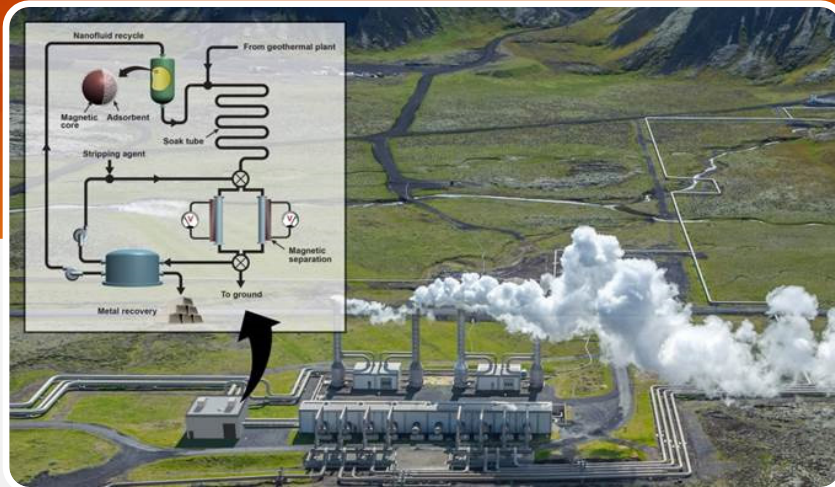




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## Magnetic Partitioning Nanofluid for Rare Earth Extraction from Geothermal Fluids

**August 2017**

BP McGrail  
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SK Nune

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# **Magnetic Partitioning Nanofluid for Rare Earth Extraction from Geothermal Fluids**

BP McGrail  
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August 2017

Prepared for  
the U.S. Department of Energy  
under Contract DE-AC05-76RL01830

Pacific Northwest National Laboratory  
Richland, Washington 99352



## Abstract

Rare earth metals are critical materials in a wide variety of applications in generating and storing renewable energy and in designing more energy efficient devices. Extracting rare earth metals from geothermal brines is a very challenging problem due to the low concentrations of these elements and engineering challenges with traditional chemical separations methods involving packed sorbent beds or membranes that would impede large volumetric flow rates of geothermal fluids transitioning through the plant. We are demonstrating a simple and highly cost-effective nanofluid-based method for extracting rare earth metals from geothermal brines. Core-shell composite nanoparticles are produced that contain a magnetic iron oxide core surrounded by a shell made of silica or metal-organic framework (MOF) sorbent functionalized with chelating ligands selective for the rare earth elements. By introducing the nanoparticles at low concentration ( $\approx 0.05$  wt%) into the geothermal brine after it passes through the plant heat exchanger, the brine is exposed to a very high concentration of chelating sites on the nanoparticles without need to pass through a large and costly traditional packed bed or membrane system where pressure drop and parasitic pumping power losses are significant issues. Instead, after a short residence time flowing with the brine, the particles are effectively separated out with an electromagnet and standard extraction methods are then applied to strip the rare earth metals from the nanoparticles, which are then recycled back to the geothermal plant. Recovery efficiency for the rare earths at ppm level has now been measured for both silica and MOF sorbents functionalized with a variety of chelating ligands. A detailed preliminary techno-economic performance analysis of extraction systems using both sorbents showed potential to generate a promising internal rate of return (IRR) up to 20%.



## Summary

Rare earth metals are critical materials in a wide variety of applications in generating and storing renewable energy and in designing more energy efficient devices.<sup>1</sup> Extracting rare earth metals from geothermal brines is a very challenging problem due to the low (ppb) concentrations of these elements and engineering challenges (pressure drop, parasitic pumping power losses) with traditional chemical separations methods involving packed sorbent beds or membranes that would impede large volumetric flow rates (>6000 gal/min for a 20 MWe plant) of geothermal fluids transitioning through the plant.<sup>2</sup> In addition, to achieve reasonable brine residence times, the packed bed or membrane systems would be very large and so pose significant challenges in fitting within an existing geothermal plant footprint and would have very high capital and operating costs.

In this project, we are demonstrating a simple and highly cost-effective nanofluid-based method for extracting rare earth metals from geothermal brines. Core-shell composite nanoparticles are produced that contain a magnetic iron oxide core surrounded by a shell made of silica or metal organic framework (MOF) sorbent functionalized with chelating ligands selective for the rare earth elements. By introducing the nanoparticles at low concentration ( $\approx 0.05$  wt%) into the geothermal brine after it passes through the plant heat exchanger, the brine is exposed to a very high concentration of chelating sites on the nanoparticles without need to pass through a large and costly traditional packed bed or membrane system where pressure drop and parasitic pumping power losses are significant issues. Instead, after a short residence time flowing with the brine, the particles are effectively separated out with an electromagnet and standard extraction methods are then applied to strip the rare earth metals from the nanoparticles, which are then recycled back to the geothermal plant.

Recovery efficiency for the rare earths have now been measured for both silica and MOF sorbents functionalized with a variety of chelating ligands and the results used to conduct a preliminary but detailed techno-economic performance analysis of extraction systems using both sorbents. Production cost estimates confirm potential to produce rare earth elements (REEs) at less than half the present commodity market value for these metals generating an IRR  $\geq 20\%$ .





## Acknowledgments

We thank the Department of Energy, Geothermal Technologies Office for supporting this work and especially Timothy Reinhardt, Joshua Mengers, and Holly Thomas for constructive criticisms over the course of the Phase I project. A portion of this research (Mossbauer, Atom probe, SEM/TEM and magnetometry) was performed in the Environmental Molecular Sciences Laboratory, a national scientific user facility sponsored by the Department of Energy's Office of Biological and Environmental Research and located at PNNL. Pacific Northwest National Laboratory is a multiprogram national laboratory operated for the U.S. Department of Energy by Battelle Memorial Institute under Contract DE-AC05-76RL01830. The Advanced Light Source is supported by the Director, Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.



## Acronyms and Abbreviations

CTAB	Hexadecyltrimethylammonium Bromide
ICP-OES	Inductively Coupled Plasma Optical Emission Spectrometry
IR	Infrared
IRR	Internal Rate of Return
K <sub>d</sub>	Partition Coefficient
MOF	Metal Organic Framework
PXRD	Powder X-ray Diffraction
REEs	Rare Earth Elements
SEM	Scanning Electron Microscopy
TEM	Transmission Electron Microscopy
TEA	Techno-economic Analysis
TEOS	Tetraethyl Orthosilicate
ICP-OES	Inductively Coupled Plasma Optical Emission Spectrometry



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# 1.0 Introduction

Rare earth metals are critical materials in a wide variety of applications in generating and storing renewable energy and in designing more energy efficient devices.<sup>1</sup> Extracting rare earth metals from geothermal brines is a very challenging problem due to the low (ppb) concentrations of these elements and engineering challenges (pressure drop, parasitic pumping power losses) with traditional chemical separations methods involving packed sorbent beds or membranes that would impede large volumetric flow rates (>6000 gal/min for a 20 MWe plant) of geothermal fluids transitioning through the plant.<sup>2</sup> In addition, to achieve reasonable brine residence times, the packed bed or membrane systems would be very large and so pose significant challenges in fitting within an existing geothermal plant footprint and would have very high capital and operating costs.

In this project, we are demonstrating a simple and highly cost-effective nanofluid-based method for extracting rare earth metals from geothermal brines that is illustrated in Figure 1. Core-shell composite nanoparticles are produced that contain a magnetic iron oxide core surrounded by a shell made of silica or metal organic framework (MOF) sorbent functionalized with chelating ligands selective for the rare earth elements. By introducing the nanoparticles at low concentration ( $\approx 0.05$  wt%) into the geothermal brine after it passes through the plant heat exchanger, the brine is exposed to a very high concentration of chelating sites on the nanoparticles without need to pass through a large and costly traditional packed bed or membrane system where pressure drop and parasitic pumping power losses are significant issues. Instead, after a short residence time flowing with the brine, the particles are effectively separated out with an electromagnet and standard extraction methods are then applied to strip the rare earth metals from the nanoparticles, which are then recycled back to the geothermal plant.

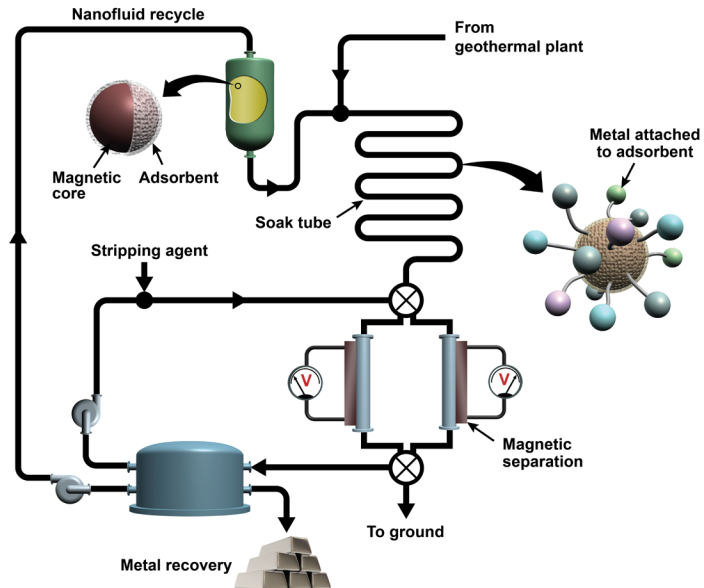


Figure 1. Conceptual drawing of magnetic partitioning nanofluid extraction system

Recovery efficiency for the rare earths have now been measured for both silica and MOF sorbents functionalized with a variety of chelating ligands and the results used to conduct a preliminary but detailed techno-economic performance analysis of extraction systems using both sorbents. Production cost estimates confirm potential to produce REEs at less than half the present commodity market value for these metals generating an IRR  $\geq 20\%$ .

## 2.0 Technical Progress Summary

Technical progress made under the first year of the project is summarized below.

### 2.1 MOF Sorbent

For brevity, we will not describe the full suite of MOF synthesis and functionalization trials that were conducted. Here, we will report on the three most promising sorbents. Several highly aqueous stable MOFs functionalized with a high density of anionic functional groups ( $-\text{COO}^-$ ,  $\text{CO}_2^-$ ,  $-\text{SO}_3^-$ ,  $\text{PO}_3^{2-}$ ) were synthesized and characterized. Batch experiments were performed by introducing synthesized MOFs to 0.005 M and 0.0005 M solutions of REE's at pH 3 to 4. REE uptake was determined by comparing inductively coupled plasma optical emission spectrometry (ICP-OES) analysis of blank reference solution samples where no sorbent was present with solution samples extracted after 5 min exposure to the MOF sorbent. Based on the ICP-OES data, the MOF-2 (Table 1) is found to be a reasonably good sorbent reaching up to a maximum of 122 mg/g (Eu) versus our 50 mg/g proposed target for the MOF based sorbents. Please note that we did not attempt to synthesize nanoparticle forms of the MOFs for these initial trials. MOFs reported on here were fine powders on the order of 50  $\mu\text{m}$  diameter. Given that our target is to have particles 1000X smaller with proportionally higher surface area, these loadings are extremely encouraging.

Table 1. REE Uptake with MOF-2: 0.005 M REE

REE	Loading (mg/g)	%Removal	$K_d$
Nd	121.6	31.4	246.4
Dy	28.7	6.83	49.3
Eu	122.5	16.78	190.2
Ce	79.03	11.46	109.8
Y	99.08	20.2	242.0

The MOF-3 sorbent was functionalized with the same anionic group and tested under identical conditions except that REE concentration was reduced 10X to 0.0005 M. The ICP-OES data (Table 2) shows the functionalized MOF-3 has over 90% removal efficiency with distribution coefficient reaching up to 40,000 mL/g (Dy), suggesting promise to quantitatively strip REEs from geothermal brines at ppb concentration.

Table 2. REE Uptake with MOF-3: 0.0005 M REE

REE	Loading (mg/g)	%Removal	$K_d$
Y	29.07	88.54	7728
Nd	64.09	94.5	12866
Dy	59.9	97.7	36244
Eu	71.64	95.99	21776
Ce	35.89	96.2	21033

Last, we covalently attached another chelating group to MOF-1 to produce MOF-1a. Experiments were conducted on this functionalized MOF-1a under identical conditions as described previously (Table 3).

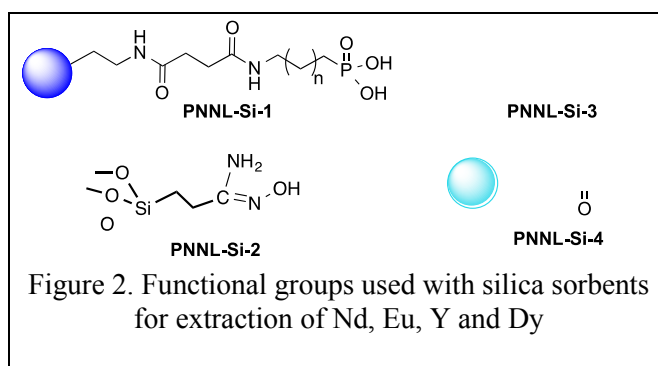
The batch experiments show MOF-1a to have the highest REE extraction performance with quantitative removal after 5 minutes of exposure.

Table 3. REE Uptake with MOF-1a: 0.0005 M REE

REE	Loading (mg/g)	%Removal	K <sub>d</sub>
Y	23.3	99.98	2328440
Nd	57.35	99.99	-
Dy	25.12	99.75	140027
Eu	53.96	99.98	5395081
Ce	31.45	99.99	791970

## 2.2 Silica Sorbent

The functional groups listed in Figure 2 were selected because they have been previously demonstrated to adsorb heavy metal ions with very high adsorption capacities. Silica particle cores were functionalized using the methods illustrated in Figure 3. All the functionalized materials prepared were thoroughly characterized by IR, PXRD, SEM and BET surface area measurements. Dried powders were redispersed into solution as agglomerates with estimated particle sizes of approximately 50  $\mu\text{m}$ .



A total of eight sorbents were evaluated for REE uptake as listed in Table 4. Systems 5-7 provided for some reproducibility assessment with different batches. SiO<sub>2</sub>-PNNL-4 included both amino groups as well amidoxime functional groups.

Sorption experiments were carried out

using similar batch methods as for the MOF sorbents described previously. In brief, a specific amount of functionalized silica was mixed with 10 mL of 0.005 M aqueous salt solutions and allowed to soak for 5 min. After the specified contact time, the mixtures were filtered using 0.2 micron filter to remove functionalized silica from supernatant salt solution. The residual concentration of rare earth metal ions in the supernatant was determined by ICP-OES.

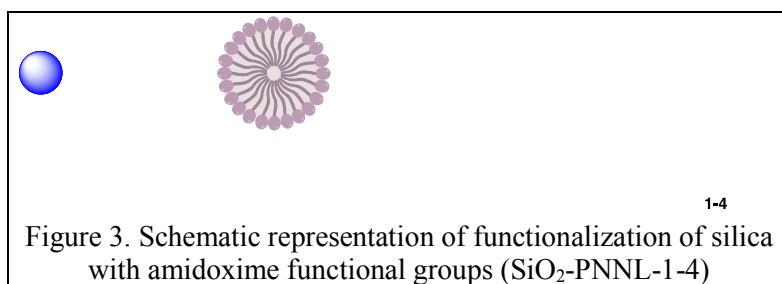


Table 4. Functionalized silica systems used for adsorption studies

	Systems	Functional group
1	Propylcarboxylic acid functionalized silica	carboxylic acid
2	Ethyl/butyl phosphonic acid silica	phosphonic acid
3	3-Propylsulfonic acid functionalized silica	sulfonic acid
4	3-(Ethylenediamino)propyl-functionalized silica	amino
5	SiO <sub>2</sub> -PNNL-1	amidoxime

6	SiO <sub>2</sub> -PNNL-2	amidoxime
7	SiO <sub>2</sub> -PNNL-3	amidoxime
8	SiO <sub>2</sub> -PNNL-4	amidoxime, NH <sub>2</sub>

The calculated adsorption uptake of Nd, Eu, Y and Dy is given in Table 5. Carboxylic acid, phosphonic acid, sulphonic acid and amino functionalized silica exhibited higher adsorption capacities for europium (53-71 mg/g) compared to neodymium (15-50 mg/g) at 5 min residence times.

Table 5. REE Uptake Measurement Results for Functionalized Silica

Sample #	Metal Salt/ Silica Sorbent	Uptake (mg/g)	% Removal
1	<b>Neodymium(III) nitrate hexahydrate</b>	NA	
2	Propylcarboxylic acid functionalized silica	15.30	2.05
3	Ethyl/butyl phosphonic acid Silica	49.70	6.80
4	3-Propylsulfonic acid-functionalized silica	-1.10	-0.16
5	3-(Ethylenediamino)propyl-functionalized silica	21.30	2.85
6	<b>Europium(III) nitrate pentahydrate</b>	NA	NA
7	Propylcarboxylic acid functionalized silica	53.80	7.23
8	Ethyl/butyl phosphonic acid Silica	65.80	9.54
9	3-Propylsulfonic acid-functionalized silica	58.60	8.64
10	3-(Ethylenediamino)propyl-functionalized silica	71.90	10.49
11	<b>Neodymium(III) nitrate hexahydrate</b>	NA	NA
12	SiO <sub>2</sub> -PNNL-1	47.40	6.35
13	SiO <sub>2</sub> -PNNL-2	23.30	3.33
14	SiO <sub>2</sub> -PNNL-3	62.50	8.64
15	SiO <sub>2</sub> -PNNL-4	48.60	7.10
16	<b>Europium(III) nitrate pentahydrate</b>	NA	NA
17	SiO <sub>2</sub> -PNNL-1	29.50	3.97
18	SiO <sub>2</sub> -PNNL-2	13.60	1.90
19	SiO <sub>2</sub> -PNNL-3	36.60	5.01
20	SiO <sub>2</sub> -PNNL-4	3.70	0.52
21	<b>Yttrium(III) nitrate hexahydrate</b>	NA	NA
22	SiO <sub>2</sub> -PNNL-1	-0.60	-0.13
23	SiO <sub>2</sub> -PNNL-2	28.20	6.27
24	SiO <sub>2</sub> -PNNL-3	5.40	1.28
25	SiO <sub>2</sub> -PNNL-4	2.70	0.61
26	<b>Dysprosium(III) nitrate hydrate</b>	NA	NA
27	SiO <sub>2</sub> -PNNL-1	-7.20	-1.34
28	SiO <sub>2</sub> -PNNL-2	-2.70	-0.50
29	SiO <sub>2</sub> -PNNL-3	37.90	7.04
30	SiO <sub>2</sub> -PNNL-4	-13.50	-2.71

## 2.3 Techno-Economic Performance Analysis

The data described in the previous Section was used to analyze the techno-economic performance of the rare earth metal extraction process using magnetic nanofluids. Costs for the magnetic nanoparticle adsorbents were estimated based on the raw material costs and complexity of the preparation processes. The performance of the MOFs and modified silica adsorbents were also projected for designed parameters based on the available data presented previously. Capital and operating costs, including energy, equipment, labor, taxes and depreciation were determined using a pre-set calculation template for the nanofluid extraction process.

### 2.3.1 Adsorbent Performance

Because the screening adsorption experiments could not be conducted under the exact conditions expected in the real system, extrapolation methods were used to project REE adsorption capacity under typical geothermal brine REE concentrations (ppb level) and shorter contact times on the order of <1 min. The particle sizes of the tested adsorbents are around 50  $\mu\text{m}$  and the contact time between the REE solution and adsorbents was 5 min. For the same mass of sorbent, the surface area is increased 1000X when the particle size is reduced to 50 nm in the actual extraction system. Consequently, we will use this scaling factor to adjust for both shorter contact time and lower REE concentrations in the actual situation. However, not all of the surface area will be available to chelate REE metal ions due to diffusion time required to access the interior pore surfaces. So an adjustment factor of 0.2 is applied reducing the scaling factor to 200X for the 50 nm nanoparticles. With these assumptions, the projected loading of selected REE metal ions for some MOF candidates at typical geothermal brine conditions are summarized in Table 6. In the last row, the required adsorbent mass was calculated for all the metals based on the projected loadings and assuming 90% of metal ions will be removed. We have conservatively assumed that incremental adsorbent is needed to remove all of the five REE candidates, i.e. the required sorbent mass is the summation of the required adsorbent mass for each REE metal. When the data is not available for all five REE metals, the results were normalized to calculate the maximum adsorbent mass. The estimated maximum adsorbent mass needed for the MOF-3 and MOF-1a are 3.9 kg and 5.6 kg, respectively. For reference, our estimated required sorbent mass in the original proposal was 7.4 kg.

Table 6. Projected REE metal loadings and estimated adsorbent mass for MOFs

MOF sample REE	MOF-3 (mg/g)	MOF-1 (mg/g)	MOF-1a (mg/g)	MOF-2 (mg/g)
Y	2.62	1.98	2.10	0.89
Nd	2.37	0.44	2.12	0.45
Dy	0.29	0.11	0.12	0.01
Eu	0.19	-	0.14	0.03
Ce	3.42	1.84	2.99	0.75
Adsorbent (kg)	3.9	8.6	5.6	30.2

Similar projections were made for REE extraction at typical geothermal brine conditions for the modified silica sorbent. Only the samples with experimental data on multiple REE metal ions were selected and the maximum adsorbent masses were calculated after normalization. The results are summarized in Table 7. It is clear that the projected loadings for modified silica are smaller compared to the best MOF candidates shown in Table 6. The two best silica candidates are ethyl phosphonic acid

modified silica and SiO<sub>2</sub>-PNNL-2. The estimated maximum adsorbent mass needed for those two modified silica are 36.8 kg and 42.3 kg, respectively. We now turn to the development of extraction cost comparisons for the MOFs and modified silica adsorbents.

Table 7. Projected REE metal loadings and estimated adsorbent mass for modified silica

REE \ Silica sample	Propylcarboxylic acid-silica (mg/g)	Ethly phosphonic acid-silica (mg/g)	3-Propylsulfoneic acid-silica (mg/g)	SiO <sub>2</sub> -PNNL-2 (mg/g)
Y	-	0.27	0.05	-
Nd	0.06	0.19	-	0.24
Dy	-	-	0.03	-
Eu	0.02	0.02	0.02	0.01
Ce	-	-	-	-
Adsorbent (kg)	85	36.8	100.2	42.3

### 2.3.2 Cost comparison

It is necessary to synthesize the magnetic core nanoparticles in bulk to significantly reduce cost. Assuming a reported procedure can be scaled up to synthesize Fe<sub>3</sub>O<sub>4</sub> nanoparticles with size of 13-20 nm<sup>3</sup>, the cost was estimated to be \$34.4/kg as shown in Table 8. The cost includes cost of chemicals, energy, equipment, and labor. The labor cost is the major factor because of the batch reaction.

Table 8. Estimated cost to prepare Fe<sub>3</sub>O<sub>4</sub> nanoparticles with size from 13-20 nm in kg level

Material	Energy	Separation	Equipment	Labor	Total
\$3.14/kg	\$1.26/kg	\$2.64/kg	\$5.21/kg	\$22.22/kg	\$34.4/kg

The costs of the adsorbents will be estimated using the material costs, labor costs, processing costs, and modification costs. The labor cost is estimated to be \$22/kg similar to that of the Fe<sub>3</sub>O<sub>4</sub> nanoparticles and the processing cost is estimated to be two times of the material cost. The modification cost will be estimated as 50% of the total cost of the base adsorbent including labor cost, processing cost and material cost. There will be no modification cost for the adsorbents that do not need modification. The yield and magnetic core cost will also be considered and included into the cost. The core-shell preparation cost will be estimated to be 20% of the magnetic nanoparticles cost.

A general formula can be written as below:

$$\begin{aligned}
 & \text{Adsorbent cost} = \frac{\left[ \underbrace{(\text{Metal salt cost} + \text{Organic linker cost} + \text{Solvent cost} + \text{Other cost})}_{\text{Modification cost}} \times 3 + \underbrace{\text{Labor cost}}_{\text{Core-shell cost}} \right]}{(1 + 50\%) \div \text{Yield} + \text{Fe}_3\text{O}_4 \text{ cost}} \times (1 + 20\%)
 \end{aligned}$$

Using the strategy described above, the adsorbent cost for all the four candidates are calculated and summarized in Table 9. Together with the required maximum adsorbent mass estimated in Section 2.3.1, the estimated total annual adsorbent costs were also included in the table assuming 6000 hour lifetime for all the adsorbents.

Table 9. Estimated cost to prepare and use magnetic core-shell nano-adsorbent

	Metal (\$/kg)	Linker (\$/kg)	Solvent (\$/kg)	Other (\$/kg)	Labor (\$/kg)	Yield	Fe <sub>3</sub> O <sub>4</sub> (\$/kg)	Adsorbent cost (\$/kg)	Adsorbent mass (kg)	Total adsorbent cost (\$/year)
<b>MOF-1a</b>	0.9	171.8	142.9	0.8	22	0.90	34.4	1983.68	5.6	16219
<b>MOF-3</b>	1	110	99	0.25	22	0.90	34.4	911.61	3.9	5191
<b>Ethly phosphonic acid-silica</b>	9.4	0.77	36.1	44	22	0.95	34.4	596.08	36.8	32026
<b>SiO<sub>2</sub>-PNNL-2</b>	9.4	0.77	36.1	90	22	0.95	34.4	857.55	42.3	52961

The cost impacts when considering recovery of multiple REE metals using the nanofluid extraction process with the four best sorbent candidates are shown in Table 10. Potential annual revenue is estimated at \$806,371/year. The estimated cost for all the adsorbent candidates are pretty close except for the MOF-1a. However, the difference in the annual material cost for the candidates are within reasonable range at this early R&D stage.

Table 10. Updated cost impacts using the nanofluid extraction process

Parameter		Ce	Dy	Eu	Nd	Y
Recovery Efficiency	90%					
Brine Flow Rate (gal/min)	6000					
Metal Concentration in Brine (ppb)		500	30	15	200	300
Metal Production Rate (kg/yr)	12235	5854	351	176	2342	3512
Metal Sales Price \$/kg		10	475	1000	83	60
Annual Revenue \$	\$806,371	\$58,540	\$166,725	\$176,000	\$194,386	\$210,720
Adsorbent candidate	<b>MOF-1a</b>	<b>MOF-3</b>	<b>Ethly phosphonic acid-silica</b>	<b>SiO<sub>2</sub>-PNNL-2</b>		
Nanoparticle Charge (kg)	5.6	3.9	36.8	42.3		
Nanoparticle lifetime (h)	6000	6000	6000	6000		
Nanoparticle cost (\$/kg)	1983.7	911.6	596.1	857.6		
Metal Recovery Cost \$/kg	5.6	5.6	5.6	5.6		
Annual Material Cost \$	\$84,735	\$73,707	\$100,543	\$121,480		
Annual Raw Profit \$	\$721,636	\$732,664	\$705,828	\$684,891		

### 2.3.3 Complete Process TEA

#### 2.3.3.1 Flowsheet and equipment

The magnetic nanofluid extraction process for the rare earth metals can be modeled in the flowsheet shown in Figure 4. Basically, the magnetic nanofluid is mixed with the feed brine and then the mixture passes through pipes that provide residence time to extract REE. Then the nanoparticles are separated out from the brine using electromagnetic force. Two magnetic separators are placed to make the separation a continuous process. Strip agent will be used to desorb the REE and regenerate the magnetic nanoparticles. The necessary equipment for this process is listed Table 11 below.

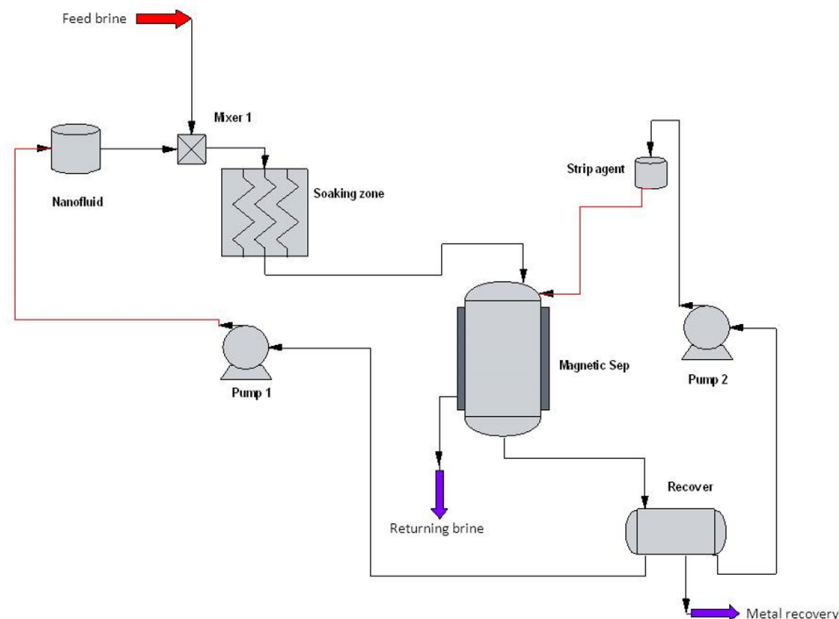


Figure 4. Rare earth metal extracting process using magnetic nanofluids

Table 11. Estimated cost for the equipment in the magnetic nanofluid extraction process

ID	Qu.	Equipment	Size	units	Cost Basis		Scaling Factor	Installation Factor	Current Cost	Installed Cost (each) (low ris)	Installed Costs (ISBL)
					Cost	Year					
1	1	Pump 1 for nanofluid	1.5	kW	\$ 1,280	2015	0.7	2	\$ 1,941	\$ 3,883	\$ 4,582
2	1	Pump 2 for stripe agent	1.5	kW	\$ 1,280	2015	0.7	2	\$ 1,941	\$ 3,883	\$ 4,582
3	1	Residence tube	35.6	m	\$ 53,400	2015	0.7	2	\$ 80,991	\$ 161,982	\$ 191,139
4	2	Separator and magnets	7.6	m <sup>3</sup>	\$ 8,000	2015	0.7	2	\$ 12,133	\$ 24,267	\$ 57,270
5	1	Vessel for nanofluid	13.6	m <sup>3</sup>	\$ 5,000	2015	0.7	2	\$ 7,583	\$ 15,167	\$ 17,897
6	1	Vessel for stripe agent	1.4	m <sup>3</sup>	\$ 2,500	2015	0.7	2	\$ 3,792	\$ 7,583	\$ 8,948
7	1	Vessel for recovery	1.36	m <sup>3</sup>	\$ 34,675	2015	0.7	2	\$ 52,591	\$ 105,182	\$ 124,115
8	1	Miscellaneous Tube and valves	1	m <sup>3</sup>	\$ 20,000	2015	0.7	2	\$ 30,334	\$ 60,667	\$ 71,587

Costs were estimated using the method of Guthrie, which generally includes four steps:<sup>4</sup>

1. Sizing the reactor or vessel based on the known flow rates and assumed residence time
2. Estimating purchase cost based on empirical design data (Year 2002) (Williams power law)\*
3. Estimating total cost by including the installation module factor: 2.0 ( includes labor, piping and accessories cost)
4. Converting to today's cost by considering the Chemical Engineering Plant Cost Index: 2002 (395.6) vs. 2015 (600, estimated)

The total installed equipment cost was estimated to be \$480,119.

### 2.3.3.2 Capital and Operating Costs

The capital and operation costs were estimated using a calculation template that was provided by ARPA-E for use on another project requiring cost estimation for a chemical processing plant. Reasonable



complexity was added to simulate cost analysis for a practical project.<sup>5-11</sup> The capital investment estimated results are shown in Table 12.

Table 12. Capital investment summary for the magnetic nanofluid extraction process

<b>Installed Costs (ISBL+)</b>			<b>\$ 480,119</b>
Auxiliaries	30.0% of ISBL+	\$	144,036
Buildings	20.0% of ISBL+	\$	96,024
Site development	5.0% of ISBL+	\$	24,006
Land	2.5% of ISBL+	\$	11,855
Spare parts	0.5% of ISBL+	\$	2,401
<b>Fixed Capital Investment (FCI)</b>		<b>\$</b>	<b>758,440</b>
Working Capital	19.0% of FCI	\$	144,104
Start-up Costs	8.0% of FCI	\$	60,675
<b>Total Capital Investment (TCI)</b>		<b>\$</b>	<b>963,219</b>

Similarly, the operation expense for the magnetic nanofluid process is summarized in Table 13. The plant was assumed to be running at 95% capacity factor. The labor and utility costs were positively related with this capacity factor. It is observed that the labor related costs were the major cost for daily operation. The raw material cost included the adsorbent cost and the metal recovery cost. Here, the MOF-3 was selected as an example in the raw material cost.

Table 13. Operation expense summary for the magnetic nanofluid extraction process

Plant capacity factor			95%
<b>Fixed Costs</b>			
Maintenance	5.0% of FCI	\$	37,922
Operating Labor (OL)	25 FTEs	\$	208,050
Laboratory Costs	10.0% of OL	\$	20,805
Supervision	20.0% of OL	\$	41,610
Plant Overheads	30.0% of OL	\$	62,415
Insurance	1.0% of FCI	\$	7,584
Royalties	1.0% of FCI	\$	7,584
<b>Variable Costs</b>			
Raw Materials (RM)		\$	73,707
Miscellaneous Materials	10.0% of RM	\$	7,371
Utilities			5,344
<b>Indirect Costs</b>	10.0% of Costs	<b>\$</b>	<b>47,239</b>
<b>Annual Operating Costs</b>		<b>\$</b>	<b>519,632</b>

### 2.3.3.3 Financial analysis and IRR

Financial analysis was conducted using the previous capital and operation costs. The results are summarized in Table 14. The production and values of different REE metals were normalized into one product to facilitate the analysis. The annual total production of REE was estimated to be 12,235 kg and the average value for the REE was estimated to be \$65.9/kg based on the conditions listed in Table 10. The plant operation time was assumed to be 30 years and the payment time for debt was assumed to be 10 years. The IRR was calculated to be 20% for the MOF-3 using the capital costs and corresponding operation costs. The IRRs for other adsorbents MOF-1a, ethly phosphonic acid-silica, and amidoxime-silica were estimated to be 19%, 17%, and 15%, respectively.

Table 14. Financial analysis for the magnetic nanofluid extraction process

Parameters				
FCI				\$ 758,440
TCI				\$ 963,219
Debt		45%		
Equity		55%		
Interest on debt		4.5%		
Preferred dividend rate		0.00%		
Repayment term of debt		10	years	
Capital Expenditure Period		3	years	
completion in year	0	0%		
completion in year	1	10%		
completion in year	2	60%		
completion in year	3	30%		
completion in year	4	0%		
completion in year	5	0%		
Operation begins at year		4		
Operational Period		30	years	
Ramp Up Period				
capacity in year	4	100%		
capacity in year	5	100%		
capacity in year	6	100%		
Escalation of O&M, fuel, revs		3.00%		
Discount rate		10.00%		
Capital Cost Escalation prior to operation		0.397%		
Capital Depreciation period		20	years	
Depreciation X-declining balance		150%		
Corporate Tax Rate (fed+state)		38%		
Effective Annual Rate of Equity				
Cost of Capital				
Cost-Year Dollars		2015		
WACC		12.29%		
IRROE		20%		

### 3.0 Summary and Conclusion

Adsorbent performance at typical geothermal brine conditions for both MOFs and modified silica materials were projected based on currently available data. The adsorbent costs were estimated based on material cost and modification complexity. The MOF sorbents offer the best tradeoff in terms of sorbent performance and balance of plant capital and operations costs. However, the differences in IRR between the best MOF and best silica candidate ended up being relatively small. Looking forward, the benefit of that finding is that if an unexpected problem develops during development of the MOF sorbent, a switch to the silica sorbent can be done relatively easily and with little impact on overall economics of the process.

A quite conservative financial analysis of the complete nanofluid REE extraction process was conducted and an IRR of about 20% was estimated for the best candidate sorbent. This exceeds our goal to project a 15% IRR for the process. Further work justifying less conservative assumptions is likely to improve this first IRR estimate. In summary, the work conducted in this project clearly supports proceeding with R&D to further develop the nanofluid REE extraction process and demonstrate cycle performance and lifetime of the nano-sorbents under more realistic operating conditions.

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