

Technical Report

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Evaluation of Advanced Sorbent Structures for Recovery of Rare Earths, Precious Metals and other Critical Materials from Geothermal Waters –Preliminary Results

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Abstract

We developed and demonstrated high value strategic mineral extraction technology for geothermal solutions to provide additional revenue for geothermal operations. This was 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 sorbent materials were configured for collection of trace levels of rare earth elements (REEs), and other valuable minerals from geothermal fluids such as zinc, manganese, copper, and uranium. Sorbent performance was determined in different geothermal brines at room temperature up to 95 °C. A large assessment effort found that the preferred sorbent chemistries for trace mineral collection from geothermal fluids were phosphonic acids, thiols, iron oxides, manganese oxides and combinations of these chemical modalities. A multiparametric engineering feasibility analysis found the preferred sorbent form factors for utilization in the challenging conditions in geothermal plants were; packed bed/column, fluidized/expanded bed, moving slurry bed, polymer sorbent composite coating. A techno-economic analysis (TEA) was 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 TEA analysis showed the process to provide significant return of investment with the potential to substantially reduce the cost of geothermal power; particularly at sites with good mineral content in the geothermal brines. The variability of dissolved minerals and their concentrations in geothermal fluids will make return on investment strongly site dependent.

1. Background

1.1 *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 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 copper⁶, 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 water², 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}

1.2 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 reusability 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 250-350°C depending upon composition. The modified metal oxide sorbents are believed to be stable to over 400°C.

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 published or 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.

2. Project Summary

The objective of this program was to evaluate, develop and demonstrate flexible, scalable mineral extraction technology from geothermal brines based upon solid phase sorbent materials with a specific focus upon rare earth elements (REEs). The sorbent technology was iteratively developed with preferred configurations demonstrated to provide effective mineral extraction of REEs and other valuable minerals from geothermal fluids at temperatures up to 95 °C. A techno-economic analysis showed the process to provide significant return of investment with the potential to substantially reduce the cost of geothermal power; particularly at sites with good mineral content in the geothermal brines. The variability of dissolved minerals and their concentrations in geothermal fluids will make return on investment strongly site dependent. All program objectives and milestones were successfully completed and provided a demonstrated, industrially viable, technology at the TRL 3-4 level ready for scale-up testing and evaluation.

This project explored and developed a process based upon proven industrial methods (solid state sorbent technology) and leveraged recent advances in sorbent chemistry, material science, and nanoscience to provide a fast, flexible, scalable, efficient, environmentally friendly technology for the recovery of trace levels of valuable minerals from geothermal fluids. Key critical parameters were identified that would enable the economically viable utilization of solid-state sorbent technology for mineral extraction at geothermal power plants. Program efforts focused on resolving these critical issues which include sorbent; chemical affinity, capacity, kinetics, lifetime, form factor, mineral recovery and regeneration process, and cost effectiveness. A large assessment effort found that the preferred sorbent chemistries for trace mineral collection from geothermal fluids were phosphonic acids, thiols, iron oxides, manganese oxides and combinations of these chemical modalities. A multiparametric engineering feasibility analysis found the preferred sorbent form factors for utilization in the challenging conditions in geothermal plants were; packed bed/column, fluidized/expanded bed, moving slurry bed, polymer sorbent composite coating.

Techno-economic analysis (TEA) was done to determine the conditions where the developed technology would be viable. The TEA was a comprehensive end-to-end system analysis including capital and operating expenses, all major steps of mineral extraction (sorption, stripping, concentrate preparation) from geothermal brine, shipping and concentrate processing/refining into metal products. The TEA modeling showed the developed process can provide significant additional revenue for geothermal operations at sites with “average” mineralization and excellent return on investment at sites with high mineral content in geothermal fluids (such as the Salton Sea). While REEs can be collected from geothermal fluids, other minerals were found to provide the positive economic benefits for the process. A key point to note is that the process is enabled and economical only because of the performance provided by advanced solid phase sorbent material developed on this project—existing sorbent technology does not provide sufficient performance to provide and economic process.

Program Structure and summary results by Task:

FY 15, as per Statement of project objectives (SOPO) work was undertaken on Tasks 1 and 2 and successfully completed. The details of work was reported in GTO Technical Report of FY15

- **Task 1. Program Initiation and Analysis of Geothermal Fluids (M1-M6)**
All actives completed and milestones achieved in Q1 and Q2 of FY15
- **Task 2. Evaluation of Solid-State Sorbent Technology (M1-M12).**
All actives completed and milestones achieved in Q3 and Q4 of FY15

FY 16, work was undertaken on Tasks 3 and 4 and successfully completed. Specifically focused FY16 efforts were undertaken on:

- **Task 3. Demonstration of Solid-State Sorbent Technology (M13-21)**
 - Milestone 3.1 Complete Evaluation of Preferred Sorbent Materials (M18)
 - Milestone 3.2: Demonstration of Preferred Sorbent Materials (M21).
- **Task 4 Techno-economic Analysis of Solid State Sorbent Technology for Cost-Effective Geothermal Mineral Extraction (M13 –M24)**
 - Milestone 4.1: Complete Basic Conceptual TEA Model for use of Solid State Sorbent Technology in Brines (M15)
 - Milestone 4.2: Complete Preliminary TEA for Solid State Sorbent Technology for Cost Effective Geothermal Mineral Extraction (M24)

Successful completion of FY16 work positions the technology for scale up and evaluation. The program team will need to be expanded to include expertise in geothermal power facilities.

3. Results of Task 3: Demonstration of Solid-State Sorbent Technology

3.1 Task 3 Summary:

This task improved and evaluated the solid state sorbent technology identified in the first year of the project. The performance of solid-state sorbent materials with preferred surface chemistry and structure sorbent was then demonstrated and evaluated in geothermal brines.

The preferred sorbent's surface chemistries for trace mineral collection from geothermal fluids were phosphonic acids, thiols, iron oxides, manganese oxides and combinations of these chemical modalities. They have shown high performance and potential to be stable and operated above 200 °C in different brines. Four different sorbent form factors were suggested to be effective for collection of dissolved minerals and operated with in the geothermal power plants including, traditional packed beds, packed bed/column, fluidized/expanded bed, moving slurry bed, and composite thin film configuration. The preferred supports for installation of surface chemistries depend on structure or configurations of solid-state sorbents. The packed column (PC) particles is suitable for packed bed extraction configuration, the submicron size of nanofiber (NF) silica is suitable for fluidized bed and composite thin film configuration. Nanostructured silica (NS) or nanoporous silica (NP) and magnetic particles (MNP) are suitable for both composite thin film and moving slurry bed configurations.

Specific results from this effort are discussed in context below;

- The preferred sorbent surface chemistries (Phosphonic acid and Mn oxide surface chemistry) were effective for a range of brine types and pH conditions.
- Phosphonic acids based sorbent (Diphos and PropPhos) showed high performance for the collection of Eu in all geothermal brines, Diphos-SH-based materials showed good collection of all metal ions in all brines.
- Metal oxides showed good collection efficiencies for Eu, however their affinity for Cu and Ag were reduced in high ionic strength water.
- Similar performance of preferred sorbent's surface chemistries can be seen from room temperature to 95 °C
- Diphos-SH-NF Silica has high potential to be an effective sorbent for extraction of minerals from geothermal fluids at evaluate temperature with the fluidized bed system, as well as Mn- Fe₃O₄ MNP (8 nm) is suitable for the moving slurry bed system.
- Organic sorbent (Diphos and PropPhos) and inorganic (MnO₂) sorbent integrated with Nafion polymer, become a composite thin film, showed retention of their good performance for adsorption of intermediate metals (Cu and Zn), hard metals (REEs) and soft/precious metals (Ag).

3.2 Sorbent Material Selected for Final Evaluation

The high performance sorbent materials for adsorption of dissolved rare earth elements (REEs) and other trace metal ions in Sharkey Hot Spring water (results from Task 2 in FY15) were selected for further evaluation of soft, intermediate and hard metal ions in various brine waters at room temperature. Cu, Ag and Eu were chosen to represent soft, intermediate and hard

metal ions respectively (as defined by Pearson acid base concept). This selection of metal ions allows a reasonable understanding of how most minerals will behave in a particular chemical system. As determined in Task 2 the preferred sorbent chemistries for trace mineral collection from geothermal fluids were phosphonic acids, thiols (SH), iron oxides, manganese oxides and combinations of these chemical modalities. The preferred organic based surface chemistries are shown in Figure 3.1. Thiols are effective for soft metal ions and the phosphonic acids are effective for the harder metal ions. Manganese oxides and iron oxides are generally effective sorbent materials and have affinity for several metal ions.

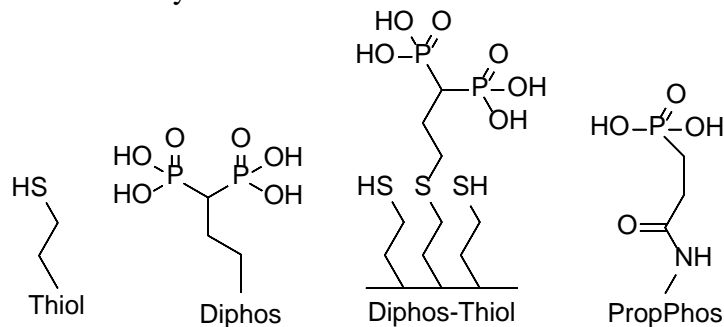


Figure 3.1 Chemical structure of preferred organic surface chemistries

The preferred support materials are nanofiber silica (NF silica), nanoporous silica (NP silica), porous column silica, (PC silica), nanostructured silica (NS silica), and Fe_3O_4 Magnetic nanoparticle (MNP), their characteristics are shown in Table 3.1. These support materials enable the preferred sorbent structures/separation processes identified in Task 2. The application of sorbents build on these materials is summarized below;

- NF-Silica, NP silica, and Fe_3O_4 MNP are fine particles, can be modified with selective surface chemistry and provide high performance of collection of dissolved metals of interests in solution. They can be utilized in various configurations especially for integration with polymer become thin films and application in fluidized beds.
- NS silica and PC silica are suitable for traditional packed bed column application or expanded bed since their particle sizes and high surface area provide high sorption capacity with minimum backpressure from the fluid flow. Their surfaces also can be functionalized with organic chemistry, as well as inorganic chemistry).
- Fe_3O_4 MNP (as well as other magnetic nanoparticles) has strong magnetic properties that can support multiple material uses in magnetic separation. Its particle size and surface chemistry is adjustable for improving the performance.

Table 3.1 Characterization of preferred support sorbents

Sorbent Material	Particle Size (µm)	Mean Pore Diameter (Å)	Surface Area (m ² /g)
NF Silica	0.2-0.3	225	307
NP Silica	1-5	56.5	550
NS Silica	63–106	61	549
PC Silica	250-500	153	291
Fe ₃ O ₄ MNP	6-8 nm	-	120

NF= nanofiber Silica, NP= nanoporous Silica, NS= nanostructured Silica, PC= Packed Column Silica

3.3 Performance of selected sorbent materials in geothermal brines (at room temperature)

The high performance sorbent materials for adsorption of dissolved REEs and other trace metal ions in Sharkey Hot Spring water (results from Task 2 of FY15) were selected for further performance evaluation in various brines at room temperature. Cu, Ag and Eu were chosen to represent soft, intermediate and hard metal ions, respectively. The performances of selected sorbents are shown in Table 3.2.

Table 3.2. Performance of selected sorbents in various brine solutions at room temperature

Sorbents	Sharkey Hot Spring water			Columbia River water			Seawater			Desalination brine			Synthetic GTO simple brine			Diluted Great Salt Lake water*			Great Salt Lake water		
	Cu	Ag	Eu	Cu	Ag	Eu	Cu	Ag	Eu	Cu	Ag	Eu	Cu	Ag	Eu	Cu	Ag	Eu	Cu	Ag	Eu
<i>Phosphonic group</i>																					
Diphos-SH-NF Silica	96	83	91	80	79	64	83	98	99	58	91	100	61	89	77	60	95	97	0	87	90
Diphos-SH-PC Silica	91	40	76	82	66	59	88	98	94	54	90	95	60	86	78	66	95	96	7	85	91
PropPhos-NP Silica	67	19	94	22	16	71	53	0	98	3	0	93	0	0	60	25	0	86	0	0	64
<i>Thiol Group</i>																					
SH-NF Silica	100	98	12	91	97	62	94	98	4	79	94	0	87	97	0	92	97	7	55	96	10
SH-PC Silica	100	94	6	100	93	23	95	98	3	83	96	0	97	97	0	94	98	1	49	97	12
<i>Metal Oxide surface</i>																					
Mn- Fe ₃ O ₄ MNP (8nm)	100	69	99	57	29	90	91	3	99	46	0	100	51	2	66	64	0	100	5	0	99
MnO ₂ -NS Composites	92	66	95	93	91	99	90	0	98	66	0	99	0	3	0	64	0	98	0	0	92
<i>Commercial</i>																					
Actinide Resin	13	0	98	16	0	52	26	0	93	18	0	0	0	2	78	8	0	53	0	0	29
Activated carbon	59	74	29	72	31	83	58	0	17	61	89	77	0	0	0	50	0	9	0	0	15
<i>Equilibrium pH</i>	8.5			7.9			7.9			8.4			4.9			8.3			8.1		
<i>Ionic strength (M)</i>	0.5			0.07			0.7			1.4			0.9			2.3			4.7		

Equilibrium pH is the pH after stock dissolved metals were added in water and agitated for 2 hours. The initial concentration of Cu, Ag, Eu are ~ 52, 35 and 45 ppb, respectively, in a 2 hour batch contact experiment with agitation at L/S ratio of 5 x10⁴ mL/g sorbent at room temperature. Desalination is obtained from concentration of seawater for 2 times. Synthetic GTO simple brine obtained from Idaho National Laboratory and is primarily NaCl (see appendix A for all composition). NF= nanofiber Silica, NP= nanoporous Silica, NS= nanostructured Silica, PC= Packed Column Silica. Experimental details are provided in appendix A.

The results from Table 3.2 are summarized as below;

- Phosphonic acid based (Diphos, PropPhos) showed high performance for the collection of Eu in all geothermal brines including very high ionic strength of Great Salt Lake water.
- Diphos-SH-based materials showed good collection of all metal ions in all brines, however only good collection of Ag and Eu can be seen in Great Salt Lake water.
- Diphos-SH-ligands functionalized sorbent materials showed higher performance for the collection of Ag and Cu than did PropPhos ligands functionalized sorbent material in all brines. This is expected since Diphos is bidentate and binds stronger than PropPhos which is monodentate (see Figure 3.1).
- Metal oxides showed collection efficiencies similar to phosphonic acid groups functionalized sorbent materials for Eu collection.
- Both metal oxide sorbents showed good uptake of Cu and Ag, however, their performances was reduced when ionic strength of brines increased.

3.4 Performance of selected sorbent materials in geothermal brines at elevated temperatures.

The target of this technology is to extract minerals from the brine that being discharge from geothermal plant where the temperature of the brine are low, normally above 57 °C. The temperature of 60 °C and 90 °C was selected because it was experimentally advantageous and it represented conditions that can occur at the output of low-temperature geothermal plants.

Table 3.3. The performance of selected sorbents in geothermal waters at 60 °C

Sorbent	Sharkey Hot Spring water			Seawater			Synthetic GTO simple brine			Dilute Great Salt Lake water*		
	Cu	Ag	Eu	Cu	Ag	Eu	Cu	Ag	Eu	Cu	Ag	Eu
<i>Phosphonic acid surface chemistry</i>												
Diphos-SH-NF Silica	99	98	94	73	100	99	70	80	92	64	99	94
Diphos-SH-PC Silica	99	70	73	89	100	94	72	75	91	55	96	95
PropPhos-NP Silica	74	45	95	57	0	96	15	5	85	25	0	83
<i>Thiol surface chemistry</i>												
SH-NF Silica	99	100	5	97	100	0	90	100	0	76	100	46
SH-PC Silica	99	100	2	97	100	0	94	100	0	78	100	30
<i>Metal oxide surface</i>												
Mn-Fe ₃ O ₄ MNP (8nm)	99	89	100	97	0	100	76	0	89	62	0	100
MnO ₂ -NS Composite	99	88	100	97	0	100	46	1	61	58	0	97
<i>Preferred commercial sorbent</i>												
Actinide Resin	6	5	100	37	0	75	26	5	91	4	0	37
Activated Carbon	68	90	66	60	0	33	13	3	5	29	0	36
<i>Equilibrium pH</i>	8.5			8.1			4.9			8.4		
<i>Ionic strength (M)</i>	0.5			0.7			0.9			2.3		

Equilibrium pH is the pH after stock dissolved metals were added in water and agitated for 2 hours at 60 °C. The initial concentration of Cu, Ag, Eu are ~ 45, 39 and 35 ppb, respectively, in a 2 hour batch contact experiment with agitation at L/S ratio of 5 x 10⁴ mL/g sorbent. * 2x dilution of Great Salt Lake solution. Experimental details are available in appendix A. NF= nanofiber Silica, NP= nanoporous Silica, NS= nanostructured Silica, PC= Packed Column Silica

The performances of preferred sorbent materials are shown in Tables 3.2 and 3.3. It can clearly be seen that the preferred sorbent materials are very effective for a range of brine types and pH conditions. Due to their high affinity and selectivity, the preferred sorbents can be seen to demonstrate similar chemical activity in brines for temperatures ranging from room temperature to 95 °C (data shown Table 3.4 and discussed in subsequent section). Thermogravimetric data suggests the potential for operation up to 200 °C for the polyfunctional organic sorbent and over 400 °C for the metals oxides.

3.5 Evaluation and Summary of Sorbent Structures Applicable to Geothermal Fluids

Geothermal fluids are very challenging solutions to perform trace mineral extractions is due to the high temperature, high salt levels, high flow rates, and high levels of dissolved solids. Previous work has identified preferred sorbent materials and structures (Milestone 3.1 of this task) and Task 2.2 in FY15). A wide range of form factors have been evaluated and four form factors were found to have the best promise for viable operation in geothermal fluids; pack beds/columns, fluidized beds, moving slurry bed, thin film sorbent coating on separation structures (i.e., filters, separator belts). A brief description of the preferred structures/configurations for the use of solid-state sorbents in geothermal fluids is given below.

- Packed bed/column

A packed bed or packed column is a tube filled with sorbent particles of desired composition (size, surface chemistry). The fluid is forced through the packed similar to water flowing through coarse sand. This configuration provides good contact efficiency and simply effective separation system which makes it an industrial standard with a wide range of solution processing applications ranking from analytical microextraction to industrial scale water clean up. The major drawback to this configuration is the high back pressures (resistance to flow) that can develop during the extraction. Further, the fluid flow can compress the column, break down the sorbent material, and deliver debris that plugs up the interstitial spaces between the sorbent particles—all of these processes can drive up the backpressure and even plug the sorbent bed completely. The proven industrial solution “backflush” the column when back pressures become unacceptable. Backflushing drives solution in reverse through the column (than typical operation) reversing some the compression and debris in the packed sorbent bed. This allows the packed sorbents columns to be clean and reutilized for many cycles.

- Advantages: good contact efficiency, compact, modular, known technology-the industrial standard, easily incorporation into industrial flow systems.
- Challenges: back pressure, fouling and column packing
- Preferred sorbent: Diphos-SH-PC Silica and MnO₂ modified packed column grade supports. These materials can be made in particles sizes appropriate for pack bed application and provide excellent broad spectrum absorption for minerals of interest

- Fluidized bed

Fluidized bed is an extraction bed where solid sorbent and fluid is well mixed by pressurized fluid or very high velocity flows of fluid. The high velocity of fluid forces the

solid sorbent to be suspended in fluid and promotes the continuing contact with mineral metals through out the extraction process. Contact between fluid and solid sorbent material (per unit bed volume) is greatly enhanced, systems can accommodate high relative flow velocities between the fluid and the dispersed solid phase. Therefore, fouling of sorbents and plugging or clogging of the extraction bed are reduced. The size and density of particles in fluidized bed should be small enough to promote the heterogeneous mixture between fluid and solid phase but large enough to be physical stable and enable separations.

- Advantages: low pressure drop, relatively compact, resistant to fouling, facile sorbent processing, known industrial technology
 - Challenges: attrition and degradation of sorbent material
 - Preferred sorbent: Diphos-NF Silica is the most suitable for adsorption of trace metals from geothermal water in the Fluidized bed system due to the sorbent's high affinity for REEs and other trace metals. More importantly, the organic ligands are installed on a fine and micron size structure material (0.2-0.3 μm) that is easily suspended in the fluid. Moreover, since the size of the sorbent is already small in submicron size, the potential that the sorbent material will be broken into smaller size particles is reduced.
- Moving slurry bed

The moving slurry bed is where the sorbent particles move through the bed along with fluids. It is an advantageous option to consider for trace mineral concentration from large volumes of solution. The sorbent particles and fluids are well mixed throughout the moving bed by the fluid flow. Separation of the sorbent materials can be performed using magnetic forces (or gravity for nonmagnetic sorbents) at the end of the moving bed (in the geothermal plant, the pipe lines can be used as a moving bed). This system is suitable for the slow kinetics and uptake rates of inorganic sorbents since the particles have longer contact time with minerals in the fluid during moving through the pipe bed. This system offers low process handling cost, eliminates processing problem such as sorbent's fouling, back pressures and plugging or clogging of the extraction bed.

 - 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, recovery of sorbent particles injected into geothermal fluids may be a technical and regulator challenge
 - Preferred sorbent: Mn-Fe₃O₄ MNP (8nm) shows outstanding performance for adsorption of most interested dissolved trace metal in geothermal waters. Fe oxide core is used as a core material for installation of Mn oxide surface chemistry, it is nontoxic, relatively inexpensive, commercial available and has strong magnetic properties. The strong magnetic properties offer an effective and fast separation, are efficient, and avoid issues such as fouling and plugging of the separation system. Other magnetic media with high surface, high magnetic strength, high affinity surface chemistry (yet reversible), and low cost might also be viable. Other cost effective media with high surface area, appropriate surface chemistry and high relative magnetic strength may also be effective.

- Thin film sorbent coatings on separation structures

Thin film sorbents is an incorporation of high performance sorbent materials (typically nanostructured material) onto a surface. Thin films can be installed on surfaces by sintering or with polymer binders. Thin film sorbent coatings have been extensively used in separation and analytical science. The integration of the highly selective nanostructured materials into thin films can improve properties such as surface area, chemical affinity, selectivity, permeability, water adsorption, thermal stability, mechanical strength, and fouling resistance. The sorbent films can be coated on many other support structures of interest, ranging from beads for packed-columns to membranes.

- Advantages: low pressure drop, resistance to fouling, easy to incorporate in mineral extraction processes, manufacturable with flexible configurations
- Challenges: potentially lower contact/collection efficiency, novel approach
- Sorbents: Diphos-NF Silica, PropPhos-NP Silica, and MnO₂-NS composites are preferred sorbents for composite thin film configurations. All selected sorbents show outstanding performance for collection of trace metals from geothermal waters. The selected organic and inorganic sorbents are nanostructured materials, which are typically good for solution dispersion and combining with a porous polymer binder to create a composite thin film. While the normal thin films have limited mass (and low relative surface area) that limits the sorption capacity of the structure, they do provide good contact with the solutions, low backpressure, and rapid kinetics. The integration of high surface area nanostructured sorbent materials into a thin film has shown been to significantly enhance sorption capacities, mitigating the principle problem associated with thin film sorbent systems.

The preferred solid-state sorbent structures/materials are demonstrated below to provide high collection efficiencies for dissolved rare earth elements (REEs), precious metals and other trace metals from various geothermal brines at room and elevated temperatures.

3.6 Demonstration of Sorbent Particles Suitable for Fluidized Beds and Moving Slurry Beds

Both fluidized beds and moving slurry beds of magnetic media involve suspending particles in the flowing fluid from which minerals are being recovered. The key difference between the adsorption techniques is the method for recovery of the particles from the solution flow. In a fluidized bed, the suspended particles are separated by the gravity method. In magnetic media, the suspended magnetic sorbent particles are separated from the water flow by applying external magnetic fields. However, the suspended particles from both techniques are separated from the water flow after a desired contact time between suspended particles and water is reached.

For both systems, having particles with high mineral recovery performance (kinetics, collection capacity, chemical affinity for target minerals) is key for an economically viable trace mineral recovery process. The preferred high performance particulate sorbent materials for

adsorption of dissolved REEs and other trace metal ions in various brines (at 60 °C, results as shown in Table 3.3) were selected for a final demonstration. Sharkey Hot Springs water at 95 °C was used for the final evaluations with Cu, Ag and Eu chosen to represent soft, intermediate and hard/REE mineral ions, respectively.

Table 3.4 shows both particle types, with preferred organic and inorganic surface chemistries, could provide high collection efficiencies from geothermal fluids at high temperatures. Diphos-SH-NF Silica was designed to provide a broad range adsorption of trace metal ions from challenging solutions such as geothermal waters. Installation of this high performance surface chemistry on NF silica which is a fine submicron size structure makes the material direct suitable for fluidized beds and thin film sorbent film application form factors. Mn- Fe₃O₄ MNP (8 nm) is designed and made as a high performance sorbent material for magnetic separation (in moving slurry bed) since it has strong magnetic properties but can also be integrated into thin sorbent films.

Table 3.4. The performance of selected sorbents in geothermal water at 95 °C

Sorbent	Collection Efficiency (%)		
	Cu	Ag	Eu
Diphos-SH-NF silica	92	70	98
Mn-Fe ₃ O ₄ MNP (8nm)	99	60	99
Equilibrium pH	8.8		

Equilibrium pH is the pH after metals were added in water and agitated for 2 hours at 95 °C
 The initial concentration of Cu, Ag, Eu are ~ 32, 8 and 2 ppb, respectively, 2 hour batch contact with agitation at L/S ratio of 5 x10⁴ mL/g sorbent. Experimental details are provided in appendix A.
 NF= nanofiber silica, MNP= magnetic nanoparticles

The conclusions from Table 3.4 are summarized below;

- Diphos-SH-NF silica and Mn- Fe₃O₄ MNP (8 nm) showed outstanding performance for adsorption intermediate metal ions (Cu and other valuable minerals such as Zn) and hard metal ions (REE's) and good performance for soft/precious metal ions (Ag and other precious metals such as gold).
- The data clearly demonstrates that the high temperature at 95 °C did not deleteriously impact the efficacy of these surface chemistries. This is due the high chemical affinity of these sorbents for the target minerals.
- The high performance of both sorbent materials at high temperature demonstrates that the Diphos-SH-NF Silica has high potential to be an affective sorbent for extraction of minerals from geothermal fluids at evaluate temperature with the fluidized bed system, as well as Mn- Fe₃O₄ MNP (8 nm) is suitable for the moving slurry bed system.

3.7 Demonstration of Sorbent Thin Films for Mineral Extraction

Sorbent thin films on support surfaces are a novel extraction approach that was identified as a promising configuration and explored in this project. Sorbent thin films are commonly used for small scale of trace collection efforts (i.e., the wide spread use of solid phase microextraction for analytical chemistry). Thin film sorbent coatings have been extensively used in the processes requiring high surface areas and surface chemistries for interactions, such as membrane separation, sensor and fuel cell technologies. The integration of the highly selective nanostructured materials into polymer has improved desired properties of thin film sorbent, such as increased surface area, affinity, selectivity, permeability, water adsorption, thermal stability, mechanical strength, and antibiofouling. The new sorbent materials developed and demonstrated in this effort have shown significantly improved collection capacity over previous solid phase sorbent, potentially enabling utilization of this form factor at the industrial scale. As previously mentioned sorbent thin films has many potential advantages including low-pressure drop, easy to incorporate into mineral extraction processes, resistance to fouling, manufacturability and flexible configuration. The thin films can be coated on basic filtration and separation media and used for industrial processing.

High performance sorbent thin film demonstration was carried out in Sharkey Hot Spring water at room temperature. As result shown in Table 3.5, the composite thin films showed excellent performance for collecting of dissolved REEs and other valuable trace metal ions from the geothermal water. Table 3.5 shows the thin films can be effective for sorbents with both organic (Diphos and PropPhos) as well as inorganic (MnO_2) sorbent chemistries. In general all the sorbent materials showed retention of their good performance for mineral uptake when incorporated into polymer composite thin films.

Table 3.5. The performance of polymer-sorbent composite thin film

Composite thin film (sorbent/polymer)	Collection Efficiency (%) (in Sharkey Hot Springs Water)					
	Cu	Zn	Ag	La	Eu	Ho
Diphos-SH-NF Silica/Nafion	87	83	95	87	91	90
PropPhos-NP Silica/Nafion	90	55	20	98	97	98
MnO_2 -NS Composite/Nafion	100	83	75	100	100	99

Composite thin films contained of 54% (wt/wt) sorbent loaded into Nafion polymer binder. Films deposited on a stainless steel disc (diameter of 22 mm) then air-dried. The coated disc (film ~ 20 μ m thick) was placed in a 50 mL falcon tube and 10 mL (L/S ratio ~8000 mL/g-sorbent) of the geothermal water (pH~8.3) containing ~50 ppb trace metal ions was added and gentle agitation for 24 hours prior ICP-MS analysis. Experimental details are provided in appendix A. NF= nanofiber Silica, NP= nanoporous Silica, NS= nanostructured Silica

The results from Table 3.5 are summarized as below;

- Organic sorbent (Diphos and PropPhos) and inorganic (MnO_2) sorbent integrated with Nafion polymer showed retention of their good performance for adsorption of intermediate metals (Cu and Zn), hard metals (REEs) and soft/precious metals (Ag).
- The composite thin film performance (collection efficiency) is similar to the unbound sorbent particles.

- The result indicates that the sorbents affinity and ability to collect minerals was not significantly reduced by incorporation into a thin film format.
- This experiment was performed at room temperature, however the films have been found to be thermally stable at the up to 200 °C (and beyond for some formulations).

Kinetics for adsorptions by sorbent thin films are a bit more complicated than unbound sorbent particles in dispersed in solution. The kinetics or adsorption of trace mineral ions in a solution by a thin film is normally longer than when compared to the unbound sorbent. Solution contact efficiency (and contact rate) with the thin film surface is a significant factor in determining uptake rate. Thicker films have more capacity but have slower sorption kinetics (due to mass transfer resistance to sorbent material deeper into the film). These factors, along with the specific film composition, will have to be optimized for specific applications using known methods.

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4. Results for Task 4: Techno-economic Analysis of Solid State Sorbent Technology for Cost-Effective Geothermal Mineral Extraction

4.1 Task 4 Summary:

A techno-economic analysis (TEA) for geothermal mineral extraction based upon the preferred separation materials identified in Tasks 2 and 3 was conducted. The TEA was developed for the advanced sorbent systems using performance data from the preferred sorbents in actual geothermal waters. The TEA was based on proven industrial chemical processing plant principles for similar types of facilities, current mineral market values, and published literature values for mineral concentrations in geothermal brines. The TEA included principle process drivers such as material price, plant size, resource composition/concentration, and extraction efficiency. For the advanced solid-state sorbent technology, *the TEA showed the potential for substantial revenue from recovery of selected minerals with favorable to excellent returns on investment, depending on the mineral content of solution at the geothermal site.*

Using available literature values for mineral concentrations, and current mineral pricing, the results of the TEA are presented in detail subsequently and summarized below in Tables 4.1 and 4.2. The TEA results for a “typical” domestic geothermal site with moderate mineral concentrations in the brine (Table 4.1), and a site with higher concentrations of valuable minerals (Table 4.2, Salton Sea geothermal brine) are presented. Both sites show positive economics for the geothermal plant for the addition of a mineral recovery process. The higher mineralization of the Salton Sea brines provides better economics as expected. Revenue from mineral extraction may represent a significant fraction of the economic output from energy generation at some geothermal sites.

Table 4.1. Financial returns from moderately mineralized geothermal site as function of flow volume

Brine Flow (gpm)	Sorbent Plant Capital Costs ^(a)	Net Annual Profit from Mineral Sales ^(b)	Simple Annual Return on Investment	Period to Recover Capital Investment	Annual Mineral Production (kg)
3,000	\$28,900,000	\$5,100,000	18%	5.7 yr	3,464,000
6,000	\$43,800,000	\$10,200,000	19%	4.3 yr	6,927,000
12,000	\$66,400,000	\$20,300,000	28%	3.3 yr	13,855,000

a. Estimated installed cost for mineral recovery equipment
b. Assumes 72% recovery with majority of revenue from Au, Pd, Pt, Ag, Mn, Cu and Zn.
Au = \$1,250/troy ounce, Pd = \$750/troy ounce, Pt = \$1,325/troy ounce, Ag = \$20/troy ounce, Mn = \$0.75/lb, Zn = \$0.70/lb, REE considered negligible compared to other metals.

Table 4.2. Salton Sea financial returns as a function of brine flow volume

Brine Flow (gpm)	Sorbent Plant Capital Costs ^(a)	Net Annual Profit from Mineral Sales ^(b)	Simple Annual Return on Investment	Period to Recover Capital Investment	Annual Mineral Production (kg)
3,000	\$28,900,000	\$35,400,000	122%	0.8 yr	2,930,000
6,000	\$43,800,000	\$70,800,000	162%	0.6 yr	5,860,000
12,000	\$66,400,000	\$141,500,000	213%	0.5 yr	11,713,000

a, b) All assumptions same as previous table except for brine mineral content.

The financial parameters improve with higher flow rates, because more minerals are delivered to the collection facility and economies of scale work in favor of the operator. Some interesting observations from the TEA results include the following:

- Economic returns might be even higher than shown because:
 - Only the minerals listed in the table 4.3 were used to calculate ROI. Many valuable minerals (i.e., Co, Ni, Ge, etc.) did not have concentrations available in the literature and were consequently not included in the TEA but would contribute to the bottom line.
 - Mineral prices at the time of this writing are well below peak. Improved mineral prices will provide more favorable economics.
 - TEA assumes lower efficiency (net 80% for collection and stripping) than already reported with new sorbent materials.
- REEs present in the geothermal brines can be collected by the proposed technology as a potentially domestic source of these strategically critical elements. At existing mineral prices and reported concentrations these elements do not presently provide significant economic value to the process, but that could change.
- Some geothermal sites near highly mineralized regions, such as those in the Nevada Great Basin, could reasonably be expected to have economics similar to those presented for the Salton Sea.
- The process is enabled and economically viable only because of the performance provided by advanced solid phase sorbent materials developed on this project.

A detailed model description, results and discussion are presented subsequently. Note this TEA is for the technology at TRL 3/4 and during period of low mineral prices. Refinement of the TEA would be appropriate as the technology advances and mineral prices change. Future efforts could adjust the model to evaluate specific sites and conditions of interest. The model could even be applied to other technologies.

4.2 The Techno-Economic Analysis Model

The techno-economic analysis (TEA) focuses on evaluating the cost of production of target RE/PM/CMs in conjunction with geothermal energy production. The TEA includes principal process drivers such as material price, plant size, resource composition/concentration, and extraction efficiency. The basic conceptual process flow diagram that illustrates the required process steps for extraction and recovery of critical materials from geothermal brines is shown below in Figure 4.1. TEA results are based on proven industrial chemical processing plant principles for similar types of facilities, current mineral market values, and published literature values for geothermal brine mineral concentrations.

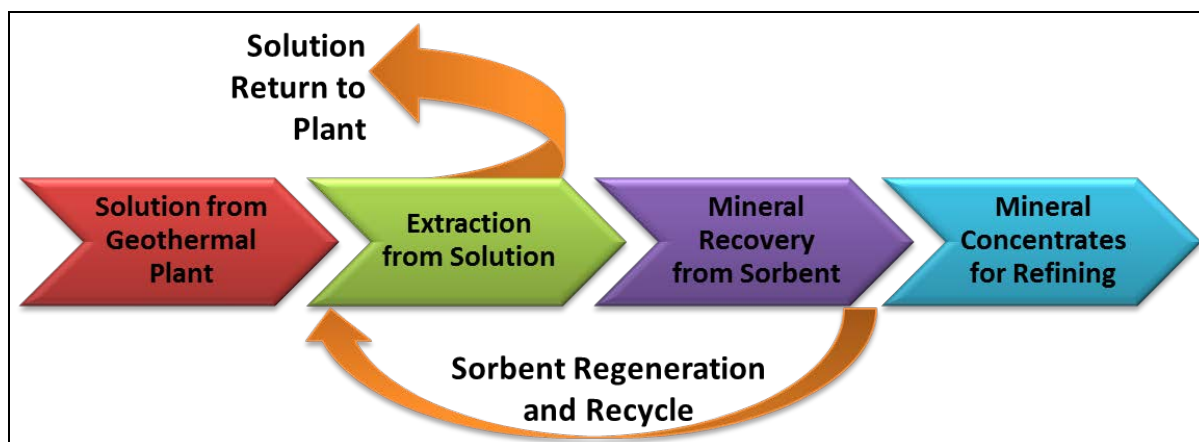


Figure 4.1. Schematic for the recovery of critical materials from geothermal solutions with advanced solid phase sorbents.

Extraction, mineral recovery, and regeneration of the sorbent are the heart of the process. Resulting mineral concentrates are suitable for specific refining and smelting operations based on classes of material – REEs, soft/precious metals, uranium, etc.

The TEA accounts for the major variables affecting both capital (Capex) and operating (Opex) expenses for mineral recovery and processing in conjunction with a geothermal plant. Since there are no published data for poly-metallic concentrates (as would be produced by our process), we evaluated the extraction, concentration, transportation, and refining on an end-to-end basis that accounted for the major steps of:

- Mineral extraction from geothermal brine, including
 - Sorption
 - Stripping
 - Concentrate preparation
- Concentrate shipping to a suitable refinery
- Concentrate processing/refining into metal products

This approach assumes the new geothermal add-on plant will extract minerals from the geothermal brine and produce polymetallic concentrate(s) suitable for feeding to a toll processor. That is, we do not include the capital cost of the metal refinery, but are including the estimated cost of toll processing the concentrate produced by the geothermal add-on plant, including the toll processor's fee/profit. By accounting for all of these major steps, we can utilize published market prices for the individual metals as the basis for the gross income from the facility. We calculate the amount and value of the finished metals produced at the refinery, and then pro-rate this value by the cost of extraction, concentration, shipping, and refining – the total Opex. This provides a net revenue stream that can be used, along with the estimated extraction plant Capex to determine relevant economic parameters for feasibility analysis.

This TEA makes the following assumptions/conditions:

1. Sorption, stripping, and concentrating of minerals at the geothermal site (using the advanced sorbent technology developed)
2. The polymetallic concentrate produced at the site is shipped to a toll refinery

3. Capex for the refinery is ignored, since it will be utilized on a contract basis that accounts for refinery costs and refiner's profit
4. The target metals are obtained from the geothermal brine at net 72% recovery
 - a. 80% recovery at geothermal site (this includes sorbent performance for collection and stripping)
 - b. 90% recovery at toll refinery
5. Shipping of polymetallic concentrate is based on
 - a. Concentrate being ~90 wt% solids (estimate from typical concentrates)
 - b. The concentrate solids contain ~45 wt% target metals
6. Shipping distance is unknown, so a flat rate of \$85 per wet ton shipping cost was used – this is based on a recently published mine/refinery feasibility study for the western US
7. Toll refiner will charge 20% markup (profit) above the actual refining costs
8. Metal processing costs, including 20% profit for toll refiner, are estimated at present prices to be (estimating assisted by a Senior Mining Consultant):
 - a. \$480 per dry ton of REE oxide
 - b. \$120 per dry ton of precious metal
 - c. \$240 per dry ton of base metal
9. All of the metal products are saleable at their currently published market value
10. 10 year operational plant life
11. Metal concentrations are from published data for geothermal domestic sites
12. Capital cost was calculated for a 3,000-gpm plant size. The industrial standard 6/10 rule was used to adjust for flow rate size (with input on actual water treatment plants from Tonka Water)
 - a. Capital cost estimate for 3,000-gpm plant is \$28.9 million
13. Brine treatment cost of \$0.88/1000 gallons (estimated by Tonka Water), including:
 - a. Sorbent
 - b. Sorbent stripping agent (acid)
 - c. Sorbent neutralizing agent (caustic)
 - d. Additional cost added for pretreatment cost

The TEA model is based on reasonable assumptions for extraction and processing costs. The capital costs, based on standard industrial plant design criteria, assume an add-on to an existing geothermal facility that produces a dewatered concentrate suitable for standard industrial processing, thus the capital cost of the metal refinery is not included in the estimate. The overall net revenue accounts for the estimated operating expenses of a chemical plant functioning in a high temperature corrosive environment. Additional unanticipated expenses were incorporated into the TEA estimates.

Because the technology under assessment is still at an early TRL(~3-4), some of the assumptions and numbers listed above will require refinement as the technology matures and is applied to specific geothermal sites. For instance, the cost of the advanced sorbent per 1,000 gal produced is difficult to calculate at this stage of technology readiness. Both sorbent production cost and its attrition rate are unknown at present. However, where possible, we have incorporated cost data from similar industrial water treatment systems in order to estimate the system Capex and some of the system Opex.

It must be emphasized that these are results from our initial TEA model. Actual economic return will be dependent on prevailing commodity prices, specific mineral concentrations in the solutions, and physical parameters of the specific site – reflecting the same hard limitations encountered by any other mining operation.

4.3 Mineral Concentrations in Geothermal Fluids

The concentration of the minerals in the geothermal fluids is a key parameter determining system performance since profitability fundamental depends on the amounts of minerals available for extraction. For our analysis we looked carefully at the peer reviewed literature for values of mineral concentrations that exist in geothermal fluids. We found that:

- Information in literature is very limited-comprehensive mineral compositions of geothermal brines have been rarely determined.
- The available information shows that the chemistry and mineral loading in geothermal brines *highly* variable.
- Some geothermal sites have very high mineral concentrations
 - i.e., Salton Sea, some undersea vents and volcanic fields
- Sampling and analysis protocol is key for reliable data
 - Minerals will precipitate with temperature changes

We chose to model 2 conditions; an “average” or typical domestic geothermal brine and a highly mineralized geothermal site. Mineral concentration values, based on peer reviewed literature, are shown below in Table 4.3. For the highly mineralize geothermal site we used the Salton Sea brine. The Salton Sea geothermal fluid has high mineral concentrations that have been carefully and extensive characterized and reported in literature.

For a geothermal solution with a “typical” mineral we averaged values found in literature. For REE concentrations we used high concentrations reported from the southern area of Idaho batholith site (Van Middlesworth and Woods, 1998). The Idaho batholith represents moderate concentrations of REEs relative to those reported at other sites in literature. For base metals (e.g., Mn, Zn, Cu) and precious metals (e.g., Au, Ag, Pt, Pd) we used an average of concentrations from all well mineralized geothermal sites around the world (including the Salton Sea site) reported in a review literature (Gallup, 1998). For Salton Sea we also used the values found in literature. For REE concentrations, we used high concentrations reported from the Death Valley Spring site (Kreamer et al., 1996). For base metals and precious metals we used concentrations reported in a literature review (Maimoni, 1982).

Table 4.3. Mineral concentrations in geothermal fluids values for “average” geothermal brines and the Salton Sea

Element	Selected Average ^{a-b} Concentration(s)		Salton Sea ^{c-d} Concentration(s)		Market Price*
Cerium Ce	1553	ng/L	700	ng/L	\$0.96/lb
Copper Cu	0.29	mg/kg	1	mg/kg	\$3/lb
Dysprosium Dy	60	ng/L	55	ng/L	\$103/lb
Erbium Er	26	ng/L	34	ng/L	\$32/lb
Europium Eu	16	ng/L	-	ng/L	\$93/lb
Gadolinium Gd	86	ng/L	14	ng/L	\$9/lb
Gold Au	17	µg/kg	100	µg/kg	\$1,250/troy ounce
Holmium Ho	10	ng/L	11	ng/L	\$25/lb
Lanthanum La	672	ng/L	367	ng/L	\$0.96/lb
Lutetium Lu	0	ng/L	7	ng/L	\$498.95/lb
Manganese Mn	499	mg/kg	500	mg/kg	\$0.74/lb
Neodymium Nd	660	ng/L	305	ng/L	\$18.10/lb
Palladium Pd	11	µg/kg	11	µg/kg	\$750/troy ounce
Platinum Pt	19	µg/kg	100	µg/kg	\$1,325/troy ounce
Praseodymium Pr	133	ng/L	77	ng/L	\$25/lb
Samarium Sm	86	ng/L	55	ng/L	\$1.18/lb
Silver Ag	259	µg/kg	600	µg/kg	\$20/troy ounce
Terbium Tb	11	ng/L	12	ng/L	\$204.12/lb
Thulium Tm	0	ng/L	5	ng/L	\$453.59/lb
Ytterbium Yb	23	ng/L	40	ng/L	\$22.68/lb
Zinc Zn	307	mg/kg	180	mg/kg	\$0.70/lb

*Values for 2016 and pricing available from:

- Argus Media Ltd. (UK)
- Stormcrow Capital Ltd. (Canada)
- <http://www.infomine.com/investment/metal-prices/manganese/1-year/>
- <http://www.infomine.com/investment/metal-prices/zinc/>

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Many valuable mineral concentrations (i.e., Co, Ni, Ga, Ge, Mo, Rh, Sb and Te) are only available in literature for some geothermal brines (i.e., Death Valley Spring site, Salton Sea) but not available in the literature for many geothermal brines, therefore, they were not included in the TEA. Further, mineral prices at the time of analysis (Feb. 2016) were well below average. Improved mineral prices and addition of other available minerals should provide more favorable process economics.

Literature sources providing even partial characterization of the mineral composition of geothermal fluids are limited and the Salton Sea geothermal brine was chosen originally for TEA efforts because of the availability of comprehensive mineralogical data on the sites brine (not its high degree of mineralization). *As subsequent analysis will show the economics for mineral extraction from the Salton Sea brines are very good.* Analogous to mining, each site is different and unique. Some geothermal sites will have brines with insufficient minerals to merit application of the technology. Some geothermal sites may have mineral concentrations higher than the Salton Sea—there is too little data in literature to know how common a site like the Salton Sea is. Geothermal sites near historic mining/mineralized regions, such as those in the Nevada Great Basin (famous for its mineral deposits and a huge geothermal energy reservoir), may have mineral solution concentration (and positive economics) similar to, or greater than, those presented for the Salton Sea.

4.4 The Techno-Economic Analysis Results for Geothermal Mineral Extraction with Advanced Solid State Sorbent Technology

The results of the TEA for advanced solid-state sorbent technology are shown below in Table 4.4 and 4.5 (and subsequently in Tables 4.6-4.8). The results are derived from the model (and assumptions) described in section 4.2 and the two geothermal solutions defined in section 4.3. The basic parameters used in the TEA are:

- Capital expenses (Capex) are based on 10 year plant life (a longer plant life time will improve ROI).
- Operating (Opex) expenses are based on standard industrial values based on mineral extraction and plant processing facilities.
- Net Annual Revenue (Gross Annual Revenue – Annual Opex)
- The return on investment (ROI) is calculated by as the ratio of net annual revenue of capital expenses. (Note that the simple ROI calculation merely evaluates net annual income as a percentage of the capital investment, assuming flat annual revenue, and does not account for inflation.)

TEA results are shown for 3000, 6000 and 12,000 gpm geothermal mineral recovery system. As shown in Tables 4.4 and 4.5 (and subsequently in Tables 4.6-4.8), the net annual revenue and the ROI provide favorable simple ROI for both geothermal sites modeled. Net revenues and ROIs can be observed to improve with flow volume, more minerals are delivered to the collection facility and economies of scale work in favor of the operator. Net revenue and ROI are based on an assumption that all produced metals are sold (this may be problematic under some market conditions for semiprecious metals such as Zn, Mn, Cu). A key point to note is that the process is enabled and economical only because of the performance provided by advanced solid-phase

sorbent material developed on this project (commercial sorbents were shown to be have insufficient performance in Tasks 2 and 3).

It is important to note, and can be clearly observed in Table 4.4 (and subsequent TEA table 4.7 based on this geothermal fluid), that net revenue and ROI are very positive for “typical” or “average” mineralization found in geothermal fluids. This means the process economics of using effective solid-state sorbent for mineral extraction from geothermal brine could potentially provide a value added process for many geothermal sites. *Revenue from mineral extraction may represent a significant fraction of the economic output from energy generation at some geothermal sites.*

Like other mineral recovery efforts, actual economic return will be dependent upon prevailing commodity prices, site-specific mineral concentrations and flow rates, and other physical constraints for the specific site. The Salton Sea has much greater concentrations for gold, platinum, and silver (as shown in Table 4.3) providing the potential to produce much more profitable returns compared to the average geothermal sites. Consequently, the net revenue and the ROI resulting from processing geothermal brines with Salton Sea mineral concentrations can be observed in Table 4.5 to be significantly greater compared to the “average” brines (Table 4.4). With ROI’s of 100-200% Salton Sea brines clearly provide a positive economic opportunity for a viable technology. While Salton Sea brines are not typical, they should not be viewed as unique. Other geothermal sites, particularly those near highly mineralized areas, such as those in the Nevada Great Basin, could reasonably be expected to have economics similar to those for the Salton Sea.

Table 4.4. TEA results for a mineral recovery process from a geothermal energy plant with “average” mineral content in the geothermal fluid*

Item	3,000 gpm	6,000 gpm	12,000 gpm
Capex	\$28,900,000	\$43,800,000	\$66,400,000
Opex			
<i>Shipping Cost</i>	\$800,000	\$1,600,000	\$3,200,000
<i>Raw Brine Treatment</i>	\$1,390,000	\$2,770,000	\$5,550,000
<i>Processing Costs</i>	\$6,400,000	\$12,800,000	\$25,700,000
Net Opex	\$8,590,000	\$17,170,000	\$34,450,000
Revenue			
<i>From REEs</i>	\$0	\$0	\$0
<i>From Precious Metals</i>	\$8,200,000	\$16,300,000	\$32,600,000
<i>From Base Metals</i>	\$5,500,000	\$11,100,000	\$22,200,000
Gross Annual Revenue	\$13,700,000	\$27,400,000	\$54,800,000
Net Annual Revenue	\$5,100,000	\$11,800,000	\$20,300,000
ROI (Net Revenue/Capex)	18%	23%	31%

**) Model assumption defined in section 4.1. Minerals utilized defined in section 4.2*

As shown in Table 4.4, the TEA results for mineral recovery process from a geothermal energy Plant with “average” or “typical mineral content are positive with an *estimated* net annual revenue of \$20.3 million against a capital investment of \$66.4 million at plant flow rate of

12,000 gpm. This translates to a 31% simple ROI, while only 18% ROI was calculated if the plant flow rate was 3,000 gpm. This data based on the prospect that all of the metals produced were sold. However, these numbers will need to be refined based upon updated market analysis and site specific details.

Table 4.5. TEA results for a mineral recovery process from a geothermal energy plant with “high” mineral content in the geothermal fluid (based on Salton Sea geothermal brines)

Item	3,000 gpm	6,000 gpm	12,000 gpm
Capex	\$28,900,000	\$43,800,000	\$66,400,000
Opex			
<i>Shipping Cost</i>	\$700,000	\$1,400,000	\$2,700,000
<i>Raw Brine Treatment</i>	\$1,390,000	\$2,770,000	\$5,550,000
<i>Processing Costs</i>	\$5,400,000	\$10,800,000	\$21,700,000
Net Opex	\$7,490,000	\$14,970,000	\$29,950,000
Revenue			
<i>From REEs</i>	\$0	\$0	\$0
<i>From Precious Metals</i>	\$38,200,000	\$76,300,000	\$152,500,000
<i>From Base Metals</i>	\$4,700,000	\$9,400,000	\$18,900,000
Gross Annual Revenue	\$42,900,000	\$85,700,000	\$171,400,000
Net Annual Revenue	\$35,400,000	\$70,800,000	\$141,500,000
ROI (Net Revenue/Capex)	122%	162%	213%

*) Model assumption defined in section 4.1. Minerals utilized defined in section 4.2

As shown in Table 4.5, the TEA results for mineral recovery process from a geothermal energy plant operating in Salton Sea brines are very positive with an *estimated* net annual revenue is \$ 141.5 million against a capital investment of \$66.4 million at plant flow rate of 12,000 gpm. This translates to an amazing 213% simple ROI, while only 122% ROI was calculated if the plant flow rate was 3,000 gpm. However, these numbers will need to be refined based upon updated market analysis and site specific details.

The TEA showed the process revenue comes from the precious metals (e.g., Pt, Au, Ag) and some base metals (e.g., Mn, Cu, and Zn). Additional evaluation is needed to confirm the validity of counting revenue from minerals like Mn and Zn, due to potential limitations in marketability. It can be observed above in Tables 4.4 and 4.5 that REEs do not provide any economic value to the process. In both cases examined the levels of total REEs were in ppt range (see Table 4.3), and current (2016) REE market prices are well below their peak, resulting in the conclusion that REE’s do not provide any measurable revenue. However, this could change if REE market prices improve significantly and other sites with more significant REE content are identified. The masses of REEs that could be extracted from the selected geothermal brines is shown in Table 4.6. Distribution of the REEs in the geothermal brines will be site dependent.

Table 4.6. Potential rare earth element recovery (kg/yr) from selected geothermal brines

Flow Rate (gpm)	1,000	3,000	6,000	7,000	12,000
Salton Sea	3	9	17	20	34
Idaho Batholith	5	14	29	33	57

It must be emphasized that these are results from our TEA modeling of a technology at the TRL3/4 and for 2016 conditions. Actual economic return will be dependent on prevailing commodity prices, specific mineral concentrations in the solutions, and physical parameters of the specific site – reflecting the same hard limitations encountered by any other mining operation. Refinement of the TEA would be appropriate as the technology advances, mineral prices change and site specific requirements (i.e., flow volume and site mineralization) are determined.

4.5 Impact of Fluid Process Volumes Upon The Techno-Economic Analysis Results

Based on initial TEA efforts, Tables 4.7 and 4.8 show how the financial returns scale as a function of plant flow rate. As expected, the financial parameters improve with higher flow rates, because more minerals are delivered to the collection facility and economies of scale work in favor of the operator. However, it must be emphasized that these are based on the limited data available from literature and a technology that is at the TRL 3-4 level. The models are based on reasonable assumptions for extraction and processing costs but need refined and verified at the industrial scale. Actual economic return will be dependent upon prevailing commodity prices, site-specific mineral concentrations and flow rates, and other physical constraints for the specific site.

For each flow rate case, we show the plant Capex, the net annual revenue, the simple ROI (Return on Investment of net annual income over Capex), the IRR (Internal Rate of Return) based on a (conservative) 10-yr plant life, and the simple payback period (Capex over net annual income). Note that the simple ROI calculation merely evaluates net annual income as a percentage of the capital investment, assuming flat annual revenue, and not accounting for inflation. The internal rate of return (IRR) is a metric used in capital budgeting that measures the profitability of potential investments. The IRR is a discount rate that makes the net present value (NPV) of all cash flows from a particular project equal to zero. The IRR in this case is based on a 10-yr plant lifetime. This is a conservative assumption that can be modified based on additional input from DOE or industry. A longer plant lifetime will provide a higher IRR. IRR calculations rely on the same formula as NPV does.

The following is the formula for calculating NPV:

$$NPV = \sum_{t=1}^T \frac{C_t}{(1+r)^t} - C_0$$

where:

C_t = net cash inflow during the period t

C₀ = total initial investment costs

r = discount rate, and

t = number of time periods

Table 4.7 uses literature value of concentrations of precious and base metals averaged over a variety of sites (as described in section 4.2). Concentrations of high value minerals are much lower than the Salton Sea and yet, the economics for “average” geothermal sites are still very positive for moderate/typical geothermal sites. The economics (ROI, IRR, etc.) for mineral extraction from the Salton Sea brines, shown in Table 4.8, are clearly very good. The Salton Sea brines should not be viewed as unique; other geothermal sites may provide mineral content as good or better. As discussed in section 4.2, limited characterization of the mineral content of geothermal brines has been conducted. It should also be pointed out that geothermal sites with low mineral concentrations will simply not yield favorable ROI and may not benefit from this technology.

Table 4.7. TEA financial returns from TEA as function of flow volume for “average” mineral content in the geothermal fluid*

Brine Flow (gpm)	CAPEX	Net Annual Revenue	ROI (simple)	IRR (10 years)	Payback Time (yrs)
1,000	\$14,900,000	\$1,700,000	11%	2%	8.8
2,000	\$22,700,000	\$3,400,000	15%	8%	6.7
3,000	\$28,900,000	\$5,100,000	18%	12%	5.7
4,000	\$34,300,000	\$6,700,000	20%	14%	5.1
5,000	\$39,300,000	\$8,500,000	22%	17%	4.6
6,000	\$43,800,000	\$10,200,000	23%	19%	4.3
7,000	\$48,000,000	\$11,800,000	25%	21%	4.1
8,000	\$52,100,000	\$13,600,000	26%	23%	3.8
9,000	\$55,900,000	\$15,300,000	27%	24%	3.7
10,000	\$59,500,000	\$16,900,000	28%	25%	3.5
11,000	\$63,000,000	\$18,700,000	30%	27%	3.4
12,000	\$66,400,000	\$20,300,000	31%	28%	3.3

*) Model assumption defined in section 4.1. Minerals utilized defined in section 4.2

Table 4.8. TEA financial returns from TEA as function of flow volume for “high” mineral content in the geothermal fluid* (based on Salton Sea Geothermal Brine)

Brine Flow (gpm)	CAPEX	Net Annual Revenue	ROI (simple)	IRR (10 years)	Payback
1,000	\$14,900,000	\$11,800,000	79%	79%	1.3
2,000	\$22,700,000	\$23,600,000	104%	104%	1.0
3,000	\$28,900,000	\$35,400,000	122%	122%	0.8
4,000	\$34,300,000	\$47,200,000	138%	138%	0.7
5,000	\$39,300,000	\$59,000,000	150%	150%	0.7
6,000	\$43,800,000	\$70,800,000	162%	162%	0.6
7,000	\$48,000,000	\$82,600,000	172%	172%	0.6
8,000	\$52,100,000	\$94,300,000	181%	181%	0.6
9,000	\$55,900,000	\$106,100,000	190%	190%	0.5
10,000	\$59,500,000	\$117,800,000	198%	198%	0.5
11,000	\$63,000,000	\$129,700,000	206%	206%	0.5
12,000	\$66,400,000	\$141,500,000	213%	213%	0.5

**) Model assumption defined in section 4.1. Minerals utilized defined in section 4.2*

The TEA capital costs, based on standard industrial plant design criteria, assume an add-on to an existing geothermal facility that produces a dewatered concentrate suitable for standard industrial processing, thus the capital cost of the metal refinery is not included in the estimate. The overall net revenue accounts for the estimated operating expenses of a chemical plant functioning in a high temperature corrosive environment. Additional unanticipated expenses were incorporated into the TEA estimates. Actual economic return will be dependent on prevailing commodity prices, specific mineral concentrations in the solutions, and physical parameters of the specific site – reflecting the same hard limitations encountered by any other extraction operation.

In summary it can be seen that all financial parameters improve with volume, as more minerals are delivered to the collection facility. ROI at the higher flow rates is very attractive, but as stated above, these numbers are based on a number of assumptions that need to be borne out.

Appendix A

Experimental

1. Sorbents and material characterization

Synthesis and characterization of organic ligands-based sorbents were previously described.¹⁻⁴ Ligands used in this work were house-synthesized including Diphosphonic (Diphos), phosphonic acid (PropPhos), Iminodiacetic acid (IDAA), the synthesized methods were explained elsewhere.²⁻⁴ Synthesis, characterization, and structure of metal oxides-based sorbents have been described elsewhere.⁵⁻⁷

The support materials such as CAB-O-SIL[®] EH5 (nanofiber, NF silica), Davisil 636 (packed column, PC silica), Davisil 635 (nanostructured, NS silica), and MCM-41 (nanoporous, NP silica) were obtained from, Cabot, Sigma-Aldrich, and ExxonMobil, respectively. Actinide Resin, Uteva Resin, RE Resin, and Diphonix[™] resin were purchased from Eichrom. The strong anionic exchange resin (SAX, AGMP-1M), and Chelex 100 Resin were purchased from Biorad. Activated carbon (Darco[®]KB-B), MnO₂ particles (<5µm and 63-250 µm), weak anionic exchange resin (WAX, CG 50), and GT74 resin were obtained from Sigma-Aldrich. MnO₂ Resin was purchased from Eichrom. The amidoxime resin Purolite[®] S910 was obtained from Purolite. All commercial materials were used as received, except the Purolite[®] S910, which was treated with 2.5% (wt) KOH at 80 °C for 1 hour before use to provide best efficacy.

Surface area and pore size data were collected using a Quantachrome QuadrasorbSI. The ligand densities were calculated from mass loss of organic attached sorbent obtained from Thermal Gravimetric Analysis (TGA). TGA was performed using a NETZSCH TG 209 F3 Tarsus in an aluminum oxide crucible under a helium purge of 10mL/min. The thermal ramp rate was 10°C/min and points were collected every 0.5 °C.

2. K_d and percent sorption measurements

The K_d is simply a mass-weighted partition coefficient between solid phase and liquid supernatant phase as shown in Equation 1. The percent sorption of REE was calculated as shown in Equation 2.

$$K_d = \frac{(C_0 - C_f) V}{C_f M} \quad (1)$$

$$\% \text{ capture} = 100 \times \frac{(C_0 - C_f)}{C_0} \quad (2)$$

where C_0 and C_f are the initial and final concentrations of the REE, respectively (at equilibrium), V is the volume of solution, and M is the mass of sorbent used.

K_d and percent sorption of REEs by sorbents were performed in different brine waters. K_d and percent sorption of REEs by sorbents were obtained through batch sorption experiments and calculated from the actual concentrations of metals detected by ICP-MS.

At room temperature, all waters were spiked with metal ions of La, Eu, Ho, Li, Mn, Ni, Cd, Ge, Mo, Hg, Pb, Zn, Cu, and Ag at ~ 50 ppb for each metal. 4.9mL of each 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 bottles were shaken for 2 hours at 200 rpm in an orbital shaker. Nonmagnetic materials were collected by filtering the solution thru 0.45- μ m syringe Nylon-membrane filters. Magnetic nanoparticles were separated from the solution using a 1.2 T NdFeB magnet. The removed supernatants were stored in 2% vol. 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.

At elevated temperature, the experiment was carried out in the same conditions as room temperature. One difference occurred at 95 °C where the temperature of the geothermal water containing the metals, ~50 ppb of Cu, Ag, and Eu, was raised up to 95 °C prior to adding the sorbent (L/S ratio of 50000 mL /g sorbent). After agitation for two hours, the sorbents were separated from the water. After ICP-MS analysis, the concentration of trace metals in control bottle (no sorbent) was significantly lower than expected, it probably due to trace metal adsorbing into the expanded plastic container at high temperature.

Brine waters were used in this work included; Sharkey Hot Spring (Sharkey, Lewis and Clark Backcountry Byway, Idaho), filtered river water (Columbia river, Washington State), filtered seawater (Sequim Bay, Washington State), Deslination (two-times concentration of Sequim Bay seawater), synthetic brine water (provided by Idaho National laboratory, INL), Great Salt Lake water (Great Salt Lake, Utah), diluted Great Salt Lake water (two-times dilution). The INL synthetic GTO simple brine solution was prepared by dissolving ACS grade salts. The compositions of the brine solution are Na⁺ (19000 ppm), Ca²⁺ (200 ppm), Mg²⁺ (100 ppm), K⁺ (700 ppm), Ba²⁺ (20 ppm), Cl⁻ (30600 ppm), TDS (50600 ppm). The ionic strength of these brines was calculated from their major ions composition and concentration, most of them were found in literatures.⁸⁻¹¹

3. Thin film application

The selected sorbents were used as a thin film configuration for recovery of REEs and other trace metals from brine solution. Thin film was prepared with 54% (wt) selected sorbent loaded into Nafion polymer; then the well-mix slurry was deposited on a cleaned surface of stainless steel disk (ID = 22mm). After air-drying, the coated disks were individually placed into 50 mL falcon tubes; then 20 mL of Sharkey water containing ~50 ppb trace metals (La, Eu, Ho, Ag, Cu, Zn) was added and gently agitated (120 rpm) for 24 hour prior to ICP-MS analysis. Experiments were performed in triplicate and the averaged values were reported

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