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Low Temperature Geothermal Mineral Recovery Program

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ABSTRACT

While geothermal power is an attractive potential source for sustainable electricity generation, the high heat temperature requirements (typically greater than 150°C) of most geothermal power systems constrain the geographic distribution and economic viability of geothermal production. At lower temperatures, the thermal conversion efficiency (converting heat to electricity) of geothermal systems is lessened, making successful developments more technically and economically challenging. The US Department of Energy Geothermal Technologies Office (GTO) has funded research to address this limitation by advancing a more non-traditional aspect of geothermal systems - strategic material or mineral recovery. By partnering with geothermal and mineral industry stakeholders to develop additional revenue streams from brines, the economic viability of geothermal projects will increase while also allowing for expanding geographic diversity of this base-load energy resource.

Geothermal fluids dissolve minerals and metals from rock formations as they flow through the Earth's subsurface. Extraction and purification of these materials recovered from geothermal brines can be viewed as "solution mining by nature." GTO issued a Funding Opportunity Announcement (FOA) in February 2014 focused on Mineral Recovery associated with these geothermal brines. This research seeks to further the development of technologies aimed at extracting and refining these materials for beneficial purposes. GTO's objective in this FOA is to promote the advancement of thermal energy conversion processes capable of converting geothermal heat sources into power, in conjunction with the development or exploitation of technologies capable of capturing, concentrating, and/or purifying valuable materials contained within geothermal brines to economically extract resources that can provide additional revenue streams to geothermal operators.

During the summer of 2014 selections for this FOA were completed and nine awards were negotiated to begin in October 2014. These nine projects cover a broad range of approaches to determine the potential mineral value-streams associated with geothermal fluids. The ongoing work will examine the feasibility of extracting rare earth or critical elements and metals using a number of different approaches, and the economic potential for the various approaches. This paper reviews the intentions behind the GTO announcement and introduces the nine projects that are now in progress and their project goals.

1. INTRODUCTION

Geothermal power is a source of sustainable energy generation and is utilized throughout the world. In current practice, these systems usually operate using fluids in excess of 150°C. Because these high temperature resources are geographically limited, most geothermal capture systems are constrained. With improved knowledge, experience and materials, the thermal limitations and economic barriers may be overcome so that these lower temperature thermal resources can become economically competitive.

Geothermal fluids dissolve minerals and metals from the rock formations they contact as the fluids flow through the Earth's subsurface. This is effectively 'solution mining by nature', and minerals dissolved in these fluids represent potential resources. The economic extraction and purification of the dissolved materials from geothermal brines will soon be demonstrated at Simbol Inc.'s Salton Sea operation. At this facility, Simbol is partnering with geothermal power producers in Southern California's Imperial Valley to produce lithium, manganese and zinc compounds from the thermally-reduced geothermal fluids after they have been utilized by the power plants but prior to reinjection. Constituents of particular interest for potential extraction are the rare earth elements (REE). The high demand for REEs in a range of applications supports the opportunity for alternative approaches for REE separation and recovery in addition to traditional mining and extraction operations. Aqueous media such as brines or produced fluids from geothermal energy production, as well as conventional oil/gas and shale gas extraction operations could be potentially significant new sources of REE.

With this perspective, the US Department of Energy (US DOE) Geothermal Technologies Office (GTO) funded research to address these limitations and opportunities by advancing a more non-traditional aspect of geothermal systems – strategic material or high-value mineral recovery from geothermal fluids.

2. FUNDING OPPORTUNITY ANNOUCEMENT

2.1 Purpose and requirements of the FOA

GTO issued the Low Temperature Geothermal Mineral Recovery Program Funding Opportunity Announcement (FOA) in February 2014 to focus on the recovery of critical materials from geothermal fluids. The EERE objective of work through this FOA is to support advancement of thermal energy conversion processes capable of converting geothermal energy to power, as well as developing or exploiting technologies that capture, concentrate and purify valuable materials contained in geothermal brines. The goal of this FOA is to initiate work to demonstrate the technical and economic feasibility of material extraction and geothermal energy production through innovative methods.

The FOA sought applications with feasibility studies that include fully-developed business plans defining the technical feasibility and economic viability of mineral extraction technology(s) combined with geothermal power production at new or existing geothermal resources, based upon known or available data on the chemical composition of the geothermal fluids at that site(s). Research results will be used to promote the advancement of technologies capable of providing additional revenue streams to geothermal operators.

An additional area of interest in the FOA was assessments of the current rare earth and near-critical metal resource base, with potential extraction volumes/rates coupled with a techno-economic analysis. Assessments were encouraged to focus on identifying viable mineral types located within the United States, as well as potential mining technology and extraction volumes for any selected material(s). Evaluation of the current state of extraction technologies for the various mineral types and an economic analysis to determine the viability of developing mineral extraction facilities could also be proposed.

Finally, applied research and development (R&D) for innovative extraction technologies with accompanying feasibility studies of currently available technologies and/or potentially novel alternatives, and modeled test results for the most promising candidates were encouraged in the Funding Opportunity. R&D projects that included evaluations of their feasibility as selective extraction mechanisms from known brine chemistries and bench testing were encouraged. Geochemical modeling and leaching experiments to optimize the composition of down-hole fluids and identify additives that selectively leach high value strategic elements were also acceptable topics.

2.2 FOA Process and Response

Approximately $4 million was planned for the awards which are to be completed in 24 months or less. The review leading to selection of the awards was conducted in two separate steps. The first step was a required Concept Paper, summarizing the idea and limited to five pages. This approach allowed applicants to have their ideas evaluated before investing a significant amount of time in a full application. After the Concept Papers were reviewed, applicants were either encouraged or discouraged from completing a full application. For this FOA, 46 concept papers were submitted, of these, 39 were encouraged to submit full applications. Of the 27 full applications received, nine were selected and awards negotiated.

The nine projects selected all fall under one of two general categories: Assessment or Applied Research and Development (R&D). The Assessment projects are utilizing different approaches to determine the potential mineral value-streams associated with geothermal fluids in the U.S. The R&D projects are examining the feasibility of extracting rare earth and other critical elements and metals using a broad range of technologies, while also assessing the economic potential for the various approaches. The awards are alphabetically listed by category in Table 1, and the individual award plans are described in Section 3.

Table 1: Projects Competitively Selected from the Low Temperature Critical Materials Recovery Funding Opportunity Announcement.

Awardee Name	Project Title	DOE Funding	Awardee Cost Share
RESOURCE ASSESSMENT			
University of CA - Davis	Maximizing REE Recovery in Geothermal Systems	$500,000	$67,307
Simbol Materials	Determination of Rare Earths in Geothermal Brines and Evaluation of Potential Extraction Techniques	$250,000	$113,007
APPLIED RESEARCH AND DEVELOPMENT			
Carnegie Mellon University	Chelating Resins for Selective Separation and Recovery of Rare Earth Elements from Low Temperature Geothermal Water	$500,000	$64,061
Lawrence Berkeley National Laboratory (LBNL)	Engineering Thermophilic Microorganisms To Selectively Extract Strategic Metals From Low Temperature Geothermal Brines	$500,000	$55,556
Pacific Northwest National Laboratory (PNNL)	Magnetic Partitioning Nanofluid for Rare Earth Extraction from Geothermal Fluids	$495,000	$55,000
Pacific Northwest National Laboratory (PNNL)	Recovery of Rare Earths, Precious Metals and other Critical Materials from Geothermal Waters with Advanced Sorbent Structures	$375,000	$273,337
Southern Research Institute	Geothermal Thermoelectric Generation (G-TEG) with Integrated Temperature Driven Membrane Distillation and Novel Manganese Oxide for Lithium Extraction	$499,944	$63,466
SRI International	Selective Recovery of Metals From Geothermal Brines	$449,961	$50,000
Tusaar Corp.	Environmentally Friendly Economical Sequestration Of Rare Earth Metals From Geothermal Waters	$499,999	$215,164
	TOTAL	$4,069,904	$956,898

3. FOA AWARDS

Two projects, one with Simbol Materials, and one with University of California at Davis, are in the Resource Assessment category. These projects will populate the National Geothermal Data System (NGDS) with information about the potential REE and critical minerals contained within US geothermal and fluids co-produced from oil and gas operations. The remaining seven awards fall under the Applied R&D category.

3.1 Resource Assessment: Simbol Materials

Simbol Materials is one of the awards working to build information about the presence of REE in the geothermal and process waters in the US. They will be establishing sampling and analytical approaches for the assessment of valuable mineral concentrations in geofluids while considering the impact of high concentrations of dissolved salts in these fluids. They will also be evaluating different methods for extracting REE from geothermal fluids. As with other awards, Simbol's approach is to determine the quality and variability of US geothermal fluids, then evaluate various extraction technologies across the range of brine chemistries. Based upon their results they will then conduct an engineering economic review to determine the most feasible approaches.

The initial step will be to define sampling protocols for collecting geothermal fluids from geothermal power plants, oil and gas wells, and other wells with geothermal power generation potential (e.g. > 100^0C). Wherever possible, operating wells in the western US will be sampled as well as other wells and fields. These fluids will be analyzed to both characterize their general constituents and determine the concentrations of REEs using inductively coupled plasma-optical emission spectroscopy (ICP-OES) and ion chromatography (IC). Simbol will compile the test results into a database of REE concentrations in a range of US geothermal fluids. Using the analyzed composition of the various fluids, Simbol will test potential REE extraction techniques for their success with the various unique fluid chemistries. These results will be incorporated into a model to establish a preliminary economic feasibility assessment for mineral recovery, potentially identifying optimal fluids and feasible REE concentrations.

3.2 Resource Assessment: University of California - Davis

The University of California at Davis is teamed with University of Oregon to achieve two closely-related goals. First, the team will provide quality data quantifying the concentration of REE in fluids from a range of US geothermal fields. Second, the team plans to combine the information about the dominant controls on REE concentration in geothermal fluids to (i.e. temperature, pH, salinity, complexing agents, and phase separation history). The team will utilize the fluid data combined with analysis of the REE concentration in resident alteration minerals to constrain geochemical models, and identify processes that result in downhole loss of REE due to phase changes and/or subsurface mineral precipitation. The team will conduct downhole fluid sampling to quantify REE partitioning resulting from fluid production.

The team has successfully utilized technologies for in-situ measurement of REE concentrations in individual primary igneous and hydrothermal mineral phases in the Reykjanes, Iceland geothermal system. They have also demonstrated the ability to analyze REE at low concentration levels in highly saline geothermal fluids. Data from that work demonstrates it is possible to predict enrichment of REE in geothermal fluids. The team's approach is to use high-temperature down-hole sampling equipment to quantify the possible partitioning of REE in geothermal fluids during phase separation in the well bore and/or production facilities as a function of pressure and temperature. If validated, the ability to estimate fluid compositions from mineral analysis, using both LA-ICP-MS and geochemical modeling, the information will help to identify geothermal systems that have the highest potential for economic REE extraction in the US and allow industry to better target geothermal prospects most suitable for REE recovery.

3.3 Applied R&D: Carnegie Mellon University

The Carnegie Mellon University (CMU) team plans a 24-month project to evaluate selective, reusable, high capacity resins to effectively and economically extract rare earth elements from geothermal fluids and low-temperature co-produced fluids. The approach is to systematically study resins functionalized with organic ligands to selectively separate and recover lanthanides from fluids similar to the brines of geothermal power plants. Ligands with known ability to bond selectively with REE in aqueous solution will be examined for application in this solid-phase extraction approach, illustrated in Figure 1. As had been demonstrated in other industries, this approach offers the advantage that separations can be performed rapidly with few process steps, and scale-up of this approach is generally relatively straightforward.

CMU is working to develop low-cost, reusable chelating resins and solid supports that demonstrate the ability to selectively recover the desired critical elements from synthetic geothermal fluids. Candidate ligands will be tested in simulated low-temperature geothermal brines under simulated extraction process conditions. For the highest performing candidates, larger-scale tests will be conducted to demonstrate and evaluate an in-line REE recovery system at constant flow and required temperatures and pressures expected in a geothermal power plant.

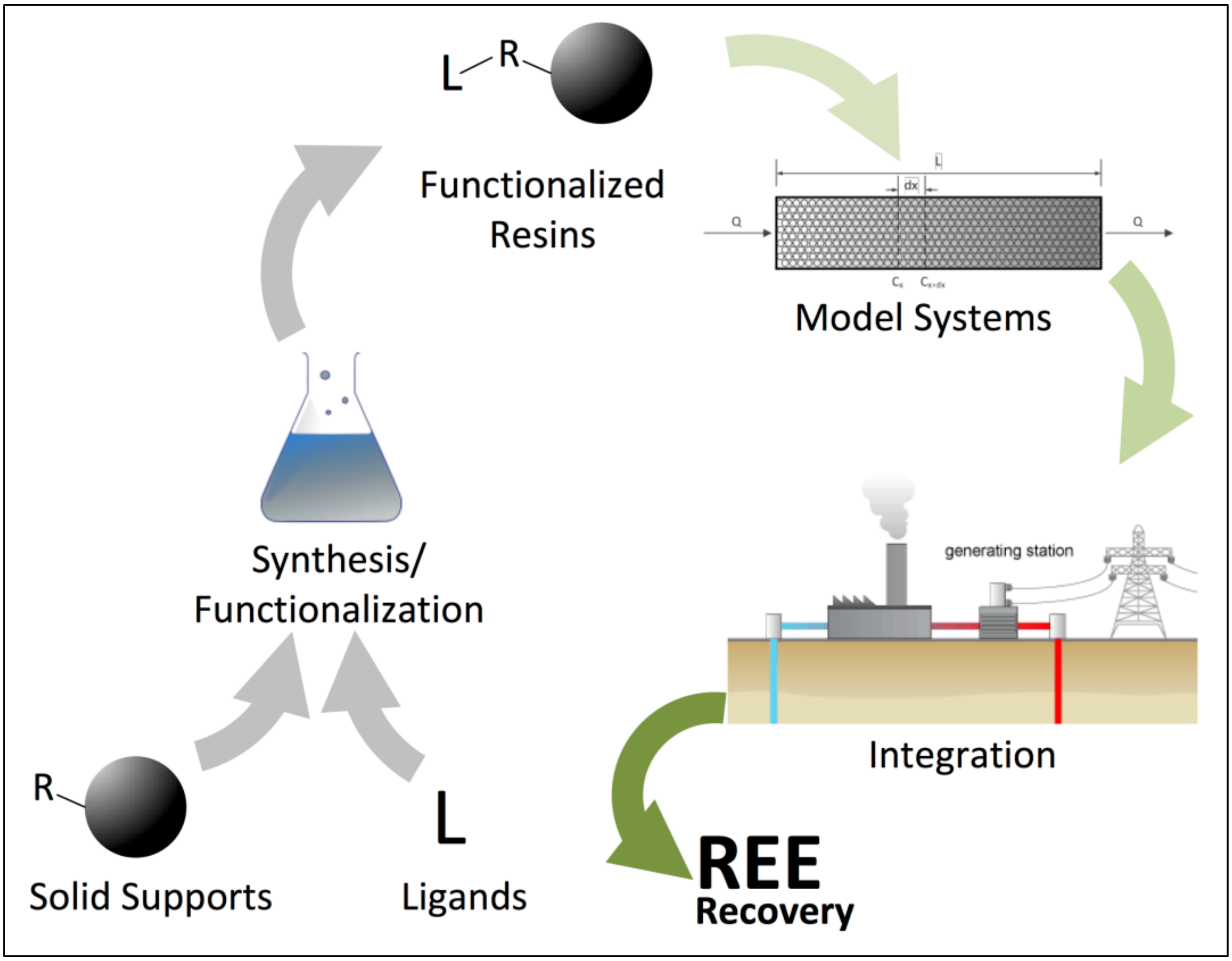

Figure 1: Schematic of the solid Phase Extraction process proposed by Carnegie Mellon University. (Karamaldis,A. 2014)

3.4 Applied R&D: Lawrence Berkeley National Laboratory

The Lawrence Berkeley National Laboratory (LBNL) approach to extract high-value metals, and/or critical metals is through combining their emerging capabilities in synthetic biology and materials science with their expertise in geothermal systems. The approach uses engineered thermophilic microbes as a low-cost, selective, and reversible metal adsorbent. It also addresses the most critical aspect of this technology – the ability to selectively bind specific strategic metals. To test this approach, the team will design and create engineered thermophilic microorganisms that display biomolecules known to selectively adsorb strategic metals, initially targeting Zinc and Gadolinium. For the successful thermophile designs, the team will conduct bench-scale experiments using both naturally-occurring and analogue geothermal brines doped with the target metals to assess the feasibility of this approach. Mass-transport, diffusion, and sorption processes will be modeled to assess the applicability to various commercial process scenarios and tested in flow-through or batch reactor systems. The process envisioned for this work is illustrated in Figure 2. If this approach successfully demonstrates the anticipated features, it will have broad ranging implications including extraction of critical materials from on-shore fields as well as remediation of contaminated sites.

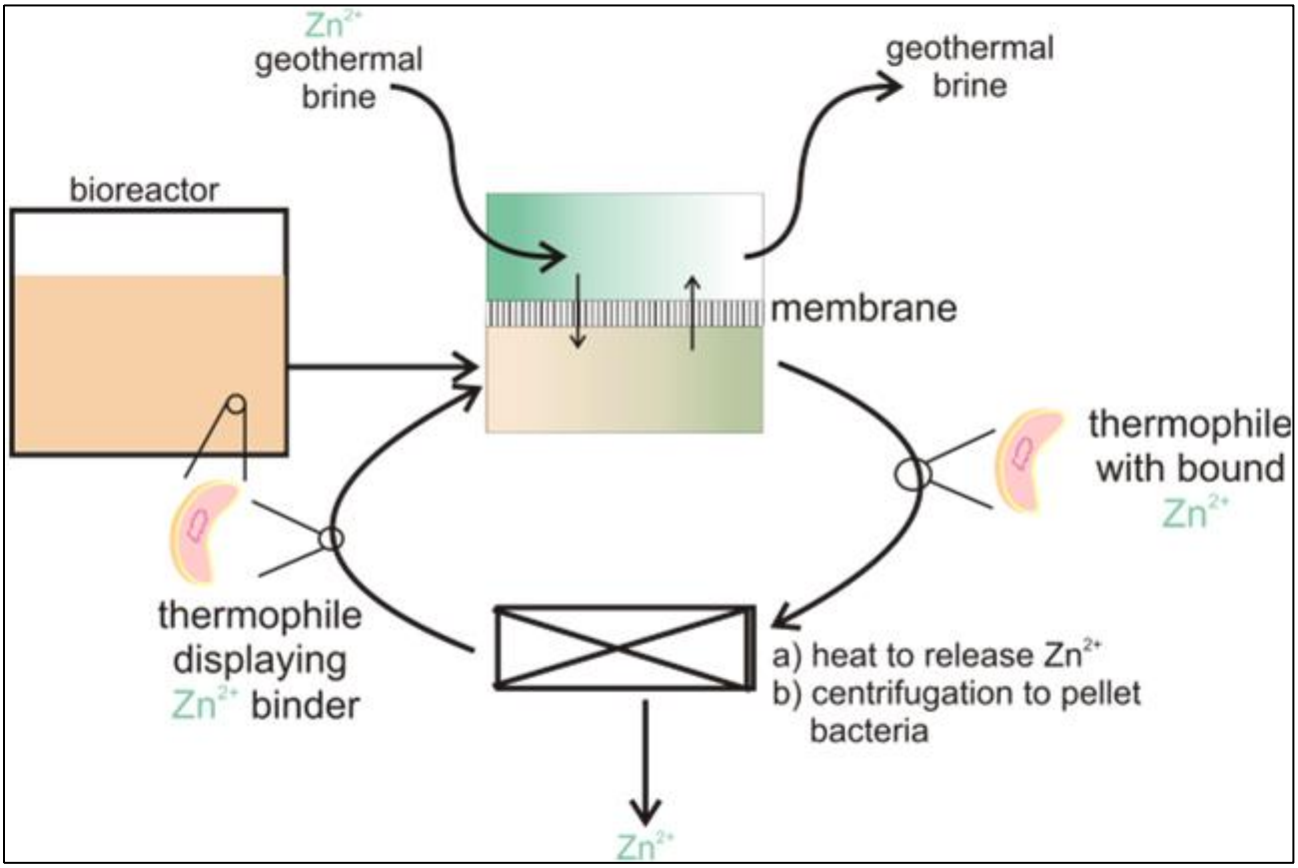

Figure 2: Schematic of the potential operating conditions for selectively-designed thermophiles with zinc ions as an example. (Ajo-Franklin et al, 2014)

3.5 Applied R&D: Pacific Northwest National Laboratory - *Magnetic Partitioning Nanofluid for Rare Earth Extraction from Geothermal Fluids*

Pacific Northwest National Laboratory (PNNL) is currently developing a new class of nanofluids called metal-organic heat carriers (MOHC) to improve efficiency of organic Rankine cycle power conversion equipment used for low-temperature geothermal resources as part of another project with GTO. However, applying nanofluids in chemical separation processes have yet to be exploited. PNNL has teamed with partner Global Seawater Extraction Technologies, LLC to demonstrate a nanofluid-based method for extracting rare earth metals from geothermal brines in a process that is simple and has the potential to be highly cost-effective.

The approach is to model and develop composite nanoparticles produced in a core-shell design that are introduced into geothermal fluids. The particle core will contain a magnetic iron oxide and the highly selective functionalized shell will be either silica or a metal organic framework (MOF) sorbent. The proposed structures are illustrated in Figure 3.

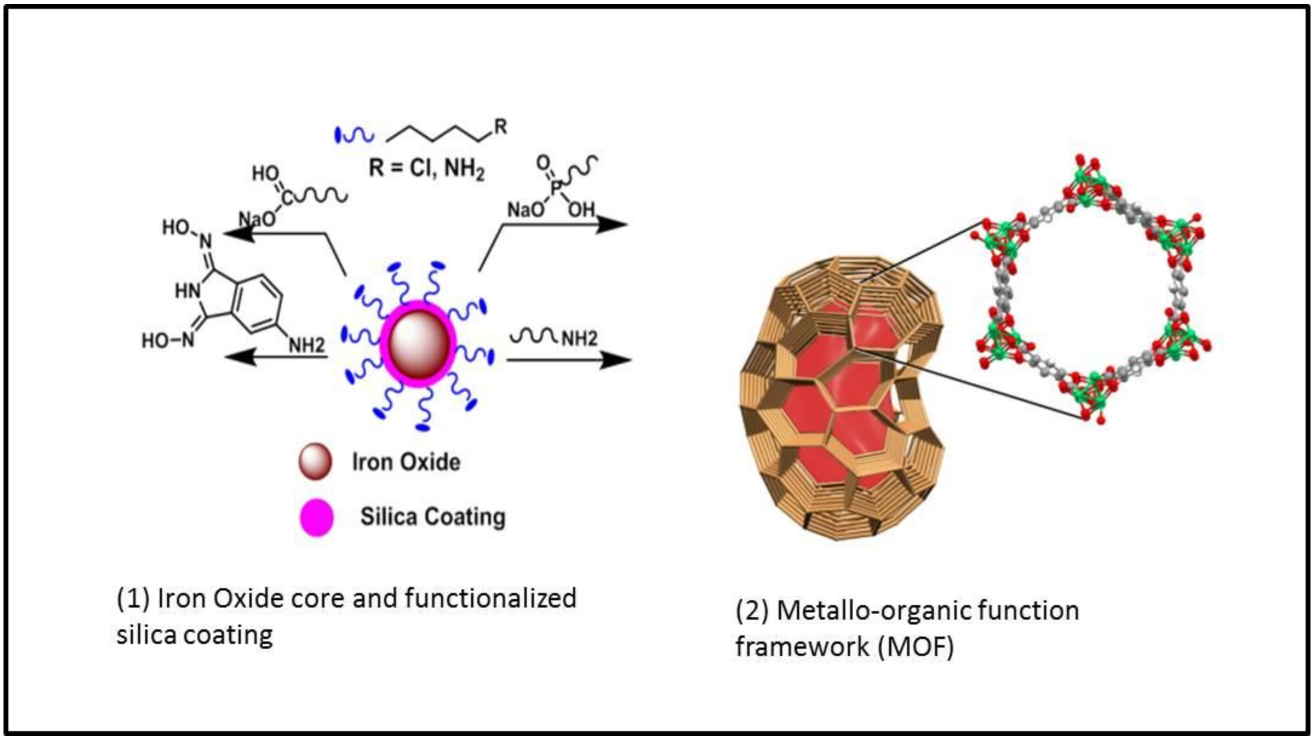

Figure 3: Illustration of the Structures of the PNNL Functionalized Nanoparticle Options. (McGrail et al 2014)

PNNL's proposed process is to introduce low concentrations of the nanoparticles into the geothermal brine after it has passed through the plant heat exchanger. This approach exposes the lower-temperature brine to a very high concentration of chelating sites on the nanoparticles without the need to pass through a traditional packed bed or membrane system. These more traditional approaches tend to introduce a pressure drop and parasitic pumping power losses that add costs and more complicated system designs. The PNNL plan incorporates a short residence time for the particles to flow with the brine to bind the REEs in the solution, then to magnetically separate out the loaded particles utilizing the particles' magnetic iron oxide core. After separation, standard extraction methods strip the REEs from the loaded nanoparticles, which can then be recycled.

As part of this work, the stripping efficiency for the REEs will be measured for both silica and MOF sorbents functionalized with a variety of chelating ligands to identify the most efficient composition. The team will conduct a techno-economic performance analysis of extraction systems using both sorbents. The sorbent providing the lowest overall production cost estimate for the REE extraction will be used to test cycling performance for an extended bench-scale demonstration of the process. The approach has the potential attributes of low parasitic losses and minimal operating and maintenance costs. PNNL's preliminary estimates using this nanofluid-based method suggest recovery efficiencies exceeding 90% and production costs for Neodymium, Dysprosium, Yttrium, and Europium that could be less than half the present commodity market value for these metals.

3.6 Applied R&D: Pacific Northwest National Laboratory – *Recovery of Rare Earths, Precious Metals and other Critical Materials from Geothermal Waters with Advanced Sorbent Structures*

For this project, Pacific Northwest Laboratory (PNNL) has partnered with Star Minerals Group and University of Oregon to develop and demonstrate new solid-phase sorbents to extract high value minerals from geothermal brines and potentially other process streams. If successful, their approach will establish a compact, clean, scalable, flexible, and efficient extraction technology. Recent developments integrating the principles of chemical and materials science with nanoscience for new solid-phase extraction materials promise to provide a mineral recovery technology with attractive attributes such as scalability and high processing speed. PNNL has conducted preliminary tests and their results are quite promising. Table 2 compares the recovery rates that have already been demonstrated by advanced composites for solvent extraction for a range of materials of interest.

Table 2: Comparative extraction performance in simulated geothermal brines (measured by chemical affinity, $K_d x10^3$ mL/g). (Addleman et al 2014)

Extraction Methodologies Compared				
Element Tested	**Advanced Composite Sorbant**	**Ion Exchange Resins**	**Chelating Resin**	**Activated Carbon**
REE	~ 4,300	2 to 40	3	12
Gallium	530	20 to 90	7	6
Ruthenium	1200	20 to 40	49	38
Silver	230	15 to 80	16	8
Uranium	3,500	50 to 70	44	130

Based upon their early results, PNNL anticipates that these advanced composite sorbent technologies will enable cost-effective recovery of valuable materials from low-concentration sources, such as geothermal brines.
Their approach is to test the most promising materials to assess the ability of these novel advanced solid-state sorbent materials to extract trace levels of REEs, precious metals and other critical materials from geothermal fluids As part of this project, PNNL will conduct a detailed engineering economic feasibility analysis to help determine the critical parameters bounding the viability of the composite sorbent technology as a value-added extraction processes for geothermal energy systems. It is anticipated that the advanced sorbent materials and engineering analysis will be applicable to other industrial processes in which secondary recovery of valuable materials may provide economic benefit.

3.7 Applied R&D: Southern Research Institute

Southern Research Institute (Southern) is teamed with partners Novus Energy Technologies, Carus Corporation, Applied Membrane Technology, Inc., and Magma Energy Corporation, to develop an innovative 'Geothermal ThermoElectric Generation' (G-TEG) system to both produce electricity and extract lithium from low-temperature geothermal brines. The G-TEG system is illustrated in Figure 5. In this approach, incoming brine is treated, then passed through a thermally-driven direct contact membrane distillation system. Electricity is generated when the latent heat in the water vapor passing through the distillation membrane is captured in the thermoelectric module before it condenses on contact with the cold side heat exchanger. The distillation leaves a stream of concentrated brine. This brine containing any dissolved minerals can then be processed for mineral recovery. For this project, the team is specifically evaluating the use of the Carus sorbent technology to recover lithium from the brine effluent.

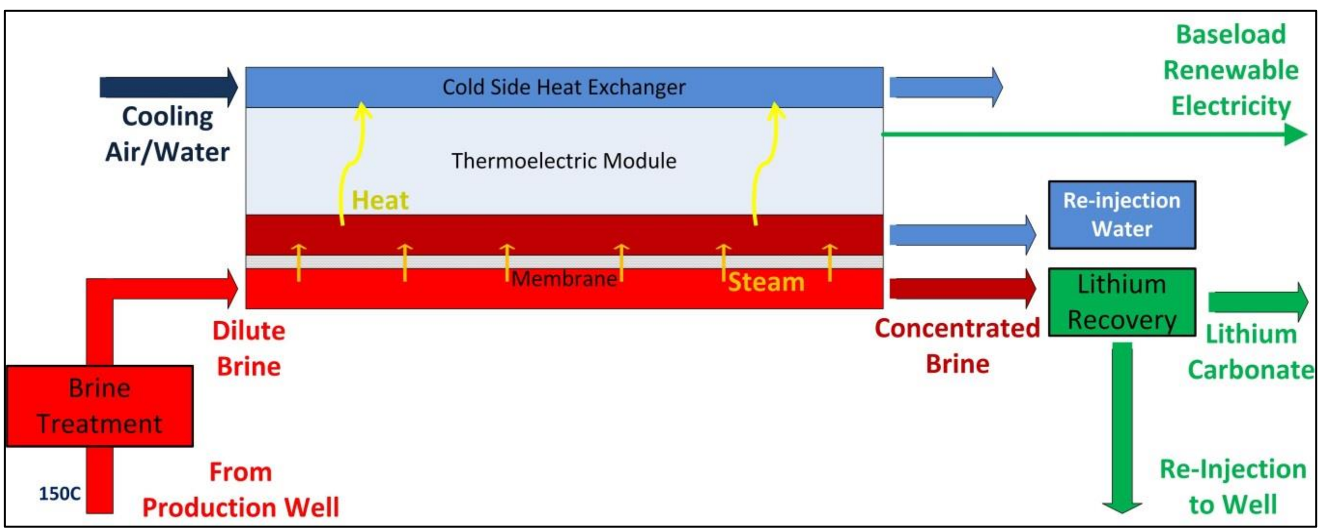

Figure 4: Process Flow Diagram of G-TEG and Mineral Recovery System. (Renew, J. 2014)

Over the course of this project, the team will model components and systems and conduct bench tests of the filters and sorbents. The test results will provide the necessary information to support a techno-economic feasibility study of the proposed system and its integration with low temperature, mineral rich geothermal or other process water sources.

3.8 Applied R&D: SRI International

SRI has teamed with Simbol Materials to develop and validate a new generation of highly selective ion exchange resins to separate metals from geothermal fluids more efficiently and at lower cost than current processes. SRI is designing the resins for integration into the power production systems of medium-to-low temperature geothermal power plants, and may be applicable to other fluids as well.

The focus for this work is to design resins to selectively bind lithium and manganese ions for recovery through the novel process of metal ion imprinting polymer beads as illustrated in Figure 5. During the planned 18 months of this project, SRI will determine the ability of the new resin to extract lithium and manganese from low-to-medium temperature (up to 100^{o}C) geothermal brines. Testing will also quantify the sorbents' binding capacity, selectivity for the ions, and sensitivities to a range of geothermal fluid compositions. As part of the resin development, appropriate processes to both strip the metals and regenerate the resins for repeated use will be determined and validated as well as the overall durability of the sorbent. Both batch and flow-through process approaches will be evaluated. Partner Simbol will work with SRI to validate the effectiveness of the resin's binding and regeneration capabilities at its facilities.

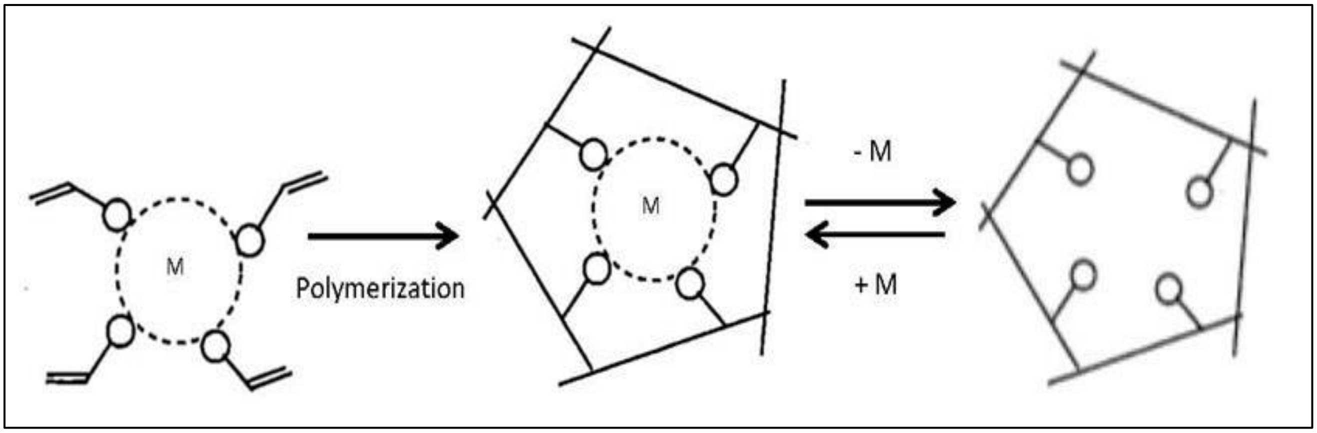

Figure 5: Schematic diagram of macroporous beads imprinted for selective metal ion extraction. (Ventura, S., 2014)

3.9 Applied R&D: Tusaar

Tusaar has developed a patented media that extracts metals from an aqueous stream. Pilots and installed systems using their proprietary materials have already demonstrated that their product, doped granulated activated carbon, is robust and environmentally friendly. Tusaar is now working with the Colorado School of Mines to evaluate the effectiveness of their product for selectively recovering critical metals including REEs from geothermal fluids.

Tusaar's product uses no toxic chemicals, has proven to be economical, and has demonstrated its durability for regeneration and reuse for more than 250 cycles. Tusaar manufactures the media by surface preparation of select granular activated carbons (GACs) followed by treatment with commercially available organic ligands. To date, the media has been robust and works in a range of environments. Figure 6 illustrates the effectiveness of the media in removing uranium from acid mine drainage fluids. Using synthetic solutions containing the target metals and all other constituents known to exist in two or more different geothermal brines, Tusaar will evaluate its product in laboratory-scale batch and column tests. The media's metal sequestration and recovery capabilities from geothermal fluids will be assessed. The Tusaar media will then be further optimized for the target metals and the challenges posed by the hardness, expected flow rates, water temperature, total dissolved solids, and selectivity toward competing metals. After experimental results are available, Tusaar will complete a detailed economic analysis for the use of this technology to recover critical minerals.

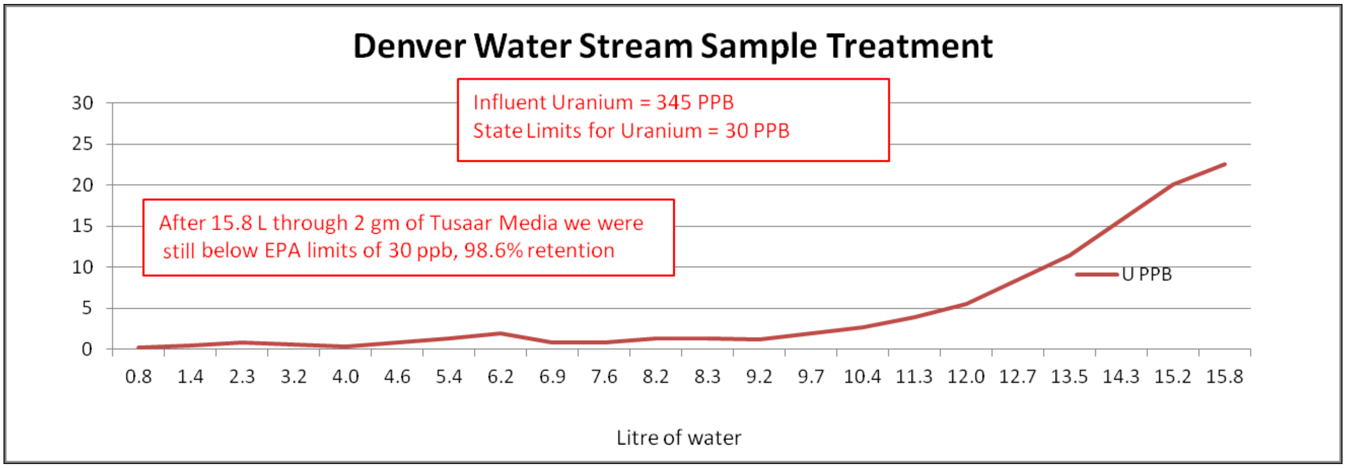

Figure 6: Demonstration of Tusaar media capability to sequester uranium from acid mine drainage. (Stull 2014)

4. ANCILLARY WORK

In addition to the research described in Section 3, a technical monitoring team (TMT) supports the GTO team to evaluate research success and to act as a resource to the researchers in problem solving for the project research teams. The TMT consists of six members from Idaho National Laboratory (INL), Sandia National Laboratory (SNL) and the National Renewable Energy Laboratory (NREL). Generally, the team joins the DOE manager and the awardee on a regular basis, providing technical feedback to both the awardees and the DOE project managers.

A second key area of support for these awards is monitoring the quality and consistency of the data reported to the NGDS. This is accomplished through an annual operating plan (AOP) project with NREL. A key element of the effort is to make sure the data obtained by the various research teams is consistently recorded and reported. The objective is to ensure the data collected from these projects is made available to the broader community as quickly as possible, in formats that are accessible for research others may want to conduct in geothermal or related projects. The intention is to enable more rapid technology transfer to support expansion of the US geothermal market.

5. CONCLUSIONS

GTO launched an extensive initiative to support creation of a systematic assessment of the available critical and REE materials dissolved in US geothermal fluids, and to evaluate new materials and advanced technologies for their ability to economically remove critical or high-value minerals from solution. This is a two-pronged approach to both populate the NGDS with data sets consisting of rigorously quantified geothermal fluid characteristics, as well as evaluating promising technologies for obtaining additional value from these fluids. The partners in these projects are also examining co-produced fluids from other processes, such as the brines produced from oil and gas operations.

Projects began in October 2014, and with only a few months of work, some key observations have been made. The projects have highlighted the variability of information pertaining to the constituents of geothermal fluids, and existing analysis of high value minerals contained within brines is generally lacking. In addition, the characteristics of geothermal fluids are highly variable, as illustrated in the Piper diagram in Figure 8 below. This is an added complexity for determining useful extraction procedures, and will require rigorous evaluation to identify the most promising approaches.

Success in this initiative can be measured in several ways. First, detailed, publicly available geothermal and process waters analyzed for these high value and critical materials will be publicly available. Second, an assessment of various recovery approaches from biological to adsorption techniques to nanofluids will have been evaluated and a library of experiences will be made available. Strengthening the US strategic position regarding these resources also offers the potential to bolster domestic advanced manufacturing. Lastly, and most importantly, economic recovery of critical materials from produced fluids will boost the geothermal industry.

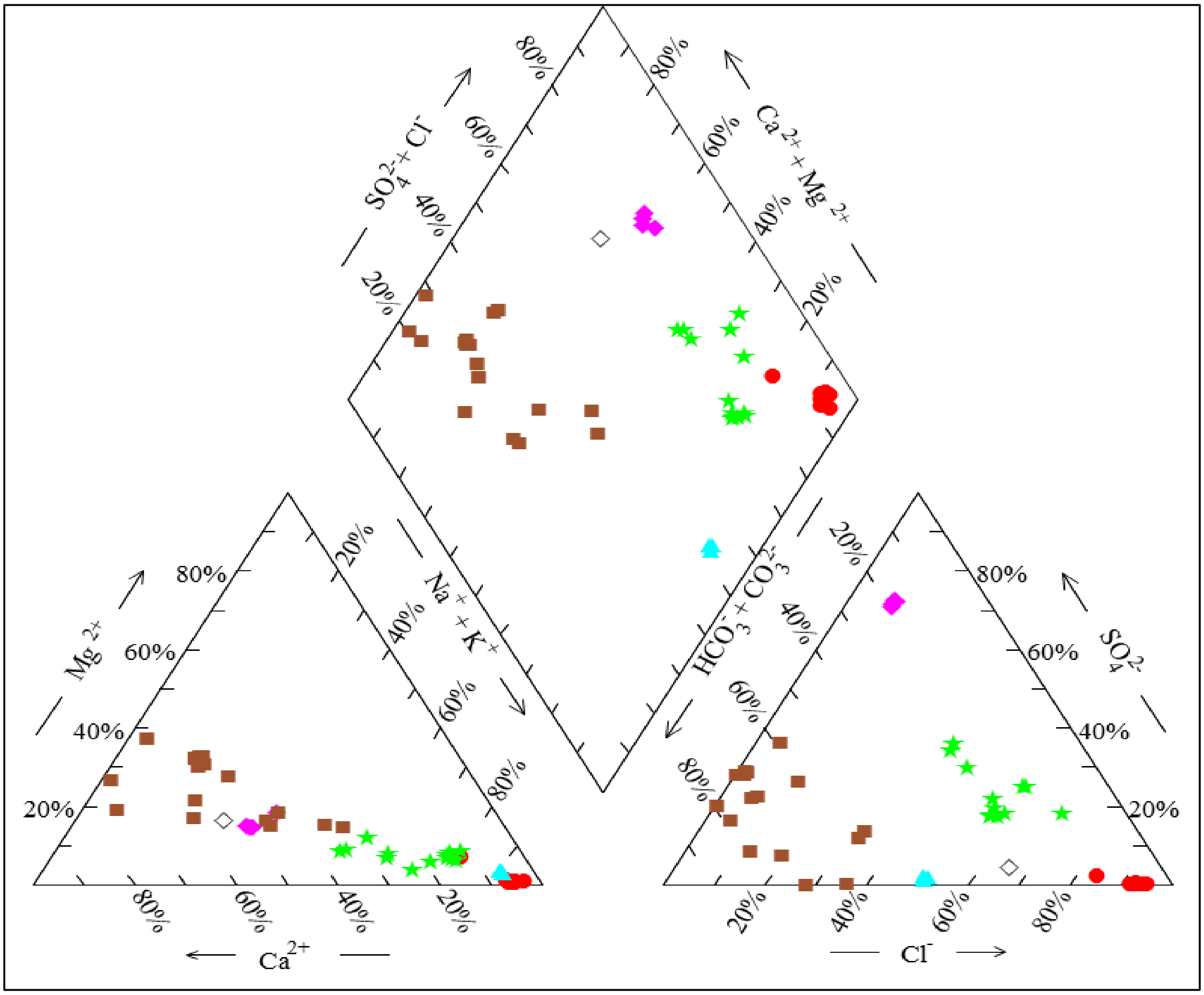

Figure 7: Reported chemistry of waters measured from several hot/warm springs and wells located in southeastern Idaho. (Neupane et al 2015)

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