Recovery of Rare Earths, Precious Metals and other Critical Materials from Geothermal Waters with Advanced Sorbent Structures

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**Abstract**

We develop and demonstrate high value strategic mineral extraction technology for geothermal solutions to provide additional revenue for geothermal operations. This is accomplished with high performance solid state sorbent materials. The best industrial materials as well as new PNNL patented technology, which has demonstrated unequalled chemical affinity for trace element collection. The high performance collection materials will enable superior performance and will enable low cost capture of high value materials creating a secondary revenue stream for geothermal projects. The sorbent materials are configured for collection of trace levels of rare earths (REEs), precious metals (PMs), and other critical/strategically valuable materials (CMs) such as zinc, manganese, copper, and uranium. Sorbent performance is determined in actual geothermal water of Sharkey Hot Springs, Idaho. We develop and demonstrate reusable sorbent materials capable of high efficiency collection of trace levels of REE from geothermal waters. A technoeconomic analysis is conducted to determine the viability of the sorbent technology in general, and the new high performance materials in particular, as a value added extraction process for geothermal energy systems. The project measures and provides the information of the concentration of REEs, PMs, and CMs at established geothermal sites and at hot springs in the vicinity of relevant mineral deposits, to identify geothermal brines of potential interest that could supply essential metals for clean-energy technologies and other industries. The developed and demonstrated technology and economic analysis will have applications to other industries where recovery of trace minerals from solutions (*i.e.,* low grade sources, recycling processes, industrial by product flows and tailings/waste streams) would provide a value-added price.

**Background**

The Promise and Abundance of Critical Minerals in Geothermal Resources

Geothermal brines represent a potential new source for strategic materials but the abundance of minerals and cost effective technology for separation from geothermal brines are unknown. Recent GTO partnering efforts have demonstrated effective extraction of lithium, manganese, and zinc from geothermal brines, providing proof of principle that additional revenue streams may be realized from mineral recovery in geothermal power operations (and potentially from other low concentration sources).

The rare earth (RE) elements occur at generally low concentration in geothermal fluids in the range from a few hundred picograms to several micrograms per liter.1-3 For example, at a thermal spring associated with Idaho batholith, in unfiltered samples1, total REs content varies from ~0.05-3.24 µg/L, with an average ~0.63 µg/L. The most abundant REs in these geothermal fluids are lanthanum (La), cerium (Ce) and neodymium (Nd) with average concentration of ~0.14, 0.26 and 0.35 µg/L, respectively. It should to be noted that unfiltered samples often contain much higher concentration of RE than filtered samples. At acidic hot springs in the Kusatsu-shirane volcano region of Japan2, total RE concentrations range from ~15.0-718.5 µg/L, and average ~210.7 µg/L. The most abundant REs in these geothermal fluids are La, Ce and Nd with average concentrations of ~31.9, 75.4 and 33.8 µg/L, respectively. Although La, Ce and Nd display higher concentration than other REs in many hydrothermal fluids, Eu content in hydrothermal fluids from the Mid-Atlantic Ridge was slightly higher than Nd, the average concentration of these metals was 0.26, 0.33, 0.17 and 0.19 µg/L, respectively.3 The variation in concentration and the fractionation of REs are results of the location, source rocks and temperature.1, 2, 4, 5 Speciation of REs in geothermal fluids depends on the types and relative concentration of ligands/complexing agents, as well as pH.

The precious metals (PMs) silver (Ag), gold (Au), palladium (Pd) and platinum (Pt) can be present in geothermal fluids at trace level in ppb range.6, 7 The geothermal fluids typically contain PMs below 20 ppb (µg/kg), however, Ag has been reported at levels 10-100 times higher than other precious metals in the Salton Sea and Raft River, USA.6 Similar to REs, PMs occur in varying degrees, depending on the concentration of complexing materials in the local geothermal fluids.6

Base metals occur in geothermal fluids in trace concentration in the ppm range (mg/kg).6 The abundant base metals and their concentrations in geothermal fluids are variable, and are found to depend on the geothermal systems and conditions. For examples, manganese (Mn), Zinc (Zn), and lead (Pb) were reported as the primary ions in geothermal brines and in greater concentrations than copper 6 , but different compositions of metals were found in spring waters.1, 2, 7 The concentrations of Mn and Zn were found to be ~500-1500 ppm in geothermal brines of Salton Sea, USA, ~1-2 ppm of Mn were reported in Bandaiko hot string water 2, and only < 1 ppb of both metals was detected in carbonate spring water7. The geothermal fluids also contain other metals, such as antimony, chromium, iron, nickel, arsenic, and tellurium at varying trace concentrations.1-3, 6, 7

*Advanced Separation Materials*

PNNL has recently developed collection materials and green extraction methods that enable recovery of critical resources, such as PMs and REs, from previously nonviable low grade sources. Collection of valuable resources from dilute industrial waste streams and other low concentration sources reduces emission of toxic metals into the environment while providing a value added process for recovery and recycling of metals. PNNL’s novel sorbent materials significantly outperform other sorbents in the extraction (and subsequent release) of low levels of valuable metals from various acidic and high salt solutions. As shown in Tables 1 and 2 below, the PNNL materials have demonstrated unequalled chemical affinity for trace element collection relevant to geothermal mineral extraction, typically 10-1000x better than comparable sorbents while allowing for facile release of captured material and subsequent regeneration of the sorbent. This superior sorbent performance results from careful integration of inexpensive polymers, high surface area ceramics, and novel selective (and very high affinity) capture chemistries installed at high densities. The excellent affinity, selectivity, capacity, and reusablility of the PNNL composite sorbent materials provide multiplicative benefits. The high affinity enables capture of ultra-trace level metals from solutions where recovery was not previously possible. For select applications environmentally benign methods have been developed for cost effective recovery (stripping) of the collected metal and for regeneration of the sorbent material which provides multiple reuse cycles. These optimizations further reduce costs and improve process viability. All sorbents can be stripped and regenerated with standard acid processes. The organic chelator based sorbents are stable up to 250-350oC depending upon composition. The modified metal oxide sorbents are believed to be stable to over 400oC.

Work to date has shown the sorbent material to be easily integrated with a wide range of metal, ceramic, and polymeric support structures that can be optimized for different applications including traditional packed beds, various filter structures, and novel membranes. Rapid kinetics, demonstrated with the composite thin film and fiber configuration of these sorbents, may also provide lower process cost as well as reduced biofouling issues. Patents have been granted or are pending and manuscripts are in preparation.8-13

Other organizations have been developing new commercial off the shelf (COTS) sorbent materials that merit comparative and competitive evaluation in this effort. Promising new COTS sorbent materials are available from a number of companies including; Eichrom Technologies, Steward Advanced Materials, IBC, Silicyle, IntelliMet, Rohm and Hass, and others. Novel separation materials may also be available from DOE funded effort at the Critical Materials Hub as well as the DOE-NE efforts for uranium recovery from seawater. Materials made available from commercial sources and government sources will be evaluated and their expertise will be collaboratively engaged as these companies choose to interact.

**Project Summary and Status**

The objective of this program is to evaluate, develop and demonstrate flexible, scalable mineral extraction technology for geothermal brines based upon solid phase sorbent materials with a specific focus upon rare earth elements (REEs). The process is based upon proven industrial methods (solid state sorbent technology) and will provide a valuable secondary product stream to reduce the cost of geothermal energy while providing a domestic, environmentally benevolent, source of critical minerals. Further, the technology will be scalable and flexible to accommodate the different mineralogy of geothermal sites and plant sizes. Initial FY15 work consisted of the development, evaluation and demonstration of sorbent materials that can effectively perform mineral extraction in the extraordinarily harsh geothermal solution conditions. This project is DOE sponsored and the discussions of the works are related to the milestones of the project which were agreed upon with DOE.

**Program Structure and summary results by Task:**

**Summary of Results for Task 1: Program Initiation and Analysis of Geothermal Fluids**

*Task 1 Summary:*

This task provided a programmatic kickoff and supported extensive critical discussions among the diverse multidisciplinary team members (academic, industrial, national laboratory) to refine keys issues that need to be resolved to make the technology viable. The effort also involved an initial analysis to determine the composition of geothermal waters and define the appropriate solution test conditions. Specific results from this effort are discussed in context with specific milestones.

*Milestone 1.1 Assemble Core List of Critical Challenges for Solid State Sorbent Technology for Geothermal Mineral Extraction.*

PNNL hosted a kickoff meeting upon receipt of funds to facilitate immediate interactions, information sharing and coordination for the entire project. The team meeting provided a valuable face to face cohesive interaction for the diverse team members. In addition to the group orientation/coordination on the diverse technologies involved in this effort a specific outcome of this meeting was to refine a list of critical challenges for the application of solid state sorbent technology for the economically viable extraction of geothermal minerals. The key critical parameters were found to be:

* Sorbent affinity and capacity
* Sorbent kinetics
* Sorbent lifetime
* Sorbent form factor
* Mineral recovery from sorbents and sorbent regeneration
* Cost effectiveness (materials, recovery process, space, installation and operation)

All of these material performance parameters must be achieved and successfully coordinated for an effective chemical extraction process to be achieved. Some additional details are available in Appendix A.

*The critical challenges for successful application of solid state sorbent technology for geothermal mineral extraction will be addressed in detail in multiple upcoming publications.* The results of the effort will have application to this and other projects (or future efforts) for low temperature mineral recovery.

*Milestone 1.2 Complete Analysis of Geothermal Fluids*

The performance of any collection process depends upon both the nature of the extraction chemistry as well as the capture chemistry. The Geothermal Program Office did not have a “standard” solution to test separation technology performance against so efforts were undertaken to ascertain appropriate conditions (and obtain geothermal solutions to test REE collection material against). Further, this program suggested to the Geothermal Program Office that a standard solution, as wells as test and evaluation conditions, be established for consistent assessment of the mineral collection technology. To enable completion of program goals (both for this project’s specific objectives as well overall DOE programmatic efforts) this effort:

* Performed a literature review for the solution chemistry and concentration of REEs and other metals in geothermal fluids.
* Identified promising regions in the United States for the value added recovery of minerals from geothermal fluids
* Collected geothermal waters for test and evaluation from a promising site for REE enrichment. *(test solutions were collected from Sharkey Hot Springs Idaho, which is in a region with known REE deposits. See Appendix B)*

To capture the accumulated relevant information and make it available for future efforts a review article entitled “*A Review of Rare Earths in Geothermal Fluids; the chemistry, abundance, distribution, analysis, and economic potential*” is presently being assembled in a manuscript for publication in the peer reviewed journal Hydrogeology.

*A key and critical factor that became apparent upon review of literature and available data was the variability in the water chemistry of the geothermal fluids in its impact probably on geothermal mineral extraction technology.* As expected that concentrations of dissolved minerals vary sustainably site to site. More significantly to the development of mineral recovery technology was that the concentrations of dissolved solids and anions (such as carbonate, sulfide and chloride) are highly variable and present at much higher concentrations than the trace minerals. These anions determine the chemical form of the trace minerals in geothermal solution and will significantly impact extraction efficacy for any mineral recovery technology. Hence mineral recovery technology may need to be optimized for solution chemistry of specific geothermal sites where valuable minerals exist in viable concentrations. *An advantage of the solid state sorbent technology proposed is the ability to tune the sorbent material composition for the site specific application (mineral type, solution composition, etc.)*

The outcomes from the literature review and solution analysis have been integrated and applied to the sorbent evaluation and development in Task 2. It was interesting to note that many (but not all) REE and other valuable mineral deposits occur in areas of geothermal activity and potential for geothermal activity. This strongly supports the concept that *recovery of valuable minerals from geothermal brines with new technology could be viable—at select locations with sufficient mineral content in the geothermal solutions to provide a value added process.* Further, like any other mining location the mineralization is going to be the site specific—suggesting a flexible, adaptable and scalable technology would be preferred for extraction of value added minerals from geothermal (or hydrothermal) brines.

**Summary of Results for Task 2: Evaluation of Solid-State Sorbent Technology**

*Task 2 Summary:*

The purpose of this task is to evaluate solid state sorbent materials for the extraction of valuable minerals from geothermal solutions. The work was conducted in two subtasks to separately evaluate sorbent chemistry and sorbent structure. The results of this task will enable the selection of preferred sorbent chemistries and structures for integration, optimization and demonstration of metal recovery from geothermal fluids in year 2. Specific results from this effort are discussed in context with specific milestones with additional information provided in appendices C and D).

*Subtask 2.1 Evaluate and Select Effective Surface Chemistry*

Two types of surface chemistries have been evaluated for REE collection; a) Organic functional groups, and b) Inorganic (metal oxides) surface chemistries. To cover the range of water chemistries encountered in geothermal solutions, initial screening work was done in fresh water (river), seawater (brine) and moderately acidic solutions. Final sorbent assessment work and reusability of preferred sorbents (details provided in appendix C) were done with geothermal waters (Sharkley Hot Springs in Idaho which are near proven REE mineral deposits under assessment/development—see appendix B).

We demonstrate greater than 75% extraction of selected metals (including Ag, Eu, Zn) from geothermal brines by preferred/particularly effective sorbents, as summarized in Table 1. Many sorbent materials were explored (see Appendix C for more information) and the preferred sorbent chemistries were found to be:

* Diphosphonic acid: this surface chemistry has a ligand that contains two phosphonic acid groups (shown in Figure 1). It is stable in a wide pH range and has shown high affinity for hard Lewis acid metals such as REEs and harder transition metals. However the high chemical affinity can make stripping of the mineral for the sorbent challenging.
* Phosphonic acids: this surface chemistry contains single phosphonic acid groups (shown in Figure 1). It is stable in a wide pH range (0-8.5) and has shown good affinity for hard Lewis acid metals such as REEs, uranium and “harder” transition metals. The synthesis of the materials is simpler than diphosphonic acid. Further, recovery of collected materials from phosphonic acid based sorbents is typically easier (when compared to diphosphonic acid) supporting more economical processing and longer sorbent life times.
* Thiol (sulfur): based surface chemistry has no efficacy for the collection of REEs. However, this ligand shows very high affinity for valuable “soft” metals such as Au, Ag, Cu, and Zn as well as secondary metals such as (Pb, Cd, Hg and other toxic heavy metals) that are more soluble/potentially present at higher concentrations than REEs in geothermal waters.
* Manganese oxides and doped manganese oxides: these inorganic materials are relatively inexpensive, stable over a high temperature range and we have shown them to be effective for collection of REEs and other metals. However, they lack selectivity and have slower kinetics than organic surface chemistries. These materials *may* enable effective collection of Li and Mn.

**Table 1. The performance of organic and inorganic sorbent materials**

**for collection of REEs and selected metals from geothermal water**

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Sorbent | Adsorption of REEs and other trace metals  In geothermal water (%) | | | | | |
| La | Eu | Ho | Ag | Zn | Cu |
| *Organic sorbent chemistries* | | | |  |  |  |
| Diphos on silica supports | 96 | 99 | 99 | 97 | 62 | 51 |
| PropPhos on silica supports | 98 | 99 | 100 | 23 | 100 | 93 |
| *Inorganic sorbent materials* | | | |  |  |  |
| Mn doped on Fe3O4 supports | 99 | 100 | 95 | 80 | 99 | 96 |
| MnO2 on silica supports | 99 | 100 | 99 | 89 | 84 | 96 |

Initial concentrations of REEs, Ag and Zn were ~40, ~19 and 80 ppb respectively. Test solution was geothermal solution from Sharkley hot spring in Idaho—a region with rich mineralization, including REEs. pH~7.7, liquid to sorbent ratio of 50,000 mL/g, 2 hour batch contact adsorption with gentle agitation.

Additional experimental details available in appendix E. Location Sharkley hot springs and mineralogy shown in appendix B.

The preferred sorbents materials in Table 1 significantly outperformed other custom and commercial sorbent materials evaluated. The organic surface phase sorbents have the advantages of faster kinetics whiles the inorganic materials have higher thermal stability (over 400oC). Note that to provide sufficient chemical affinity and capacity both inorganic and organic surface chemistries had to be installed on nanostructured supports. Data not shown demonstrates that thiol surface chemistry was extremely effective for “softer” heavy metals such as Au, Ag, Cu, and Zn. These metals are known to have higher solubility and more abundance than REEs in geothermal waters. *Work is underway to combine thiol chemistries with the other preferred sorbent chemistries (e.g., Diphos and PropPhos that have been shown to be effective for REEs) to provide a single polyfunctional sorbent material that is as collecting a wide range of valuable minerals from geothermal solutions.*

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**Figure 1. Chemical structure of preferred organic ligands/surface chemistries for collection of REE and other valuable minerals from geothermal waters**

The reusability of preferred sorbents is shown in Table 2. The sorbent’s ability to provide many collection and mineral recovery cycles is a key capability to enable economic viability in the evaluation operation and applications. High collection and recovery (stripping of adsorbed Eu for sorbent) efficiencies were maintained for 10 cycles for several preferred materials with trending indicating many more effective processing cycles were possible. Effective recovery of adsorbed Eu from one of the more promising materials was not achieved (Diphos on silica supports). Additional work is needed to determine a viable stripping recovery solution from this very promising sorbent material. Processing details are provided below the data tables and in appendix E.

**Table 2. 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 |
| Diphos on silica supports | 99.8±0.3 | Work in progressc |
| PropPhos on silica supports | 98.5±0.9 | 93.5±5d |
| Mn doped on Fe3O4 supports | 97.5±1.0 | 82.6±9.8e |

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.

c1M HCl was used for stripping solution. More aggressive stripping solutions are being explored.

d 0.1M HCl was used for stripping solution

e 0.01M HCl was used for stripping solution

Additional experimental details available in appendix E. Location of Sharkley hot springs and mineralogy shown in appendix B.

Eu was selected to represent REEs for recycle/recovery studies of the sorbents due to its central position in the f-block elemental sequence and its economic impact as one of the top 3 priced REE’s. HCl was chosen as a stripping agent due to previous positive results using this acid to recover minerals from high affinity sorbents and effective stabilization of the extracted REEs in solutions. Recovery chemistry is a function of both the sorbent material and the mineral of interest. Effective mineral stripping/recovery solutions for the Diphos sorbent are still under examination (1 M HCl was found to be insufficient). Processed geothermal brine will be available for reinjection with minimal change in chemistry.

A subtle but significant finding is the selective separation/removal of the soluble natural radioactive minerals that will likely be collected in the process of REE collection from geothermal brine by the sorbents. We have found that U can be selectively removed from the preferred sorbents in advance of other minerals (avoiding subsequent contamination and separation issues) with a simple 1 molar sodium carbonate rinse. Solutions for addressing the challenges with selective separation of Ra and Th are under consideration.

*Subtask 2.2* *Evaluate and Select Effective Sorbent Structures*

Given the very high volumetric flow rates and high potential for fouling by suspended solids and dissolved minerals, the sorbent structure used in this application must be carefully chosen and evaluated. Bulk precipitation of low value minerals such as silicon and iron, as well as deposition of suspended solids can act to foul the sorbent and render it ineffective in capturing the target minerals. At the same time, a sorbent system must be deployed that provides the kinetics, capacity, and durability to render it effective, efficient, and economical in capturing high-value trace minerals from this source. Addressing these various technical challenges will enable the successful utilization of solid state sorbents (advanced or otherwise) for mineral recovery (REEs or other value added products). Consequently this program explored several alternative sorbent structures for application to high-volume trace mineral collection from geothermal fluids. Operational and economic factors are major criteria for selecting the sorbent structures to operate in the collection of REEs and valuable trace metals from geothermal fluids. The team has conducted a survey and analysis of solid sorbent structures for this high-volume application based upon experience in the areas of municipal water treatment, industrial chemical processing, and mineral extraction technology. Various structures were considered based upon important system parameters such as:

* Resistance to fouling/plugging with precipitates,
* Pressure drop,
* Contact efficiency,
* Durability,
* Regenerability,
* Manufacturability,
* The need for specialized equipment.

Analysis is presently in progress. Appendix D shows some of the analysis that was conducted on alternative sorbent structures. Presently, the three most promising approaches are listed below, with a brief description for each:

* Fluidized bed
  + Advantages: low pressure drop, resistance to fouling, relatively compact, facile sorbent processing, known industrial technology
  + Challenges: attrition of sorbent material
* Moving slurry bed of magnetic media
  + Advantages: low pressure drop, resistance to fouling, relatively compact/small foot print, accelerated sorbent processing
  + Challenges: durability of sorbent material and novelty of large volume magnetic separation technology
* Polymer sorbent composite coating and surfaces
  + Advantages: low pressure drop, resistance to fouling, manufacturability and flexible configuration
  + Challenges: potentially lower contact/collection efficiency

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**Appendix A**

**Assemble Core List of Critical Challenges for Solid State Sorbent Technology for Geothermal Mineral Extraction**

As planned, PNNL hosted a kickoff meeting to facilitate immediate interactions, information sharing and coordination for the entire project. The meeting was very positive with excellent input by all program participants. A specific outcome of this meeting was the assembly of a list of critical challenges for the application of solid state sorbent technology for the extraction of geothermal minerals. The top challenges for producing an economically viable technology were identified enabling the program to address during subsequent efforts.

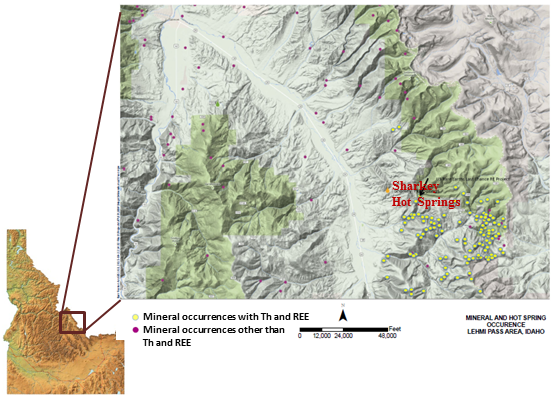
The key critical parameters for the economically viable utilization of Solid State Sorbent Technology for Geothermal Mineral Extraction where found to be:

* Sorbent affinity and capacity
  + Must be improved over existing materials
  + Must be balanced with regeneration/recovery capability, cost and kinetics
* Sorbent kinetics
  + Faster kinetics enable higher process rates, smaller equipment foot print and better economics
  + Must balance kinetics vs efficiency (in particular for collection)
  + Strongly dependent of form factor of separation media
* Sorbent lifetime
  + Thermally and chemically stable
  + Fouling-biological and chemical (iron, silica, carbonate, etc.).
  + Physical/mechanical stability
* Sorbent form factor
  + Low pressure drop and easily integrated into process
  + Function with suspended solids and surface fouling
* Mineral recovery from sorbents and sorbent regeneration
  + Minerals could be anionic, cationic, or on suspended solids
  + Chemically and physically regenerate sorbent
  + Acid stripping SOP but not ideal
  + Carbonate and peroxide
* Cost effectiveness (materials, recovery process, space, installation and operation)

All of these parameters must be achieved and successfully coordinated for an effective chemical extraction process to be created. Performance priorities and specific requirements will be situationally dependent.

**Appendix B**

**Complete Analysis of Geothermal Fluids: Location and Chemistry of Sharkley Hot Springs**

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**Figure B1. Map of Minerals and Hot Spring Occurrence in the Lemhi Pass area in Idaho**

The Lemhi Pass area is highly mineralized and has large number of sites with REE and thorium, Co and other mineral occurrences. The region also has significant hydrothermal hot spring activity and has some geothermal energy potential. However the region is remote and not near any major metropolitan energy grid.

Source: <http://www.idahogeologry.org>

**Table B1. Chemical composition of geothermal fluids in Sharkey Hot Spring, Idaho**

|  |  |  |  |
| --- | --- | --- | --- |
| **Chemical** | **Concentration**  **(mg/L, ppm)** | REE | **Concentration**  **(ng/L, ppt)** |
| pH  Temp  HCO3-  F-  Cl-  PO4-  SO42-  SiO2  Na  Mg  K  Ca | 8.01  37.5  NA  10.6  50.9  ND  151.8  38.2  288.2  0.9  14.5  0.6 | La  Ce  Pr  Nd  Sm  Eu  Gd  Tb  Dy  Ho  Er  Tm  Yb  Lu | 5.0  18.3  13.0  10.3  12.7  13.0  11.0  <12  13.0  <12  8.7  <12  8.3  <16 |

*NA= not available, ND = none detected*

**Table B2. Trace elements concentration (µg/L, ppb) in Sharkey Hot Springs, ID**

|  |  |  |  |
| --- | --- | --- | --- |
| Element | Concentration | Element | Concentration |
| Li  B  Al  Cr  Co  Ni  Cu  Zn  Ge  Rb  As  Se  Sr  Y  Zr  Rh  Mo | 596.67  1787.78  ND  0.78  0.03  0.39  5.55  2.71  7.57  90.84  19.55  0.96  443.89  0.02  0.09  0.01  13.59 | Pd  In  Sn  Te  Ru  Ag  Cd  Sb  Ba  Cs  W  Pt  Hg  Pb  Th  U | 0.21  0.01  0.14  0.02  0.33  0.04  0.03  1.79  23.72  32.57  47.59  <0.006  2.54  0.11  0.003  0.24 |

**Appendix C**

**Evaluation of Solid-State Sorbent Technology: Down-Select to the Most Effective Sorbent Chemistries**

Specific details on the performance test of selected surface chemistries evaluated are provided below. Final evaluation testing was done in geothermal water collected from Sharkley Hot springs in Idaho which are near proven REE mineral deposits under assessment and development.

1. *Organic functional groups*

The sorbents contained organic surface chemistries as shown in Figure C1 were chosen for evaluating the collection of REE and other metals from geothermal fluids. The functional groups were installed on different structures of substrates such as Cabosil (nonporous sorbent, particle size of ~0.2-0.3 µm, easily to form composite thin film with polymer), Davisil (Porous column with size particle ~250-500 µm ) and MCM41 (nanoporous materials with particle size of 1-5µm) The experiments were performed through batch contact experiment, at ~40 ppb of REE, solution’s pH ~7.7, liquid to sorbent ratio (L/S) of 50000 mL/g, and 2 hours of contact time. La, Eu and Ho were chosen to represent of light, middle and heavy REEs. The performances of the sorbents are categorized according to their surface chemistries, as results shown in Tables C1 and C2;

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**Figure C1. Chemical structure of organic ligands/surface chemistries**

*Diphosphonic and mono phosphonic groups installed sorbents provided the best performance for collection of REE from geothermal water. IDAA and SH groups installed silica materials show outstanding performance for adsorption of valuable metals (Ag), base metals and toxic materials from geothermal water.*

* Diphos-Cabosil shows a very high affinity for REEs and Ag, over 95% of these metals were collected. It offers only moderate affinity for base and toxic metals (except, the Hg). Similar performance for REE collection also can be seen from Actinide Resin; which is a commercial sorbent material and also contains diphosphonic group; however, this sorbent doesn’t show a good sorption of valuable and other metals.
* PropPhos shows outstanding performance for REE collection, over 98% of the REE were collected. It also offers excellent sorption of base metals (*i.e.,* Cu, Zn) and some toxic metals. The slightly lower performance can be seen from Ln Resin for REE collection. While Uteva resin shows no affinity for REE collection at this solution pH.
* Styrene IDAA provides low to moderate binding for REEs, lower than we expected, lower than 50% of REEs were adsorbed. While it offers excellent adsorption for Ag and most of the base and toxic metals. On other hand, very poor performance can be seen from Chelex100.
* SH shows very low affinity for REEs, but has very high affinity for Ag, Cu, Zn and toxic metals. GT-74 provides much lower performance than SH functionalized silica base substrates.
* Amidoxime installed sorbent materials show very low performance for REE collection even though the amidoxime based fiberglass were performed at lower L/S. Both types of Amidoxime functionalized polymer fibers offer excellent adsorption of Ag, Cu and Hg.
* Activated carbon and Ion exchange resins (SAX and WAX) show low to moderate affinity for REEs and other metals (except for Cu)
* The Diphos-Cabosil and styrene IDAA show excellent performance in capturing the soft metals (*i.e.,* Ag, Hg) due to it also containing SH groups as a linker on their ligands during the surface installation.

**Table C1. The performance of organic sorbent materials**

**for REE collection from geothermal water**

|  |  |  |  |
| --- | --- | --- | --- |
| Sorbent | Adsorption of REEs in geothermal water (%) | | |
| La | Eu | Ho |
| Diphosphonic group | | | |
| Diphos Cabosil | 96 | 99 | 99 |
| Diphonix Resin | 32 | 49 | 45 |
| Actinide Resin | 100 | 100 | 99 |
| *MonoPhosphonic group* | | | |
| PropPhos MCM41 | 98 | 99 | 100 |
| Ln Resin | 42 | 93 | 99 |
| Uteva Resin | 0 | 0 | 0 |
| *EDTA groups* | | | |
| styrene IDAA cab | 28 | 40 | 35 |
| styrene IDAA Davisil | 46 | 51 | 40 |
| Chelex 100 | 1 | 2 | 3 |
| *Thiol groups* | | | |
| SH Cabosil | 0 | 4 | 7 |
| SH Davisil | 0 | 2 | 3 |
| SH MCM41 | 16 | 22 | 14 |
| GT74 | 8 | 8 | 4 |
| *Amidoxime group* | | | |
| Purolite®S910 | 0 | 6 | 7 |
| Amidoxime fiberglass AF1L2R1\* | 18 | 31 | 22 |
| Amidoxime fiberglass 3495 - A18L2R2.1\* | 0 | 2 | 6 |
| *Other materials and controls* | | | |
| RE resin | 1 | 0 | 0 |
| Activated Carbon | 32 | 15 | 8 |
| AGMP 100-200 (SAX) | 21 | 41 | 36 |
| CG50 (WAX) | 47 | 69 | 67 |
| Cabosil | 7 | 22 | 23 |
| Davisil -646 | 0 | 4 | 5 |
| MCM-41 | 0 | 29 | 48 |

REE concentration ~40 ppb, Equilibrium pH~7.7, L/S 50000 mL/g, contact time for 2 hours with gentle agitation, *\*L/S =5000*

**Table C2. The performance of organic sorbent materials for**

**valuable, base and toxic metals collection from geothermal water**

|  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Sorbent | Adsorption of other metals in geothermal water (%) | | | | | | | | | | |
| Valuable metals | | | Base metals | | | | | Toxic metals | | |
| Ge | Mo | Ag | Li | Mn | Ni | Cu | Zn | Cd | Hg | Pb |
| Diphosphonic group | | | | | | | | | | | |
| Diphos Cabosil | 0 | 0 | 97 | 0 | 2 | 0 | 51 | 62 | 20 | 91 | 27 |
| Diphonix Resin | 2 | 0 | 12 | 3 | 42 | 0 | 65 | 19 | 45 | 27 | 45 |
| Actinide Resin | 4 | 26 | 4 | 0 | 28 | 37 | 6 | 0 | 42 | 0 | 0 |
| *MonoPhosphonic group* | | | | | | | | | | | |
| PropPhos SAMMS | 4 | 1 | 23 | 2 | 53 | 0 | 93 | 100 | 89 | 25 | 88 |
| Ln Resin | 4 | 0 | 0 | 0 | 3 | 6 | 5 | 0 | 0 | 2 | 6 |
| Uteva Resin | 2 | 1 | 0 | 0 | 1 | 37 | 0 | 0 | 6 | 0 | 0 |
| *EDTA groups* | | | | | | | | | | | |
| styrene IDAA cab | 2 | 0 | 82 | 3 | 21 | 89 | 96 | 97 | 82 | 91 | 82 |
| styrene IDAA davisil | 4 | 2 | 71 | 2 | 60 | 89 | 96 | 94 | 96 | 91 | 84 |
| Chelex 100 | 9 | 9 | 17 | 4 | 3 | 0 | 15 | 0 | 0 | 45 | 5 |
| *Thiol groups* |  | | | | | | | | | | |
| SH cabosil | 1 | 0 | 99 | 1 | 5 | 5 | 96 | 100 | 98 | 91 | 84 |
| SH davisil | 2 | 1 | 99 | 2 | 4 | 5 | 96 | 100 | 98 | 91 | 99 |
| SH SAMMS | 1 | 0 | 99 | 1 | 8 | 9 | 96 | 92 | 97 | 91 | 74 |
| GT74 | 3 | 2 | 53 | 3 | 13 | 7 | 40 | 0 | 14 | 86 | 26 |
| *Amidoxime group* | | | | | | | | | | | |
| Purolite®S910 | 4 | 1 | 21 | 1 | 12 | 52 | 31 | 0 | 19 | 21 | 0 |
| Amidoxime fiberglass AF1L2R1\* | 0 | 0 | 77 | 0 | 9 | 31 | 96 | 0 | 61 | 82 | 55 |
| Amidoxime fiberglass 3495 - A18L2R2.1\* | 0 | 6 | 92 | 0 | 9 | 41 | 96 | 0 | 42 | 90 | 49 |
| *Other materials and controls* | | | | | | | | | | | |
| RE resin | 2 | 1 | 0 | 3 | 2 | 0 | 10 | 0 | 0 | 5 | 7 |
| Activated Carbon | 5 | 2 | 16 | 4 | 7 | 22 | 82 | 0 | 1 | 69 | 35 |
| AGMP 100-200 (SAX) | 4 | 2 | 29 | 0 | 54 | 95 | 96 | 6 | 71 | 64 | 30 |
| CG50 (WAX) | 2 | 0 | 14 | 1 | 45 | 75 | 94 | 44 | 78 | 30 | 66 |
| Cabosil | 4 | 1 | 17 | 0 | 8 | 0 | 36 | 100 | 4 | 23 | 61 |
| Davisil -646 | 0 | 0 | 9 | 0 | 5 | 0 | 19 | 70 | 0 | 25 | 31 |
| MCM-41 | 3 | 0 | 9 | 5 | 8 | 6 | 49 | 72 | 2 | 30 | 61 |

Each metal concentration ~50-100 ppb, Equilibrium pH~7.7, L/S 50000 mL/g, contact time for 2 hours, *\*L/S =5000*

*b) Inorganic surface/metal oxide chemistries*

The inorganic metal oxides surface chemistries as the structure of the sorbents shown in Figure C2 were chosen for evaluating the collection of REEs and other metals from geothermal fluids. The experiments were performed under the same condition as the organic surface chemistry sorbent but the contact time was increased up to 2 hours due to the fact that metal oxide sorbents normally take at least 4-6 hours to reach equilibrium. The results are shown in Tables C3 and C4;

|  |  |
| --- | --- |
| C:\Users\h8906560\Desktop\SiO2FeMnO2.tif | C:\Users\h8906560\Desktop\SiO2MnO2.tif |
| A | B |
| C:\Users\h8906560\Desktop\Mn_Meso.tif | C:\Users\h8906560\Desktop\MnFe3O4(8nm).tif |
| C | D |

**Figure C2. Image of selected inorganic metals oxides; SEM of Fe/MnO2-SiO2(A), SEM of MnO2-SiO2composite (B), SEM of Mn doped Fe3O4 cluster (C), and TEM of Mn doped Fe3O4 nanoparticles (D)**

*Mn modified surfaces of magnetic particles and non-magnetic particles show the outstanding performance for collection of REEs from geothermal water, over 99% adsorption of REEs were observed from Mn-doped Fe3O4 (8nm) and MnO2-SiO2 composite (calcine). They also show excellent uptake for some base and toxic metals. The MnO2-SiO2 composite (calcine) also shows high affinity for Ag.*

* Mn modified magnetic particles show excellent uptake for REEs from geothermal water. Different sizes and structures of magnetic particle offer similar performance for REE uptake.
* Mn doped Fe3O4 (8nm) and Mn doped Fe3O4 clusters also show excellent uptake for Cu, Zn and toxic metals. But significantly increase in uptake of Ag and Mn can be seen when compared to Mn doped Fe3O4 (8nm).
* Interesting uptake of Ge, which is significantly higher that other sorbent materials including the organic sorbent materials, can be seen from Mn doped Fe3O4 (8nm) as well as Fe3O4 (8nm)
* Mn modified non-magnetic sorbents provide similar performances; over 94% of REE adsorption can be seen. Their performances are much higher than a commercial sorbent (MnO2 Eichrom) that has the same surface chemistry and similar particle size.
* While they have similar performance for REE collection, MnO2-SiO2 composite (calcined) and Fe/MnO2-SiO2 also show good uptake for valuable metals, (Ag), most of base metals and toxic metals from geothermal water.

**Table C3. The performance of inorganic metal oxide sorbents**

**for REE collection from geothermal water**

|  |  |  |  |
| --- | --- | --- | --- |
| Sorbent | Adsorption of REEs in geothermal water (%) | | |
| La | Eu | Ho |
| *Magnetic particles* |  | | |
| Mn doped Fe3O4 (8nm) | 99 | 100 | 99 |
| Mn doped Fe3O4 (25nm) | 98 | 94 | 80 |
| Mn doped Fe3O4 (cluster) | 99 | 100 | 95 |
| *None-magnetic particles* |  | | |
| MnO2-SiO2 composite | 99 | 100 | 94 |
| MnO2-SiO2 composite (calcined) | 99 | 100 | 99 |
| MnO2-Cabosil | 99 | 99 | 95 |
| Fe/MnO2-SiO2 | 99 | 100 | 96 |
| MnO2 Eichrom | 16 | 51 | 58 |
| *Bare substrates materials* | | | |
| Fe3O4 (8nm) | 99 | 98 | 87 |
| Fe3O4 (25nm) | 66 | 62 | 37 |
| Core Fe3O4 (cluster) | 93 | 83 | 64 |
| Cabosil SiO2 | 0 | 1 | 13 |
| Nanopore SiO2 (Davisil 635) | 0 | 0 | 1 |

REE concentration of ~40 ppb, Equilibrium pH~7.7, L/S 50000 mL/g, contact time for 7 hours.

**Table C4. The performance of inorganic metal oxide sorbents**

**for valuable, base and toxic metals collection from geothermal water**

|  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Sorbent | Adsorption of other metals in geothermal water (%) | | | | | | | | | | |
| Valuable metals | | | Base metals | | | | | Toxic metals | | |
| Ge | Mo | Ag | Li | Mn | Ni | Cu | Zn | Cd | Hg | Pb |
| *Magnetic particles* | | | | | | | | | | | |
| Mn doped Fe3O4 (8nm) | 16 | 0 | 30 | 3 | 0 | 66 | 96 | 99 | 98 | 73 | 96 |
| Mn doped Fe3O4 (25nm) | 5 | 0 | 28 | 3 | 0 | 27 | 96 | 93 | 58 | 41 | 96 |
| Mn doped Fe3O4 (cluster) | 0 | 0 | 80 | 2 | 69 | 63 | 96 | 99 | 98 | 65 | 96 |
| *None-magnetic particles* | | | | | | | | | | | |
| MnO2-SiO2 composite | 1 | 1 | 47 | 5 | 40 | 40 | 96 | 95 | 90 | 45 | 96 |
| MnO2-SiO2 composite (calcined) | 2 | 1 | 89 | 5 | 78 | 68 | 96 | 84 | 98 | 82 | 87 |
| MnO2 Cabosil | 7 | 4 | 81 | 6 | 0 | 79 | 96 | 61 | 98 | 83 | 79 |
| Fe/MnO2-SiO2 | 6 | 3 | 89 | 4 | 58 | 90 | 96 | 73 | 98 | 91 | 80 |
| MnO2 Eichrom | 2 | 6 | 43 | 8 | 3 | 1 | 96 | 7 | 22 | 45 | 53 |
| *Bare substrate materials* | | | | | | | | | | | |
| Fe3O4 (8nm) | 21 | 1 | 36 | 3 | 31 | 80 | 96 | 73 | 86 | 57 | 79 |
| Fe3O4 (25nm) | 5 | 0 | 34 | 3 | 7 | 20 | 96 | 55 | 32 | 29 | 77 |
| Core Fe3O4 (cluster) | 13 | 0 | 39 | 3 | 16 | 9 | 86 | 63 | 66 | 40 | 52 |
| Cabosil SiO2 | 0 | 1 | 31 | 6 | 2 | 5 | 19 | 53 | 10 | 28 | 21 |
| Nanopore SiO2 (Davisil 635) | 0 | 0 | 29 | 6 | 1 | 6 | 7 | 44 | 9 | 29 | 0 |

Each metal concentration ~50-100 ppb, Equilibrium pH~7.7, L/S 50000 mL/g, contact time for 7 hours

Specific details on the performance test of selected surface chemistries evaluated are provided below. Final evaluation testing was done in geothermal water collected from Sharkley Hot springs in Idaho which are near proven REE mineral deposits under assessment and development.

**Appendix D**

**Evaluation of Solid-State Sorbent Technology: Down-Select to the Most Effective Sorbent Structures**

To date we have identified 7 sorbent structures that could be utilized in recovering metals from geothermal brines.

* Conventional Packed Bed
* Fluidized Bed
* Mesh Screen
* Moving/Slurry Bed
* Modified Membrane system
* Polymer Braid/Rope
* Polymer Composites

Each structure is being explored in terms of important system parameters such as:

* Resistance to fouling/plugging with precipitates,
* Pressure drop,
* Contact efficiency,
* Durability,
* Regeneration,
* Manufacturability,
* The need for specialized equipment.

We have begun relative qualitative ranking the selected structures for the various critical parameters and the initial results are shown in Table D1. The potential sorbent structures are compared to the critical parameters and have been given initial rankings (1-5, 5 being most favorable).

As the project progresses, this data will become a defined database that compares the substrates on a quantitative rather than qualitative basis. We will be assigning weights to the various parameters, since some are much more likely to determine applicability than others. As we develop the techno-economic model for the system, the category weights and relative merits or each parameter will become clearer. Based on the techno-economics and the laboratory trials, those substrates that appear to be unfavorable/unacceptable in one or more areas will be removed and efforts will focus on viable candidates.

A primary barrier to mineral production from geothermal brine has historically been high TDS and bulk precipitation of low value minerals such as silicon and iron. A key technical challenge that this effort will be to address for the successful utilization of solid state sorbents (advanced or otherwise) for mineral recovery (REEs or otherwise) from geothermal waters will be resistance to fouling/plugging with silica and iron precipitates. This is one of the most important assessment parameters and will be weighted very heavily in the techno-economic assessment. Sorbent structures selected for further evaluation will be resistant to plugging/fouling by heavy precipitation (*i.e.,* fluidized bed, mesh screen, moving/slurry bed, membrane systems, polymer braids, and composite structures)

**Table D1. An Initial Assessment of Sorbent Structures with**

**Key Parameters for Trace Mineral Extraction from Geothermal Waters**



**Appendix E**

**Experimental Details for Sorbent Testing in Geothermal Waters**

*Adsorption measurement*

Percent adsorption of REEs and other trace metals by sorbents were performed in geothermal water (from Sharkley Hot springs, Idaho). The geothermal water was spiked with metal ions of La, Eu, Ho, and other trace metals at ~ 50 ppb for each metal. A 4.9mL of the metal solution was placed in a polypropylene bottle and spiked with 0.1mL sorbent suspended in DI water to obtain a liquid-to-solid ratio of 50000 (L/S in mL liquid/g sorbent). The tubes were shaken for 2 hours at 200 rpm on an orbital shaker. Then the magnetic materials were separated from the solution using a 1.2 T NdFeB magnet. The nonmagnetic materials were collected by filtering the solution thru 0.45-µm syringe Nylon-membrane filters. The removed supernatants were stored in 2% (v/v) HNO3 prior to metal analysis. The metal ion concentrations in the control (no sorbent), with and without filtration were analyzed in order to check for precipitation of metal ions and confirm concentrations. These sample solutions were analyzed using an inductively coupled plasma mass spectrometer (ICP-MS, Agilent 7500ce, Agilent Technologies, CA). All batch experiments were performed in triplicate and the averaged values were reported.

*REE collection and sorbent recycling/reuse evaluation*

The sorbents demonstrating high REE collection performance (>90% REE uptake) were selected for Eu collection and stripping study. The sorbent materials were Diphos on Silica supports, PropPhos on silica supports, and Mn doped on Fe3O4 supports. The collection of REEs from geothermal water (from Sharkley Hot springs, Idaho) and recovery of adsorbed REEs from the selected sorbent materials were obtained through batch sorption experiment. The geothermal water was spiked with Eu to approximately 50 ppb to provide sufficient concentration to enable determination of high adsorption. The pH of the geothermal water after adding Eu was 7.71. Then, 1 mL of the Eu spiked geothermal water was added in a plastic vial that contained 0.010 g sorbent material to obtain L/S ratio of 100. The vial then was placed on a shaker table for agitation at 200 rpm until contact was completed (in this study, it was completed within 1 hour). The Eu adsorbed the functional groups modified silica supports were removed from solution by centrifugation at 13000 rpm for 10 minutes. The Eu adsorbed magnetic nanoparticles were separated from the geothermal water using a 1.2T NdFeB magnet. Then, the relevant volume of stripping solution (1 mL of HCl) was added to the vial containing a sorbent to maintain the L/S of 100. The stripping solutions were separated from sorbents after they were continually shaken for 1 hour using the same technique as the collection step. The adsorption and stripping solutions were collected and stored in 2%(v/v) HNO3 for ICP-MS analysis. Note, HCl with concentrations of 1 M, 0.1 M, and 0.01 M were used as stripping solutions for removal of Eu from Diphos on Silica supports, PropPhos on silica supports, and Mn doped on Fe3O4 supports, respectively. For stripping studies a100 L/S ratio was chose to assure no limitation in recovery solution chemistry (ratio can likely be substantially reduced for preferred processing solutions). All batch experiments, adsorption and stripping steps, were performed in triplicate.