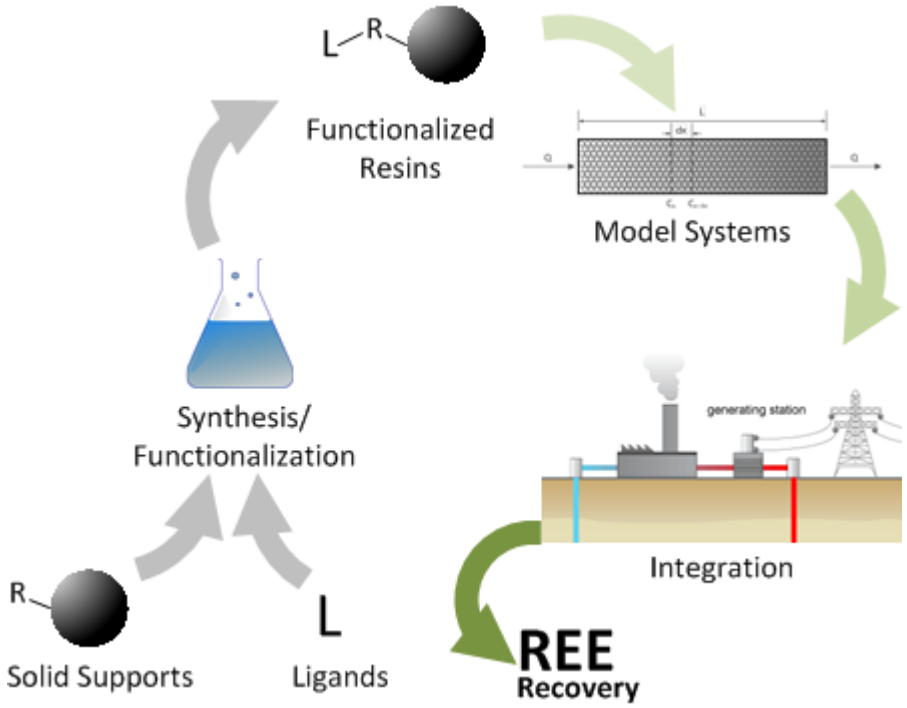

Functionalized Adsorbents for Selective Separation and Recovery of Rare Earth Elements From Low Temperature Geothermal Water

Project Officer: Arlene Anderson

Total Project Funding: $500,000

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DE-EE-0006749

Relevance/Impact of Research

Project's Key Idea

Selective and reusable functionalized adsorbents can be used to extract and quantitatively recover rare earth elements (REE) from geothermal fluids in a simple two step process

Proposed Project Goals

Development of novel selective, reusable, and high-capacity adsorbents for REE extraction from geothermal fluids and systematic study of those adsorbents in laboratory scale applications to better inform planning and design of separation columns for larger scale applications

Challenges and Innovation of this Project

- Mineral recovery from “low-value” resource streams (i.e. geothermal fluids) represents challenging separation/recovery chemistry
- Current separation strategies (e.g. solvent extraction in the mining industry) provide unsatisfactory performance for low-value resource streams
- This project draws on the knowledge of highly selective ligands for aqueous REE chelation to develop more efficient REE collectors once the ligands are immobilized on a stable substrate.
- Integration at scale can be achieved using traditional water treatment engineering techniques

Project's Main Objective

is to develop novel, functionalized adsorbents with high capacity and selectivity for rare earth elements (REEs), which can be used to separate and recover REE from brines being used in geothermal power plants. The adsorbents will be reusable and recovery of critical elements will be done in a multi-step process. The specific objectives of the proposed work are to:

1. Design optimized selective ligand-functionalized solid supports.
2. Develop optimized selective reusable adsorbents (end-product).
3. Develop a model system for pre-concentration and recovery of REEs from brines.
4. Develop modular setup for potential online integration in a geothermal power plant.

Meeting GTO objectives

- Success of this project could add financial incentives to geothermal operators through creation of new revenue stream
- Global market for REE is expanding while supplies generally stagnate
- Crisis-level supply/demand disparity (2010-2011) met through strategic reserves and sacrifices of product quality by manufacturers (i.e. substitution resulting in lower efficiency)

Major Expected Outcomes

1. development of the ability to selectively complex REEs on a functionalized adsorbent;
2. development of a technology to recover REEs from high salinity fluids;
3. development of a scheme to recover REEs from geothermal fluids using an in-line modular setup.

The proposed project focuses on developing selective adsorbents for REE extraction from geothermal fluids and the systematic study of those adsorbents in laboratory-scale applications to inform planning and design of separation columns for larger scale applications.

Impact

The proposed technology will enhance our ability to selectively complex REEs on functionalized adsorbents, treat high saline geothermal waters and recover REEs from them, and provide an approach to recover REEs systematically and continuously using an online modular setup in geothermal power plans.

Managing to develop an economical approach for separating these technological important elements from millions of gallon of produced water that generated each year will provide additional resources to the domestic economy.

Scientific/Technical approach

- Adsorbents designed using commercially available ligands and supports
- Use of synthetic solutions to match expected chemistries of geothermal fluids
- Study effect of pH, ionic strength, matrix cation competition, and temperature
- (Pseudo-) equilibrium behavior of adsorbents studied in batch reactors prior to scale up to flow through systems.

Scientific/Technical Approach

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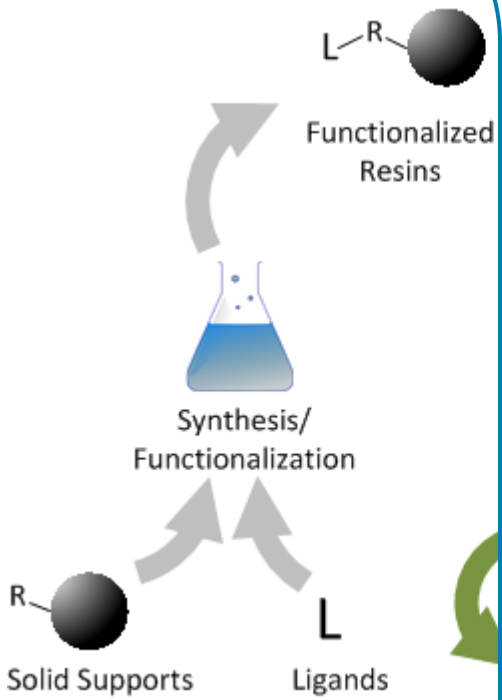
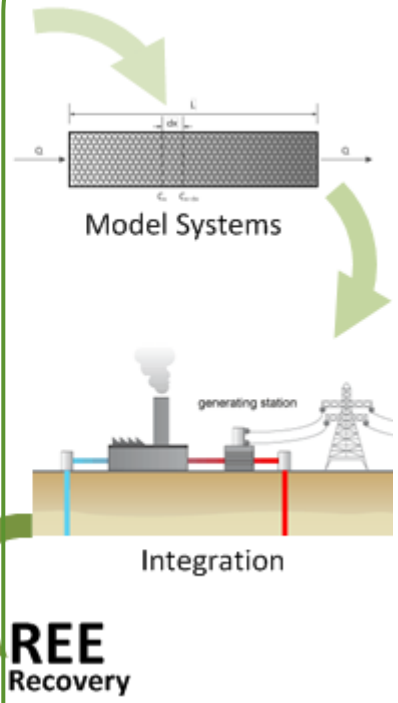
Budget Period 1

- Selection of solid supports.
- Selection of ligands.
- Functionalization of adsorbents.
- Batch testing of functionalized adsorbents in synthetic brine for selectivity, capacity, recovery, and robustness to chemical and physical variability of the brines.
- Selection of the most promising functionalized adsorbents





Budget Period 2

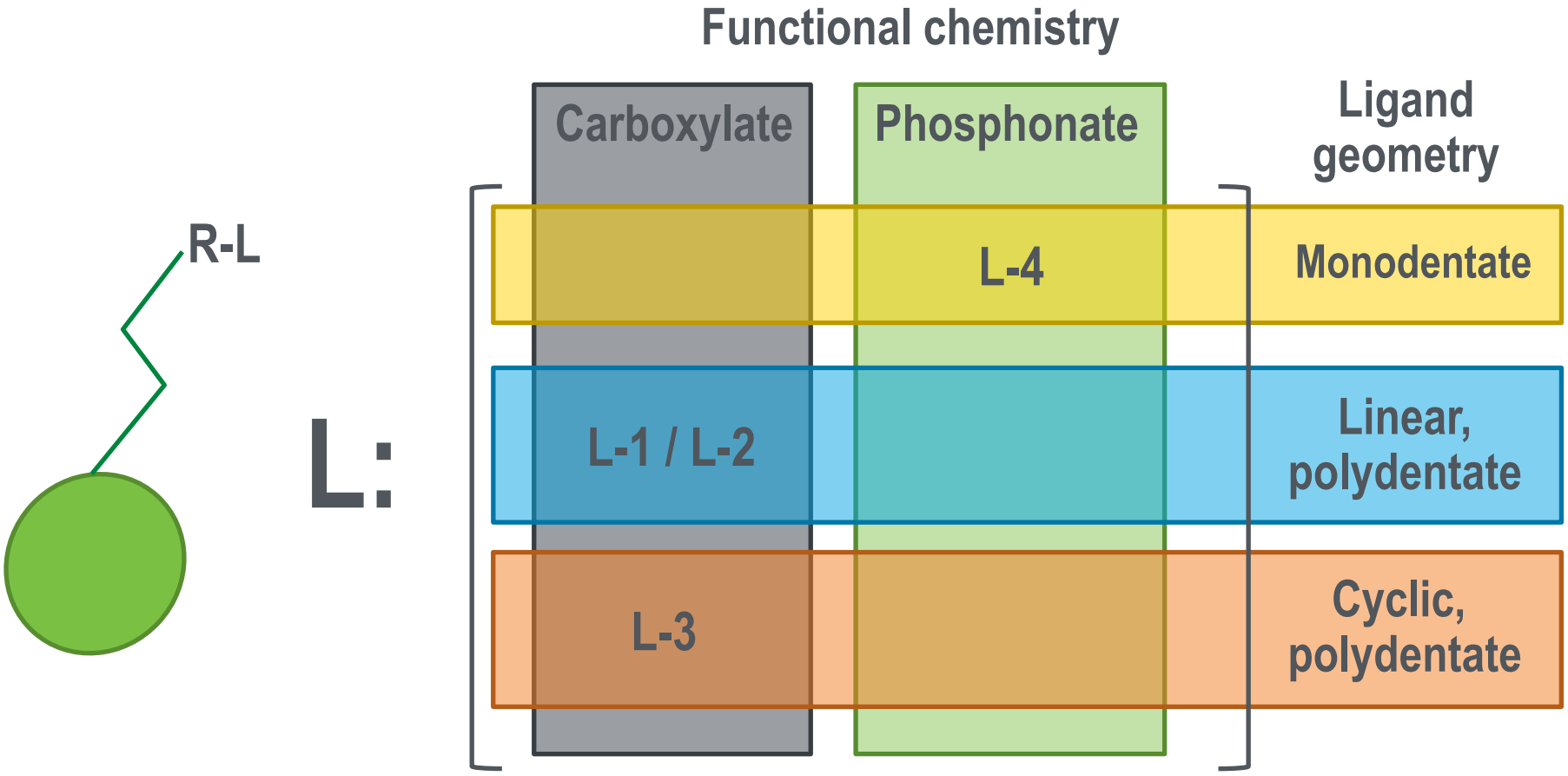
- Development of modular column system.
- Single column system lab-testing using the best performing functionalized adsorbents from BP1 with synthetic brines previously used against flow rate, temp. and pressure effects.
- Acid elution approaches for quantitative recovery of REEs.
- Modular, multi-column testing.
- Column testing with natural brines.

Completion of milestones 1 and 4

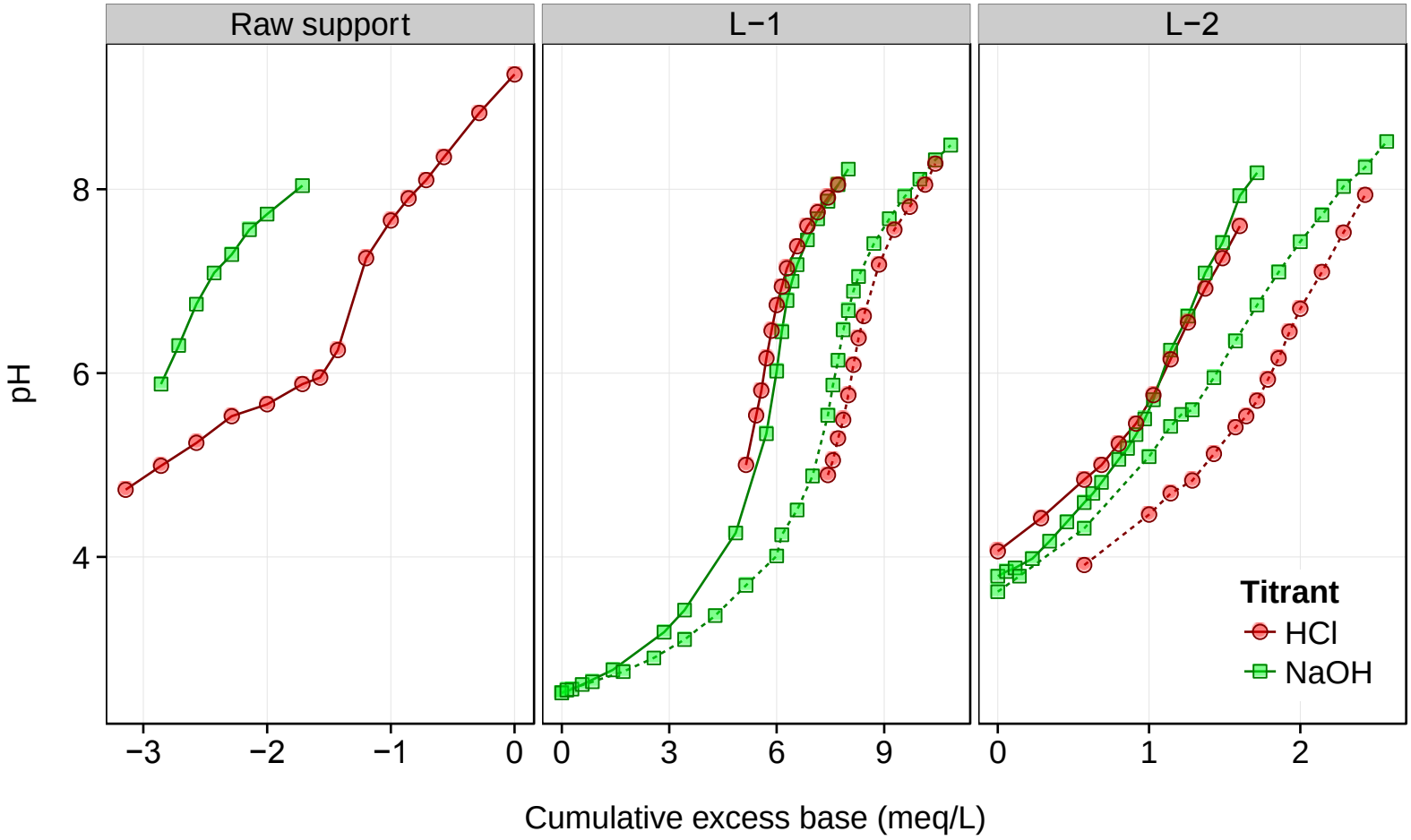
Number	Description	Verification process
M1	Completion of synthesis of three functionalized adsorbents	Aminated silica supports have been functionalized with five (5) ligands via “one-pot” reaction
M4	Completion of initial screening of functionalized adsorbents	Gd (as model REE) uptake studied for functionalized adsorbents in 0.5 M NaCl over range of relevant pH

No technical or cost variance to date

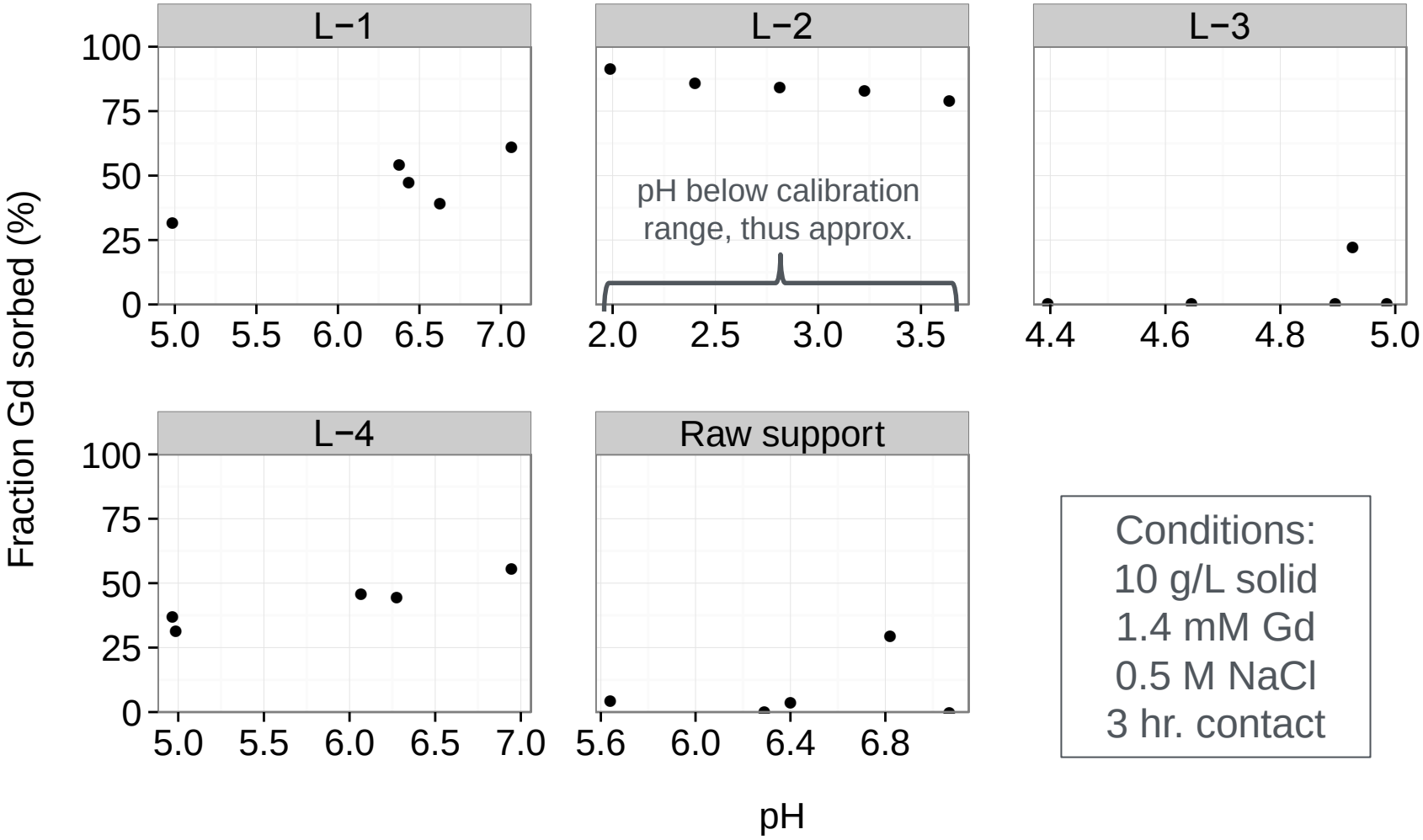
Functionalization explores differences in ligand chemistry and geometry



Change in acid-base behavior confirms modification of support surface



Early testing with Gd indicates potential best performers



Conditions:
10 g/L solid
1.4 mM Gd
0.5 M NaCl
3 hr. contact

Pathways to achieving future milestones

Number	Description	Verification process
M2	Completion of synthesis of optimized functionalized adsorbents	• Employ larger (1 mm) beads • Accurately quantify functional site density • Characterize surface chemistry
G/NG1	Selection of selective functionalized adsorbents	• Select best performers from initial screening • Test in presence of competing ions (e.g. Ca + Zn) • Test with multiple REE

Future Directions FY2015

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Milestone or Go/No-Go	Status & Expected Completion Date
Functionalization of solid supports with ligands	
Completion of synthesis of optimized and specific functionalized resins	Ongoing; July 2015
Completion of synthesis of optimized functionalized resins for model systems	Not started yet; July 2015 – June 2016
Ligand Performance Testing with batch reactors	
Selection of selective functionalized resins (GO/NO-GO)	Ongoing; October 2015
Single column plug flow reactor tests with synthetic brine	
Completion of model systems setup	Not started yet; November 2015
Completion of testing of functionalized resin with single column flow-through system	Not started yet; November 2015 - September 2016
Modular plug flow reactor tests with synthetic brine	
Completion of testing of functionalized resin with modular column flow-through system	Not started yet; November 2015 - September 2016

Mandatory Summary Slide

- Project objective is to develop a silica adsorbent with the surface bearing an REE-binding ligand that can remove REE selectively from saline geothermal waters.
- Five candidate functionalized adsorbents have been developed and subjected to preliminary testing with Gd as a model REE element in 0.5 M NaCl
- Initial screening testing indicates potential for three of the functionalized adsorbents
- Milestones to date (M1 for adsorbent synthesis and M4 for adsorbent screening) have been accomplished
- Project is on schedule and on budget

Additional Information

- Additional functionalized adsorbents will be synthesized and tested.
- Geothermal power plant experts (Thermochem) have been engaged as consultants to advise on geothermal fluid water chemistry and integration of the proposed technology with geothermal fluid cycling processes.
- Disclosure of invention/provisional patent application submitted.