasons. Progress in each area is described in the following sections.

3.1 Assessment Projects

GTO is funding two projects in this general category. The University of California at Davis was selected in the Phase I FOA. In addition, Idaho National Laboratories is providing standardized, analyzed brine samples for the Phase I participants.

3.1.1 University of California at Davis (UCD)

The goal of this work is to provide quality data quantifying the concentration and chemical speciation of REE in a wide range of geothermal fluids. The team is conducting analysis to correlate distinct types of geothermal systems (e.g. Basin and Range type, Sediment-hosted, volcanic associated, magmatic) with the presence of REE. Data included in this effort will correlate host rock, temperature, pH, salinity, complexing agents, and phase separation history with REE concentrations. One goal of the project is to quantify the potential economic benefit that could arise from co-recovery of REE elements from US geothermal fields that are producing geothermal fluids for electrical generation.

The team has already analyzed more than 20 samples from well heads and geothermal springs, and are actively seeking access to additional samples from US geothermal field operators. In an effort to advance the understanding on the geochemical controls on REE solubility and transport, the team is using Laser Ablation ICP MS to determine REE concentrations in individual crystals of host-rock and hydrothermal alteration minerals, including epidote, calcite, anhydrite, fluorite, pyroxene, amphibole, and plagioclase, where appropriate core and cuttings from geothermal wells are available.

Another focus of the project is to incorporate thermodynamic data on REE complexes and minerals into geochemical models in order to extend the applicability of the data collected to other hydrothermal systems. Existing REE data on geothermal fluids were compiled in order to assess the optimal sites for new sampling. This data is open and accessible on the DOE Geothermal Data Repository at <http://gdr.openei.org/submissions/541>. The structured dataset contains 439 samples from geothermal wells and springs, including available information on the specimen collection method, analysis date and time, fluid temperature, location, data source, units of measure, rare earth element analysis method and pH. Included in the data compilation are data from submarine hot springs on the mid-ocean ridges. Because REE solubility increases with increasing temperature, the high temperature deep sea vent fluids can be collected at pressures above the two phase separation point. These samples may provide important insight into the subsurface compositions of high temperature geothermal systems that undergo both increases in pH and cooling upon phase separation in producing wells. Thus far, data on flashed geothermal fluids analyzed in this project show strong depletion of REEs relative to their down hole concentrations indicated by LA-ICP MS analysis of cuttings and core.

A major goal for the continuation of this project is to quantify REE partitioning during phase separation by obtaining down hole fluid samples in appropriate geothermal fields. The research effort continues to be hampered by lack of access to geothermal wells. The team continues to characterize bulk REE concentrations in hydrothermal precipitates (sulfides, sulfates, and carbonates) associated with the sampled fluids to address potential partitioning of REE between the minerals and that dissolved in the fluids. UCD is also analyzing for REE partitioning into specific silicate alteration minerals e.g. barite, anhydrite, and calcite.

3.1.2 Idaho National Laboratories

To enhance the overall project and support the researchers in evaluating the measurable their extraction approaches, INL has prepared a range of standardized synthetic brines. These provide a common reference point for all the mineral recovery awardees in the Phase I FOA, providing a common reference point across the program. These representative solutions allow the teams and DOE to evaluate the effectiveness of the processes under development. INL is also writing a detailed review of REE data from thermal waters. This review will include both published and unpublished data that can be located. The data will include REE data from the more than 70 geothermal features that have been recently collected by INL. Early work by several authors has shown that the REE concentration in thermal waters and saline brines is strongly dependent on their gross geochemistry (i.e. presence of strong ligands CO₃, Cl, F, TDS, etc.) as well as the temperature of the system. INL is using this concentration dependence to bin thermal waters into generalized classifications that span the range of REE behavior.

3.2 Applied R&D

3.2.1 Carnegie Mellon University - Chelating Resins for Selective Separation and Recovery of Rare Earth Elements

The research team at Carnegie Mellon University (CMU) is developing new high capacity chelating resins to selectively separate and recover REEs from geothermal brines. CMU systematically synthesized ligands selective for REE, and is developing reusable resins with optimized ligands to be evaluated a continuous extraction and recovery process.

During this year, the team optimized five functionalized adsorbents for evaluation and have tested multiple solid supports. The most promising adsorbents have been developed using polydentate linear ligands and silica supports and work is continuing to optimize high surface area, large particle size silica supports.

The adsorption reaction kinetics of candidate resins have been evaluated for REE selectivity in various synthetic brines, and the characteristics of uptake and recovery over a range of pH and REE concentrations. Results have shown high REE affinity by silica based functionalized adsorbents, facile and efficient elution, chemical and temperature robustness of the tested functionalized adsorbents, and rapid uptake kinetics for REE (Figure 1).

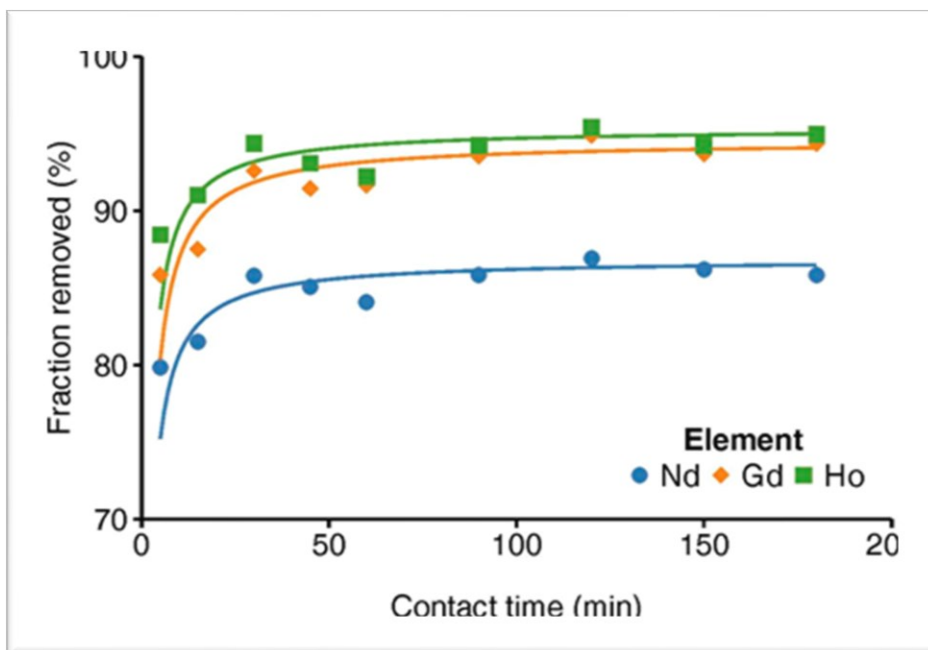


Figure 1: Example test illustrating percent uptake (% fraction removed from synthetic brine) of three model REE (i.e. Nd, Gd, Ho) over contact time (min) of functionalized adsorbents with polydentate linear ligands at pH 2.

By optimizing the ligand grafting techniques the CMU team has achieved high REE uptake (high partitioning coefficients) at pH ranges relevant to geothermal fluids and elevated temperatures. Work continues on optimizing the functionalized adsorbents, testing under a range of solution conditions. Testing is underway with small-scale, fixed-bed adsorbent column systems under continuous flow conditions.

3.2.2 Lawrence Berkeley National Laboratory - Engineering Thermophilic Microorganisms to Selectively Extract Strategic Metals

The overall goal of this work is to develop engineered thermophilic microorganisms for a new biosorbent technology that specifically binds two strategic metals, Zn²⁺ and Gd³⁺, from geothermal fluids. The key innovation of this technology will be the high density of highly-selective binding sites for Zn²⁺ or Gd³⁺ on the surface of a robust thermophilic microorganisms.

Over the past year the team demonstrated the proof-of-principle to express and purify surface (s)-layers containing these metal binding domains from *Escherichia coli* with the ultimate goal to demonstrate the process on thermophilic bacteria. The S-layers self-assemble to form two dimensional, crystalline, high-density arrays on the surface of most bacteria and are an excellent method of displaying protein domains on the extracellular surface. The team identified 2 Gd³⁺ binding domains and 3 Zn²⁺ binding domains that fit the binding and selectivity criteria necessary to achieve selective, high capacity metal binding in geothermal brines. With this information, the team generated a panel of different DNA constructs to express these desired engineered proteins in *Escherichia coli*. They were able to engineer and purify the desired S-layer proteins containing two of the three Zn²⁺-binding domains and both Gd³⁺-binding nanosheets.

With this foundation the team compared the Zn²⁺- and Gd³⁺-binding abilities of the engineered S-layer nanosheets to the native S-layer nanosheet. Induced coupled plasma mass spectrometry (ICP-MS) measurements confirm S-layer nanosheets bearing a Zn²⁺-binding domain are able to bind a higher fraction of 1200 nM Zn²⁺ than the native S-layers, with a half-maximal binding of Zn²⁺ (EC₅₀), more than factor of 2 lower than the native S-layer (EC_{50,eng'd} = 0.12 pM, EC_{50,native} = 0.30 pM). This lower EC₅₀ indicates that the engineered S-layer nanosheets bind Zn²⁺ more tightly than native S-layers. Next steps in this work are to establish that the process will apply to the thermophilic *Geobacillus stearothermophilus*.

3.2.3 Pacific Northwest National Laboratory - Magnetic Partitioning Nanofluid for Rare Earth Extraction

The purpose of this project is to develop and demonstrate a nanofluid-based method for extracting REEs. The approach is to create composite nanoparticles composed of a magnetic iron oxide core surrounded by a functionalized shell. This active shell is made of silica or a metal organic framework (MOF) sorbent functionalized with chelating ligands selective for REEs.

The planned process is to introduce the nanoparticles at low concentration (≈0.05 wt %) into the geothermal brine after it passes through the plant heat exchanger. The process allows a short residence time with the brine to bind REEs, and to then separate the particles with an electromagnet and standard extraction methods. During the past year, two MOFs were identified that when functionalized with either -SO₃- or diethylene triamine (DETA) that effectively stripped five REEs doped into a simulated brine solution in with a five-minute exposure.

The team completed a preliminary techno-economic analysis for the process. Results from this preliminary model indicate an internal rate of return of about 20%. For the remainder of the project, the research team plans to demonstrate that optimally-sized 50-100 nm core-shell nanoparticles can be prepared to increase the adsorption rate. The team will also confirm cycling stability of the nanofluid after hundreds of regeneration cycles.

3.2.4 Pacific Northwest National Laboratory - Advanced Sorbents to Recover Rare Earths, Precious Metals and Other Critical Materials

The purpose of this research is to develop and demonstrate the application of new sorbent materials with high chemical affinity and capacity for trace element collection. The work is based on the combination of novel solid-phase sorbents, high-volume industrial water-treatment technologies, and established mineral processing unit operations. This team has successfully designed and built sorbent materials to collect trace levels of REEs, precious metals, and other materials such as zinc, manganese, copper, and uranium.

Work to date demonstrate that new can be integrated into relevant mineral recovery structures such as traditional packed beds, fluidized beds, various filter structures, and novel membranes. The preferred sorbents show affinities for of economic interest with good capacities, and rapid kinetics. Patents have been granted or are pending for the PNNL materials. The table below (Table 1) illustrates the effectiveness of selected sorbents to collect materials of interest and recover for reuse,

Table 1: Sequential collection and release performance for selected sorbent materials for Eu from geothermal water throughout 10 process cycles.

Sorbent	Collection Efficiency (%) ^a	Recovery Efficiency (%) ^b
Complexing Phosphonic Acid on high surface area support	98.5±0.9	93.5±5 ^c
High surface area mixed metal oxides	97.5±1.0	82.6±9.8 ^d

a Values are average from 10 process cycles, Initial concentrations of Eu was ~50 ppb spiked into geothermal solution for Sharkley Hot springs in Idaho, solution's pH~7.7, 1 hour batch contact with gentle agitation.

b Values were average from 10 stripping/recovery cycles, 1 hour batch contact with gentle agitation.

c 0.1M HCl was used for stripping solution

d 0.01M HCl was used for stripping solution

Team member Barr Engineering completed a preliminary technoeconomic analysis of the process, indication a fairly rapid payback period of approximately 2-6 years resulting in very positive return on investment figures for the process, depending upon the possible plant size and mineral concentration in the source fluids. Over the remainder of the project the team will optimize sorbent materials, demonstrate performance in a range of geothermal fluids and refine the economic analysis of process for a process ready for scale up efforts and evaluation under operational conditions similar to those found in geothermal thermal energy plants.

Over the remainder of the project the team will optimize sorbent materials, demonstrate performance in a range of geothermal fluids and refine the economic analysis of process for a process ready for scale up efforts and evaluation under operational conditions similar to those found in geothermal thermal energy plants.

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

This combined energy production and mineral extraction project is for an innovative modular solid-state thermoelectric system to both generate electricity and extract high-value from low-temperature geothermal brines. The combination for a high efficiency thermo electric module with power production and brine concentration represents an opportunity to significantly improve the economics of dissolved mineral extraction Southern's process combines SiO₂ precipitation, nanofiltration (NF) and two stage membrane distillation (MD) with lithium recovery.

The first MD stage includes a thermoelectric power generation step to offset the fluid treatment costs. To improve the thermo-electric performance southern developed nanoelectric generators (TEG's) to produce electricity from the ~110°C temperature gradient across the device. Ongoing work includes development of thermal, fluid, and mechanical design specifications and systems models, as well as design and procurement of balance of plant, integration of the TEG with the MD system, and validation/performance testing of the sub-system.

A robust pretreatment system is needed to optimize lithium recovery. Southern's approach is to optimize removal of several of the anticipated scaling and interfering compounds in multiple treatment steps. Bench tests to remove SiO₂, Ca²⁺, and Mg²⁺ to prevent scaling in the membrane distillation system allows greater concentration in the second MD step resulting in higher lithium concentrations.

The data demonstrate that by following these steps, the process achieved almost maximum theoretical uptake on the lithium sorbent. Figure 2 shows that the LiMn₂O₄ sorbent can achieve very high Li uptake with pH adjustment, with sorption approaching 100% theoretical capacity at high pH.

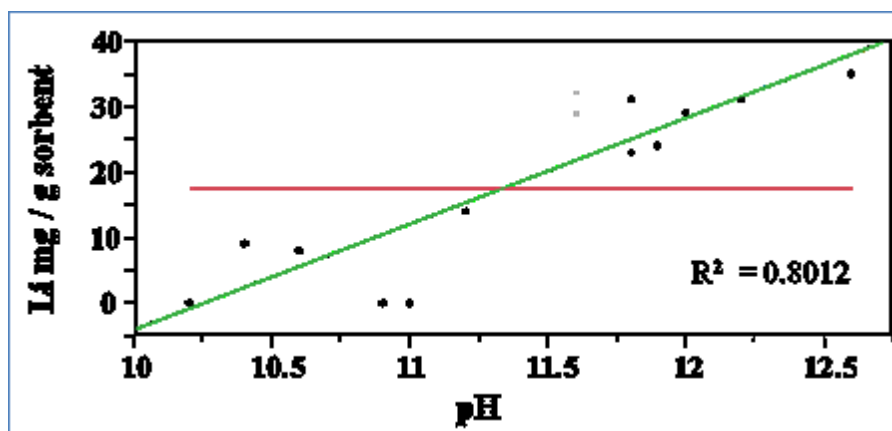


Figure 2: Impact of pH on the sorption of Li to a sorbent based on LiMn_2O_4 . Matrix was DI water, contact time was 1 hour, and the Li concentration was 70 mg/L.

3.2.6 Stanford Research Institute International - Engineered Resins for REE recovery

SRI International is developing novel low-cost reusable imprinted polymer sorbents to recover Li and Mn dissolved in geothermal brines. The approach is prepare selected polymer resins in the presence of Li or Mn ion templates such once the resins are cleaned, they have the ion size, shape, and arrangement of binding sites specific for binding the ion of choice imprinted into the resin. The result is that when a brine containing the ions of interest contacts the imprinted sorbent, the ions are captured and concentrated in the imprinted polymer.

The SRI team evaluated ion imprinted polymer sorbents for high binding capacity. Selectivity for the specific ions of interest ease of regeneration and chemical and structural stability up to 100OC. They also evaluated the ability of the sorbents to selectively bind Li^+ in the presence of competing ions such as Na^+ and K^+ . As shown in Figure 3, Li-imprinted polymers have high Li^+ binding selectivity. Lithium and Mn uptake has also been demonstrated over a range of temperatures, from 45 to 100oC.

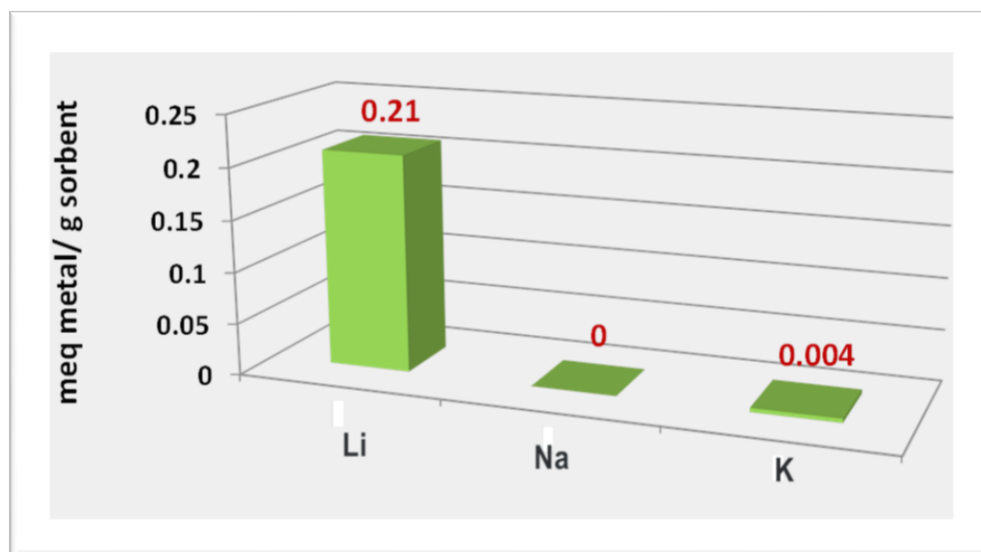


Figure 3: Li Imprinted Polymer Sorbent Selectively Binds Lithium

Experimental Conditions: $T=45\text{oC}$; Synthetic brine containing 412 mg Li/L, 405 mg Na/L and 435 mg K/L

SRI added two partners in the last year. The first, Esmeralda Minerals LLC, is a wholly-owned subsidiary of Pure Energy Minerals Ltd., an integrated lithium mining and processing developer in North America. Esmeralda is providing lithium-containing brines from their Clayton Valley, Nevada property. Nitto Innovations, Inc. is the U.S. subsidiary of a major global supplier of resins and membrane for separation processes and participating in resin development and evaluation.

3.2.7 Tusaar Corporation - Environmentally Friendly Economical Sequestration of Rare Earth Metals

The purpose of this project is to determine the feasibility of a novel metal sequestering method developed by Tusaar to extract lanthanides and other critical and valuable elements from geothermal process brines. During the past year, Tusaar has demonstrated several important aspects of the Tusaar media.

The Tusaar media effectively recovers REEs from simulated geothermal brines at temperatures up to 90oC and is insensitive to high levels of sodium, potassium and calcium in synthetic brines. Additional testing confirms that REEs can be recovered from the media through pH adjustment either in situ on the column or external to the column. The stripped media has successfully been regenerated and reused through multiple cycles without loss of the media’s sorptive capacity.

Other characteristics of the Tusaar media are shown in Table 2, illustrating the selectivity of the media for 7 target REEs. Processing studies indicate that contact times on the order of 3 to 5 minutes optimize the REE loading, although satisfactory recovery is shown under reduced contact times, although plant costs would increase.

Table 2: Sequential sorption of seven REEs of interest in synthetic brine.

Sequential REE Sorption from Model Brine at 90°C								
Brine 1M								
	La	Ce	Pr	Nd	Eu	Tb	Dy	total
Initial ppm	2.05	2.03	2.07	2.09	2.03	1.95	2.04	14.26
Final ppm	1.26	1.04	0.95	0.92	0.73	0.67	0.66	6.23
% Removed	38%	49%	54%	56%	64%	66%	68%	56%
New doped brine added to media after decanting brine								
Final ppm	1.68	1.4	1.28	1.19	0.99	0.88	0.88	8.3
% Removed	18%	31%	38%	43%	51%	55%	57%	42%
Brine 1C								
	La	Ce	Pr	Nd	Eu	Tb	Dy	total
Initial ppm	2.04	2.0	2.07	2.02	2.02	1.91	1.98	14.04
Final ppm	1.23	1.01	0.92	0.88	0.71	0.63	0.63	6.01
% Removed	40%	50%	56%	56%	65%	67%	68%	57%
New doped brine added to media after decanting brine								
Final	1.64	1.38	1.27	1.21	0.96	0.86	0.85	8.17
% Removed	20%	31%	39%	40%	52%	55%	57%	42%
* Microcosm Shaker test @ 90oC, 14 ppm REE7 in 150 ml doped brine, 2 hr contact time, 2 g Media 1 -50+100								

For the remainder of the project the team will finalize the techno-economic analysis of the Tusaar process and evaluate the most efficient methods to strip and regenerate the media.

4.0 Next Steps -Phase II Mineral Recovery

As part of the long term program plan, GTO published the FOA *Mineral Recovery Phase II: Geothermal Concepts and Approaches to Validate Extraction Technologies* in December 2015. This FOA is the next planned step in establishing the capabilities to recover the critical and strategic materials from elevated temperature fluids. The FOA invited applications applying new or improved technical approaches from existing mineral recovery from elevated temperature fluids. Ideas need to have a minimum Technical Readiness Level (TRL) of 3-4 at commencement of the effort, leading to TRL levels of 5-7 at project completion.

The FOA requests responses in two Topic Areas. Topic Area 1 is for the engineering validation of existing extraction technologies. This Topic area is further expanded into two subtopics, 1A and 1B. Topic Area 1A specifically deals with approaches to recover identified materials from geothermal fluids or produced waters. Applications could be for processes that already experimentally demonstrate effectiveness for material recovery or to evaluate the effectiveness of transferring a processes currently effective in another industry to geothermal or other elevated temperature fluids. Topic Area 1B is for approaches to mineral recovery in subsurface geothermal settings. Current practice in other industries such as enhanced geothermal operations, extractive industries such as oil and gas or mining may concentrate selected materials in the produced fluids. Responses will specifically validate the application of technologies and/or approaches for material recovery in subsurface geothermal settings.

Topic Area 2 requests applications that propose to economically and quickly build a public, U.S.-wide resource assessment of dissolved critical and high-value materials that may be site-specific, region-wide, or a national assessment.

The key Impact metric for these projects is that the work is a ground breaking approach to identify the resource potential and validate methods to recover dissolved materials contained in thermal fluids, thereby addressing DOE’s Critical Materials Hub and EERE goals.

5.0 Conclusions

The GTO has designed a multi-pronged program extending over three to five years to explore the opportunity and potential mineral recovery methods to expand the application of geothermal power to economically provide clean renewable energy. This program began with work to evaluate the REE resources in geothermal fluids and to conduct R&D to develop new methods to recover high value strategic materials from geothermal fluids. During 2015 the program was expanded to include proven processes that may be transferable from other industries, and to examine the potential for resources found in a range of elevated temperature fluids such as co-produced fluids from oil and gas or mining or other process operations. The program is intent on having the results from these efforts incorporated into the National Geothermal Database to support expanded knowledge of what is available, and extraction results for new processes.

REFERENCES

- Jan Ishee, Ethan Alpern, Alex Demas. "Going Critical: Being Strategic with Our Mineral Resources," December 13, 2013. Retrieved from website: http://www.usgs.gov/blogs/features/usgs_top_story/going-critical-being-strategic-with-our-mineral-resources/
- Strategic and Critical Materials 2013 Report on Stockpile Requirements, Office of the Under Secretary of Defense for Acquisition, Technology and Logistics, RefID: 2-9B1D9E6; January 2013.
- USGS Mineral Commodity Summaries 2015. Retrieved from website: <http://minerals.usgs.gov/minerals/pubs/mcs/2015/mcs2015.pdf>.
- Securing materials for Emerging Technologies. Retrieved from website: <http://www.aps.org/policy/reports/popa-reports/upload/elementsreport.pdf>
- Mission 2016: Strategic Mineral Management, Retrieved from website: <http://web.mit.edu/12.000/www/m2016/finalwebsite/>