PROCEEDINGS, 42nd Workshop on Geothermal Reservoir Engineering
Stanford University, Stanford, California, February 13-15, 2017
SGP-TR-212

Assessment of Mineral Resources in Geothermal Brines in the US

Ghanashyam Neupane and Daniel S Wendt

Idaho National Laboratory, Idaho Falls, ID 83415, USA

E-mail: Ghanashyam.neupane@inl.gov

Keywords: Geothermal brines, brine mining, mineral recovery

ABSTRACT

Geothermal power plants produce a large volume of brine for power generation. Since these brines are the product of long-term water-rock interactions at elevated temperatures at depth, they contain dissolved chemical components including critical and strategic mineral commodities at various concentrations. Despite the low concentrations for many of the critical and strategic minerals, significant quantities of select minerals could be recovered due to the large volumes of brine utilized by geothermal power plants. The potential economic benefits of mineral recovery from geothermal brines has long been identified, however, no commercial recovery of these materials is on-going in the US.

In this paper, we present a summary for mineral contents in geothermal brines in the US. Since the western parts of the US has substantial geothermal resources with numerous operational power plants, we have made a concerted effort to identify the potential economic minerals in geothermal brines in each of the western US geographic provinces. Our resource assessment indicates that several mineral commodities (e.g., Li, Mn, SiO_2, etc.) are present in high enough concentrations and sufficient flow rates to be economically recovered from geothermal brines.

An appraisal of mineral extraction technologies indicates availability of a number of mineral-specific to multi-minerals bench-scale extraction technologies. Some of these extraction technologies (e.g., SiO_2 and Li) have also been successfully tested with pilot-scale facilities in the US. We also present preliminary results on the potential economic values of multiple minerals for several operational power plants. Our study shows that the extraction of targeted minerals at selected sites can add an additional revenue stream. However, several outstanding technological, financial, and market challenges currently hinder the recovery of minerals from geothermal brines.

1. INTRODUCTION

Geothermal fluids are the product of water-rock interactions over a long time at a high temperature and depth. In the process of this prolonged high-temperature water-rock interaction, geothermal fluids pick up several chemical species including some valuable metals from the rock. Specifically, the chemically corrosive and complexing species such as hydrogen, chloride, sulfate, etc., ions in the geothermal fluids help leach out metals from the rocks and sustain their mobility in the geothermal brines. Therefore, the large-volume geothermal brines produced in power plants are likely to contain significant amount of valuable mineral resources. However, traditionally geothermal power plants are built to recoup heat from the brines. The post-production brines are injected back into the geologic formations without intercepting any valuable minerals therein. Therefore, development of cost-effective and deployable mineral recovery technologies can add an additional revenue stream and improve the economics of the geothermal energy.

The western states of the US have been known to have higher geothermal activities with numerous sampling features (Figure 1). Several geothermal power plants have been established at various locations in these areas over the last four decades, and there are numerous additional sites with potential power production using natural hydrothermal or engineered geothermal resources. Over the years, the chemical compositions of geothermal brines/waters of numerous hot springs and wells have been measured. In this paper, we assembled composition data for more than 2250 features scattered all over the US. The chemical dataset was used to assess the potential minerals resources in the US geothermal resources. This paper focuses the general assessment of mineral resources in the US geothermal brines and the existing/available mineral extraction technologies. We identify some target metals/minerals in geothermal brines from several western US geographic provinces. Similarly, we also present preliminary results on the economic values of several minerals in the brines of some operating power plants. Finally, we briefly present the barriers and challenges that may be hindering for the incorporation of mineral recovery facilities in power plants.

2. APPROACH

We compiled a database for US geothermal brine compositions using various sources such as past reports of the USGS, states water resources management agencies, conference papers, and journal articles. We started data compilation with the USGS open file database for geothermal brines (http://gdr.openei.org/files/194/GEOTHERM_ALL.xls). This database contains over 8000 entries for US geothermal brines. We removed incomplete and redundant data entries of this file. We also assembled as many original sources as possible to make sure the reported concentrations and units in the database were valid. We incorporated additional data to our database for geothermal features that are not included in the USGS data file, and for some features, we replaced the existing incomplete data with the complete data from other sources. For this study, we have compiled a database containing brine compositions for more than 2250 geothermal features (hot springs and wells) (Figure 1a). In addition to this, we prepared a sub-database for several operational geothermal plants (Figure 1b).

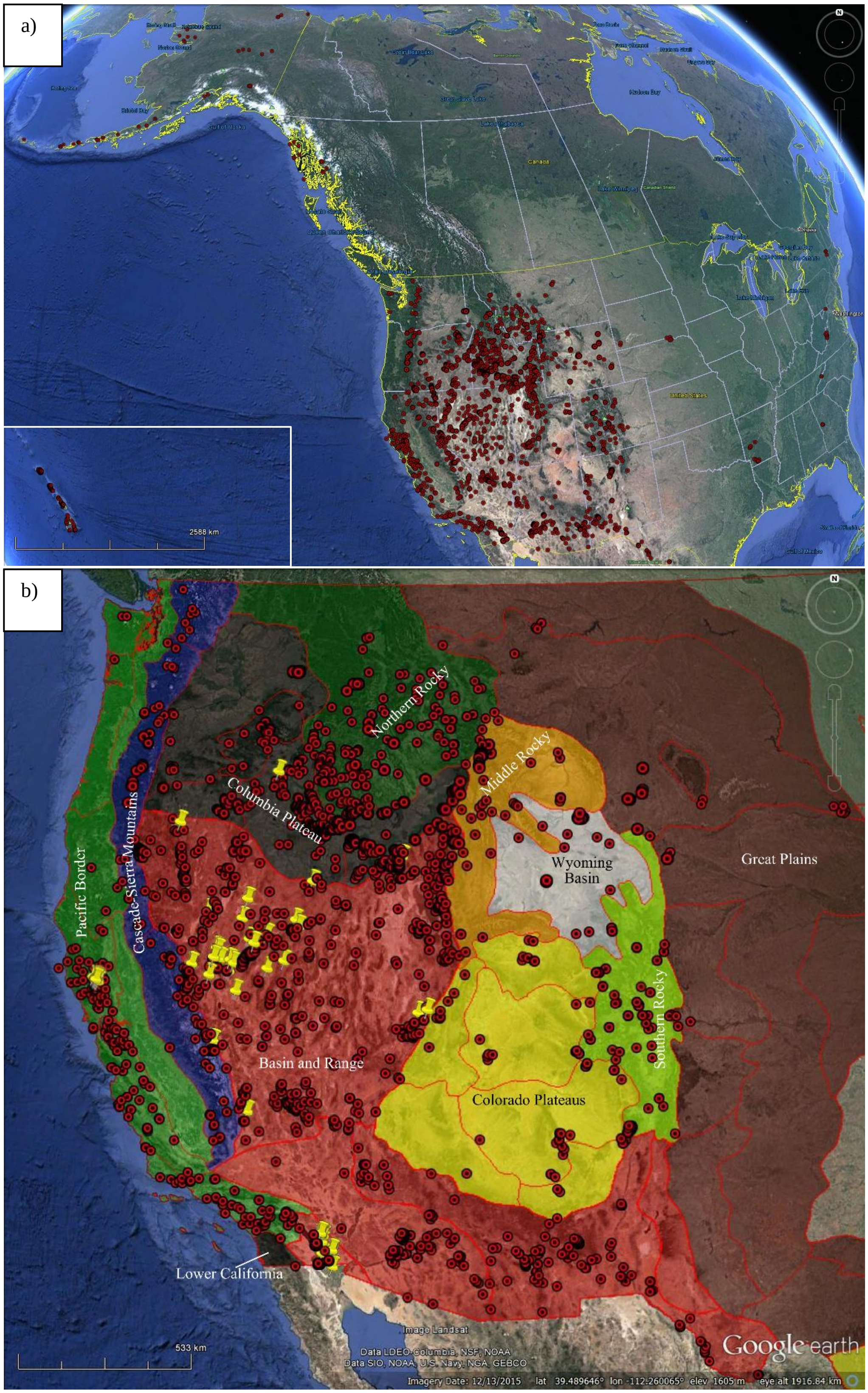

Figure 1. (a) Distribution of the US geothermal brine samples (~2275 samples) with known chemistry. (b) The western US brine samples are plotted on a map with boundaries of geographic subdivisions (Fenneman, 1917). Locations of operational (as well as a few planned) geothermal plants are indicated with yellow push pins.

A separate database was also prepared for geothermal features with known compositions of rare earth elements (REEs). The REEs data for geothermal brines were primarily assembled from reports and journal articles published by Scott Wood and his groups (e.g., Wood, 2002; Wood and Shannon, 2003; Nelson et al. 2004). Ongoing Idaho National Laboratory (INL) projects have collected and analyzed REEs in several geothermal/oil and gas wells brines of the eastern Snake River Plain (ESRP), southeastern Idaho, and Wyoming Basin. Including the INL's unpublished data, our REEs database includes measured concentrations for about 230 geothermal features in the US.

2.2 Data reduction/illustration

Two approaches were used for data reduction and illustrations. First, we treated all of the US brine samples as a single group and plotted them on a series of maps to illustrate how the concentrations of various minerals of economic interest are distributed in the US. Second, the assembled data were separated into groups depending on their geographic locations. For the contiguous US, we adopted physiographic subdivisions (provinces) given by Fenneman (1917) to separate samples into different groups. The brines samples from Alaska and Hawaii (which are given a low priority, and are not discussed in detail here) were grouped state-wise. This grouping of data helped identify potential economic minerals in each of the geographic subdivisions. Finally, annual brine flow rates produced by several geothermal power plants in the US were also assembled. The mass flow rates and concentration of minerals in the brines were used for general estimation of potential new revenue to geothermal power plants from the brine mining.

Table 1. Demand and sources of mineral commodities in the US

Minerals	Demand/ consumption	Price ($)	Purity	Domestic source	Imports (% re-calculated for non-domestic sources)	Ref.
Ag	6900^{a}	20.16^{b}	99.99%	63%	Mexico (53%), Canada (28%), Poland (6%), Peru (3%), and other (10%).	1, 2
Au	165^{a}	1335^{b}	99.99%	Net exporter^{c}	Mexico (52%), Canada (17%), Colombia (11%), Peru (7%), and other (13%).	1, 3
B	NA^{d}	630^{e}	B mineral	~100%	Turkey (81%), China (3%), Argentina (3%), Austria (2%), and other (11%).	1
$BaSO_4$	$3,420,000^{a}$	125^{e}	$BaSO_4$	21%	China (80%), India (11%), Morocco (4%), Mexico (3%), and other (2%).	1
Cs	Few thousands^{f}	2020^{g}	99.98%	None	Canada (~100%).	1
Cu	$1,830,000^{a}$	3.22^{h}	Cathode grade	69%	Chile (51%), Canada (26%), Mexico (13%), Peru (6%), and other (4%).	1
Li_2CO_3	$21300^{a,i}$	$6,600^{e}$	Li_2CO_3	<50%	Chile (50%), Argentina (46%), other (4%)	1
K_2O	$5,500,000^{a}$	730^{e}	K_2O	16%	Canada (85%), Russia (10%), Israel (2%), Chile (2%), and other (1%).	1
Mn ore	$500,000^{a}$	5.01^{e}	46-48% Mn content	None	Gabon (61%), Australia (16%), south Africa (14%), Ghana (4%), other (5%).	1
Fe-Mn	$370,000^{a}$	5.01^{e}			South Africa (57%), Norway (9%), Ukraine (8%), South Korea (7%), other (19%).	1
Si-Mn	$150,000^{a}$	5.01^{e}			South Africa (32%), Gabon (22%), Georgia (8%), Australia (12%), and other (26%).	1
Pb	$1,660,000^{a}$	1.07^{h}	Pb metal	70%	Canada (68%) Mexico (18%), Australia (5%), and other (9%).	1
Rb	2000^{f}	1472^{g}	99.75%	None	Canada (~100%).	1
SiO_2		1750^{e}	30%			4
Sn	$42,300^{a}$	8.1^{h}	Sn metal	26%	Peru (40%), Bolivia (17%), Indonesia (15%), Malaysia (12%), and other (16%).	1
Sr	$33,000^{a}$	50^{e}	Sr mineral	None	Mexico (89%), Germany (7%), China (3%), and other (1%).	1
Zn	$990,000^{a}$	1.075^{h}	Zn metal	19%	Canada (68%), Mexico (13%), Peru (9%), and other (10%).	1
Ce_2O_3	$17,000^{a}$ (total REEs)	2.5^{j}	99% Bulk	None	China (75%), France (6%), Japan (6%), Estonia (4%), and other (9%).	1, 5, 6
Dy_2O_3		250^{j}				
Eu_2O_3		225^{j}				
La_2O_3		2.5^{j}				
Nd_2O_3		46^{j}				
Pr_2O_3		62^{j}				
Sm_2O_3		3.1^{j}				
a. metric tons/year. b. per troy ounce (31.104 g). c. In 2015, US mined 211 metric tons of gold, US also imported 315 metric tons and exported 430 metric tons of gold. d. Consumption data not available, but the US also imported and exported B compounds, global production in 2014 was 3,720,000 metric tons. e. per metric ton. f. kilograms. g. per 100 grams. h. per pound. i. converted from Li content to Li_2CO_3. j. per kilograms.						
1. USGS (2015), 2. www.silverprice.org, 3. www.goldprice.org, 4. Bourcier et al. (2009), 5. Norman et al. (2014), 6. Dickson (2015).						

3. THE US DEMANDS AND SOURCES OF MINERAL COMMODITIES

We assembled the US demands, sources, and prevailing market prices of various mineral commodities (Table 1). Specifically, the latest USGS mineral commodity summary (USGS, 2015), reports of the US Congressional Research Service (e.g., Humphries, 2013), and other sources (e.g., Norman et al., 2014; Dickson 2015) were used to assemble market parameters for various mineral commodities that could potentially be recovered from the US geothermal brines. Table 1 shows that the US is completely or mostly dependent upon foreign sources for several mineral commodities. Specifically, the US is fully dependent on foreign sources for the Cs, Mn, Rb, Sr, and REEs minerals. Similarly, it imports most of the Ba, Li, K, Sn, and Zn from various countries.

4. DISTRIBUTIONS OF ECONOMIC MINERALS IN THE US GEOTHERMAL BRINES

4.1 Precious metals

More than 150 (7% of the samples in the database) of the US geothermal brine samples (mostly distributed in the Basin and Range and Columbia Plateau Provinces) have known Ag concentrations (Figure 2), and the majority (117) of them have values between 0.01 to 0.1 mg/kg. A good number of samples (ca. 15) have Ag concentration > 0.1 mg/kg, and a few samples from Salton Sea area are reported to have concentration up to 1.4 mg/kg (Cosner and Apps, 1978). Figure 3 shows the distribution of geothermal brine samples [about 90 (4% of the) samples in the database] with known Au concentrations. The reported values of Au in geothermal brines range from sub-detection limit to 0.11 mg/kg. Of the samples with known concentrations, 65 samples have Au level ca. 0.1 mg/kg, and majority of these high Au samples are located in Oregon covering both the Basin and Range Province (Great Basin Section) and the Columbia Plateau Province (Blue Mountain and Harney Sections).

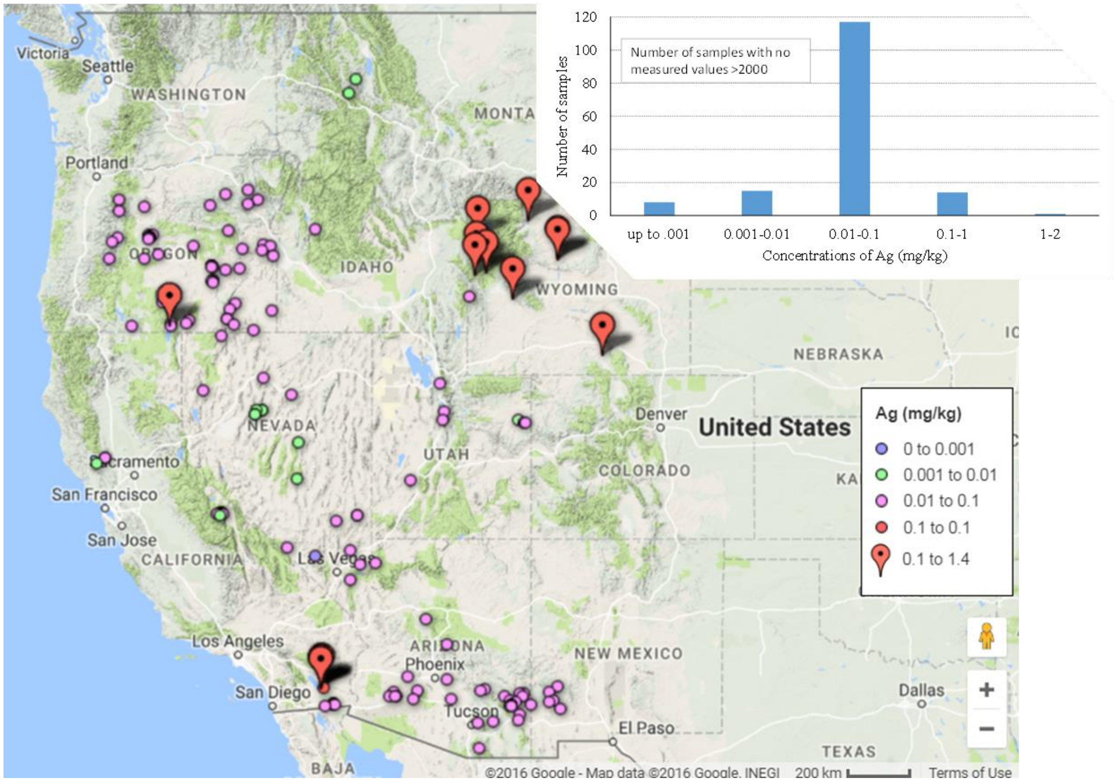

Figure 2. Distribution of geothermal brine samples with measured Ag concentrations.

4.2 Copper

In our database, about 500 (22% of the) geothermal brine samples in the database have measured Cu concentrations (Figure 4). The majority of samples with known Cu values have concentrations in the range of 0.001 to 0.01 mg/kg (230 samples) and 0.01 to 0.1 mg/kg (187 samples). About 38 samples have Cu concentrations in the range from 0.1 to 1 mg/kg. However, some samples (9) from Salton Sea area have Cu concentrations >12 mg/kg.

4.3 Lithium

Figure 5 shows the distribution of geothermal brine samples (about 1200 or 53% of the samples in the database) in the US with known Li concentrations. The majority of geothermal brines (>900 samples) have the Li concentrations <1 mg/kg. About 263 samples have concentrations in the range from 1 to 10 mg/kg, and about 14 samples are reported to have concentrations in the range from 10 to 20 mg/kg. Some brine samples (about 21) have Li concentrations >20 mg/kg. Specifically, brine samples with higher Li concentrations are confined to the Salton Sea area, and several of these brines have up to 400 mg/kg of Li. In the past, several Li extraction technologies were developed for processing brines with Li concentrations typical of the Salton Sea area, and a few of them were successfully demonstrated with a pilot scale plant (e.g., Harrison, 2014).

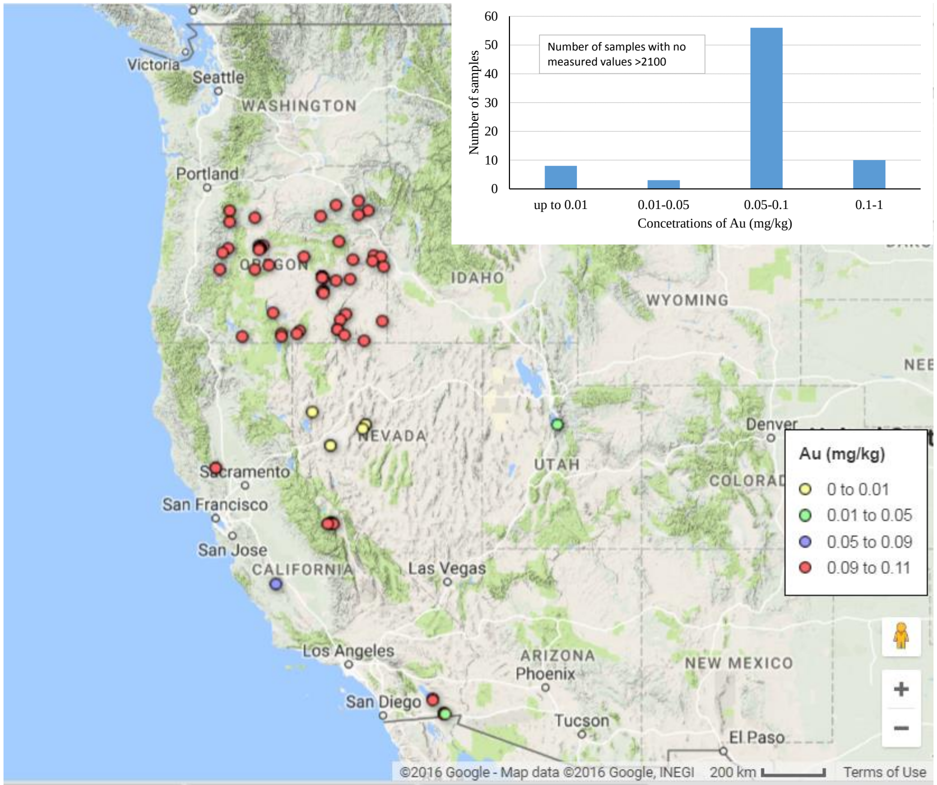

Figure 3. Distribution of geothermal brine samples with measured Au concentrations.

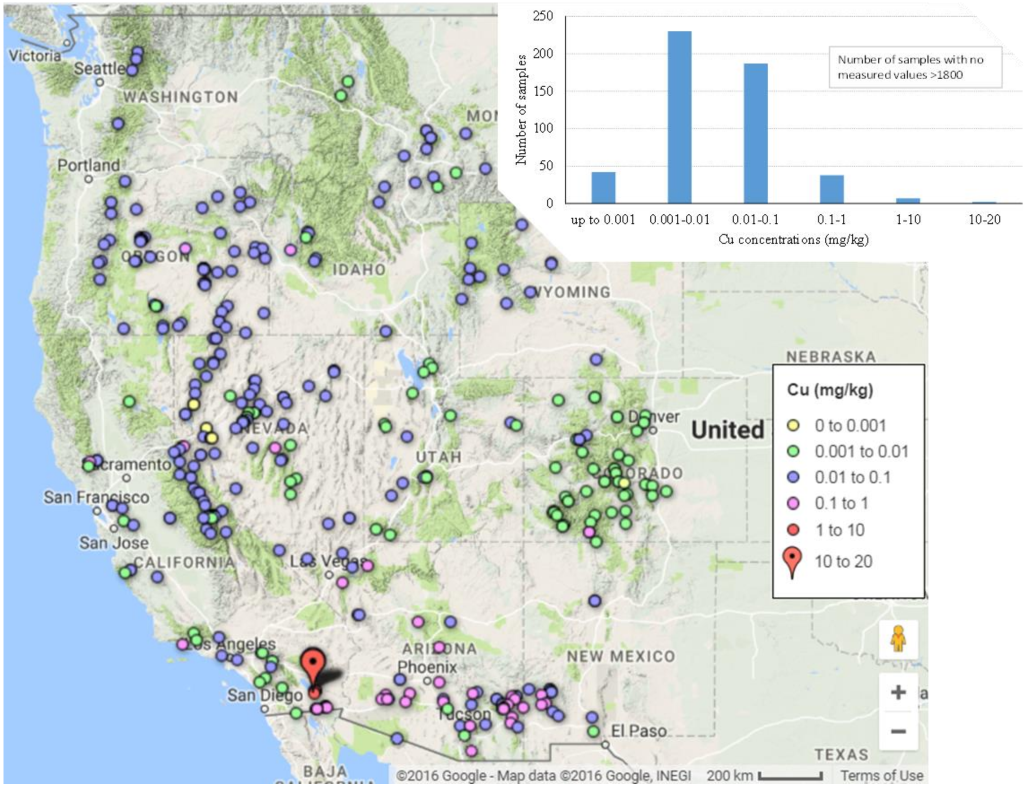

Figure 4. Distribution of geothermal brine samples with measured Cu concentrations

4.4 Manganese

Our database include about 800 (36% of the) geothermal brine samples with known Mn concentrations (Figure 6). Most of the geothermal brine samples (>700) with reported concentrations have Mn values <1 mg/kg. There are over 50 geothermal brines with Mn concentrations in the range from 1 to 10 mg/kg. Similarly, about 10 geothermal samples have Mn concentrations in the range from 10 to 50 mg/kg, and more than 15 additional samples are reported to have concentrations up to 4000 mg/kg. As with the other minerals of interest, the high Mn brine samples are confined to the Salton Sea area.

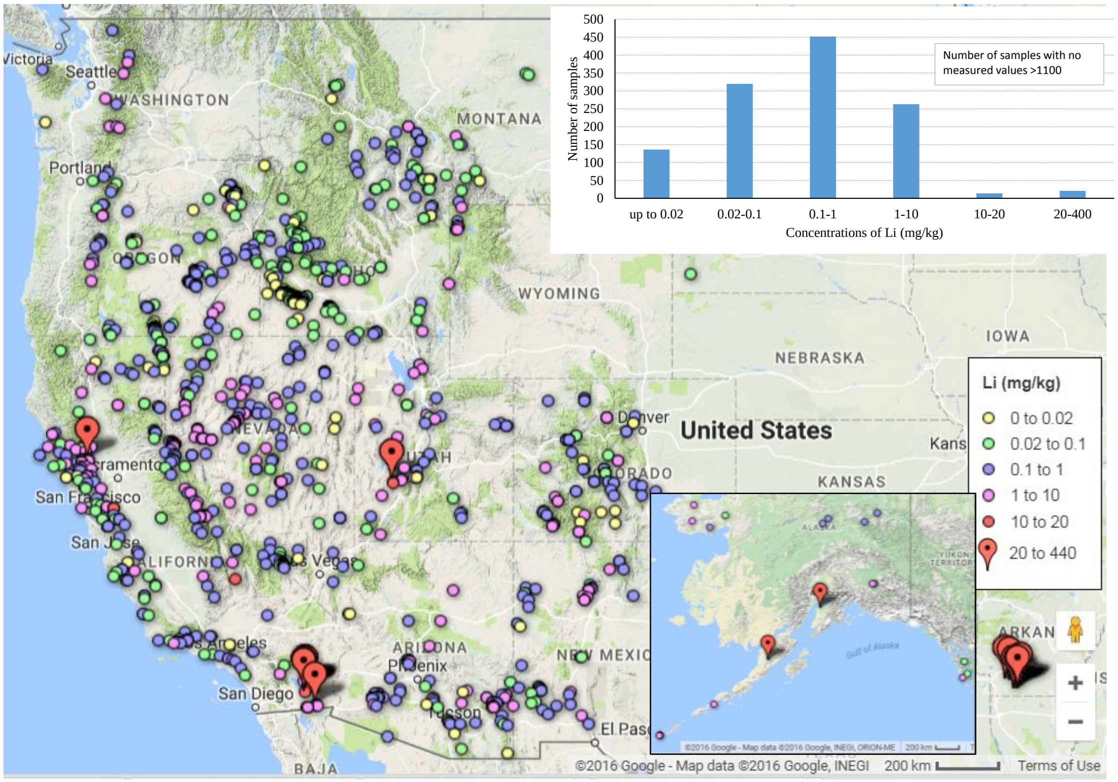

Figure 5. Distribution of geothermal brine samples with measured Li concentrations.

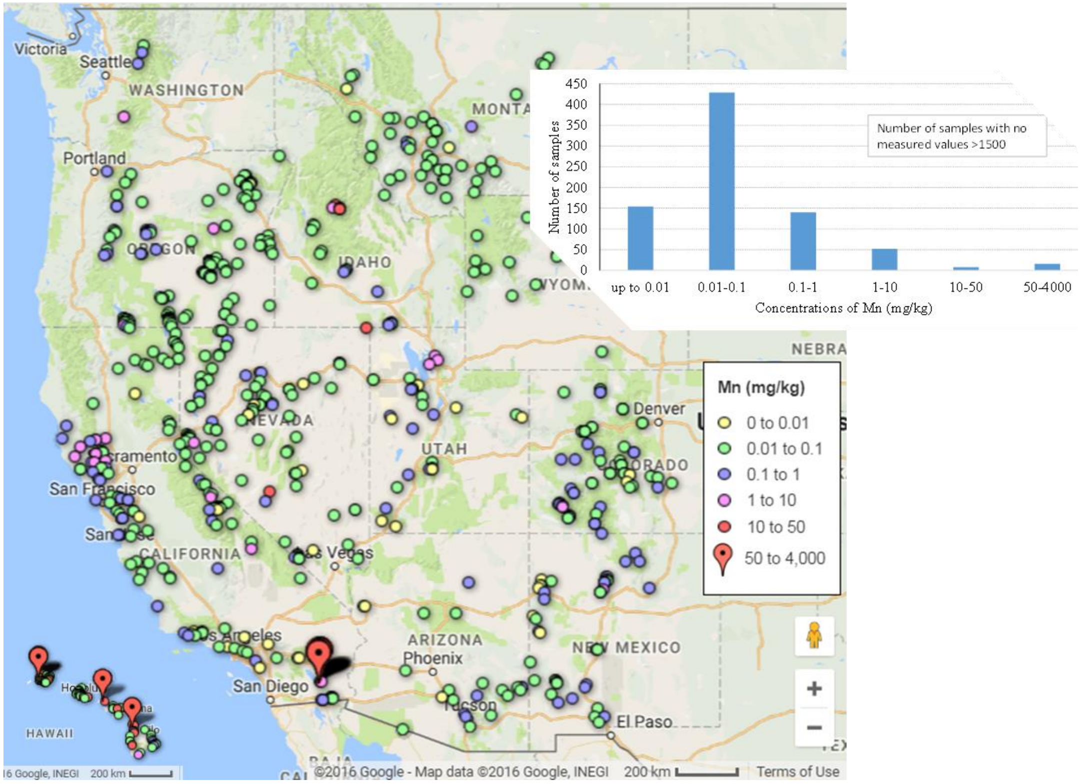

Figure 6. Distribution of geothermal brine samples with measured Mn concentrations.

4.5 REEs

Measured REEs concentrations are available (including published and unpublished data) for about 230 geothermal features and groundwater samples (Figure 7). The majority of the data represent brines collected in Oregon, Idaho, and Wyoming. A few features in California, Nevada, New Mexico, and Washington also have measured values of REEs. In general, the geothermal brines have very minute levels of REEs. With the exceptions of a few features in Yellowstone National Park in Wyoming and Valles Caldera National Preserve in New Mexico, the total REEs in filtered brine samples do not exceed 1 μg/kg (parts-per-billion, ppb). Those samples with >1 μg/kg levels of REEs are from the acidic hot springs with pH <3.5 (Figure 8). All other filtered brines with near-neutral to alkaline pH have ng/kg (parts-per-trillion, ppt) levels of REEs concentrations.

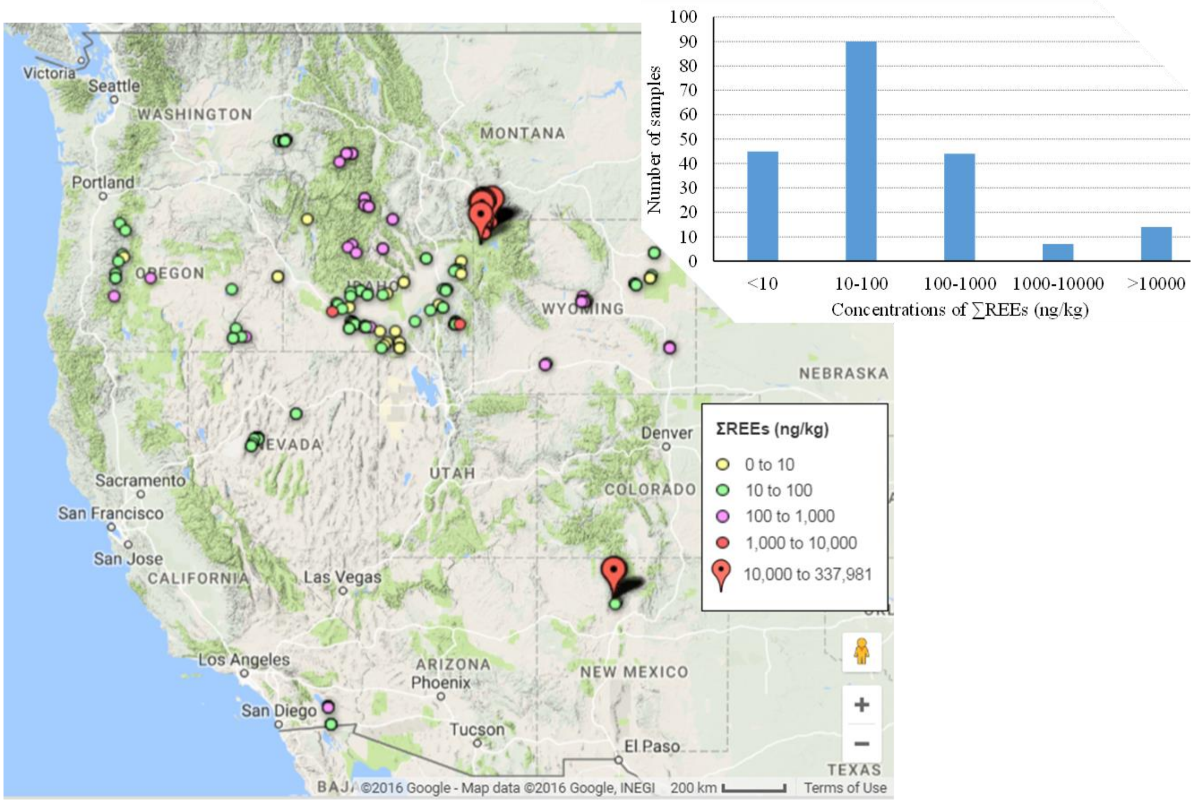

Figure 7. Distribution of geothermal brine samples with measured REEs (total REEs) concentrations.

4.6 Silica

Silica is fairly ubiquitous in geothermal brines, and its concentration is reported for most of the brines (over 2200 samples, i.e., 98% of the samples in the database have reported SiO_2 concentrations). In general, the concentration of SiO_2 increases with increasing temperature of the reservoir. Therefore, all operational geothermal power plants or the geothermal sites with potential for power production are likely to have economic level of SiO_2 in their brines. However, not all brines with very high SiO_2 concentrations are economically attractive. Harrison (2014) mentions the possibility of extracting SiO_2 and other products from hyper-saline brines, however, it could be a challenge to do so economically. In general, the brines containing relatively low total dissolved solid (TDS) and higher level of SiO_2 could produce high-value SiO_2 products with favorable economics because pre-processing of these brines to remove potential impurities can be avoided. Bourcier et al. (2006) demonstrated a SiO_2 extraction scheme with a pilot plant at the Mammoth Lake geothermal site in California. The Mammoth Lake wells produce low TDS (up to 1500 mg/L) brines containing ca. 250 mg/L of aqueous SiO_2. For direct SiO_2 extraction, this is a low level of aqueous SiO_2 and economic recovery of SiO_2 from such brines would require pre-concentration. Bourcier et al. (2006) deployed reverse osmosis to pre-concentrate aqueous SiO_2 by a factor of 2.5 to 3.5. The total TDS and SiO_2 in the pre-concentrated brine would then be present at concentrations of 5400 mg/L and 600-900 mg/L, respectively.

The TDS and SiO_2 levels in the original and pre-concentrated Mammoth Lake brines can be used to define a tentative criterion for the selection of potential SiO_2 extraction target brines (Figure 9a). The samples plotted on the lower TDS sides of T1 in Figure 9a are considered good brines for SiO_2 recovery whereas samples plotted between T1 and T2 could be useful for SiO_2 recovery. However, further geochemical analysis with specific composition will be required to assess whether the brines between T1 and T2 could produce high quality SiO_2. All samples that are plotted on the higher TDS side of T2 could potentially yield poor quality SiO_2 products without pre-removal of impurities. This selection tool indicates that there are about 164 (7% of the) geothermal brines in the database that could be used for recovery of good quality SiO_2 (Figure 9b).

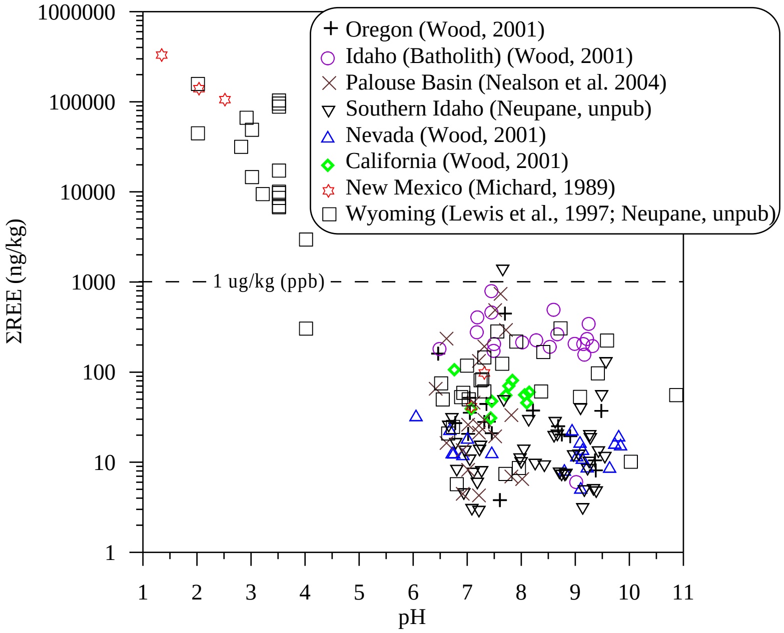

Figure 8. Brine (filtered) concentrations of total REEs plotted against pH. Only acidic brines tend to have > 1 µg/kg (ppb) levels of total REEs.

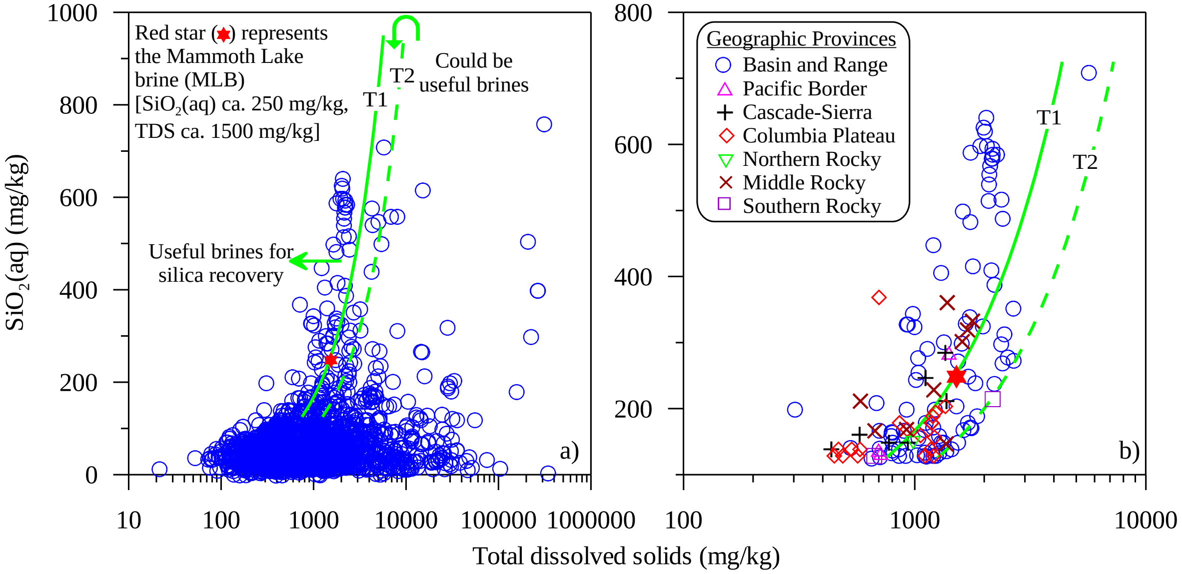

Figure 9. (a) Concentrations of aqueous SiO_2 plotted against total dissolved solids (TDS) in the US geothermal brines. The solid green line (T1) represent the reverse osmosis pre-concentration trend for the Mammoth Lake geothermal brine (MLGB) [SiO_2(aq) ca. 250 mg/kg and TDS ca. 1500 mg/kg; Bourcier et al., 2006]. The dashed green line (T2) is arbitrarily constructed to represent a trend for a brine containing the MLGB level of SiO_2(aq) and the TDS level of about (MLGB+1000) mg/kg. (b) The western US brine samples with positive attributes (TDS level on the lower side of T2 and SiO_2(aq) >125 mg/kg) are grouped according to their geographic provinces.

4.7 Potassium

Potassium is one of the major cations in the geothermal brines, and its concentration is commonly measured and reported in general water chemistry data. The majority of the samples in our database have measured concentration of K (Figure 10a). Nearly 2000 geothermal samples in the database have concentrations of K <100 mg/kg. However, there are over 150 samples that have K in excess of 100 mg/kg, and over 20 samples have K concentration >1000 mg/kg. Several hypersaline samples (mostly from the Salton Sea area) have K concentration as high as 24000 mg/kg.

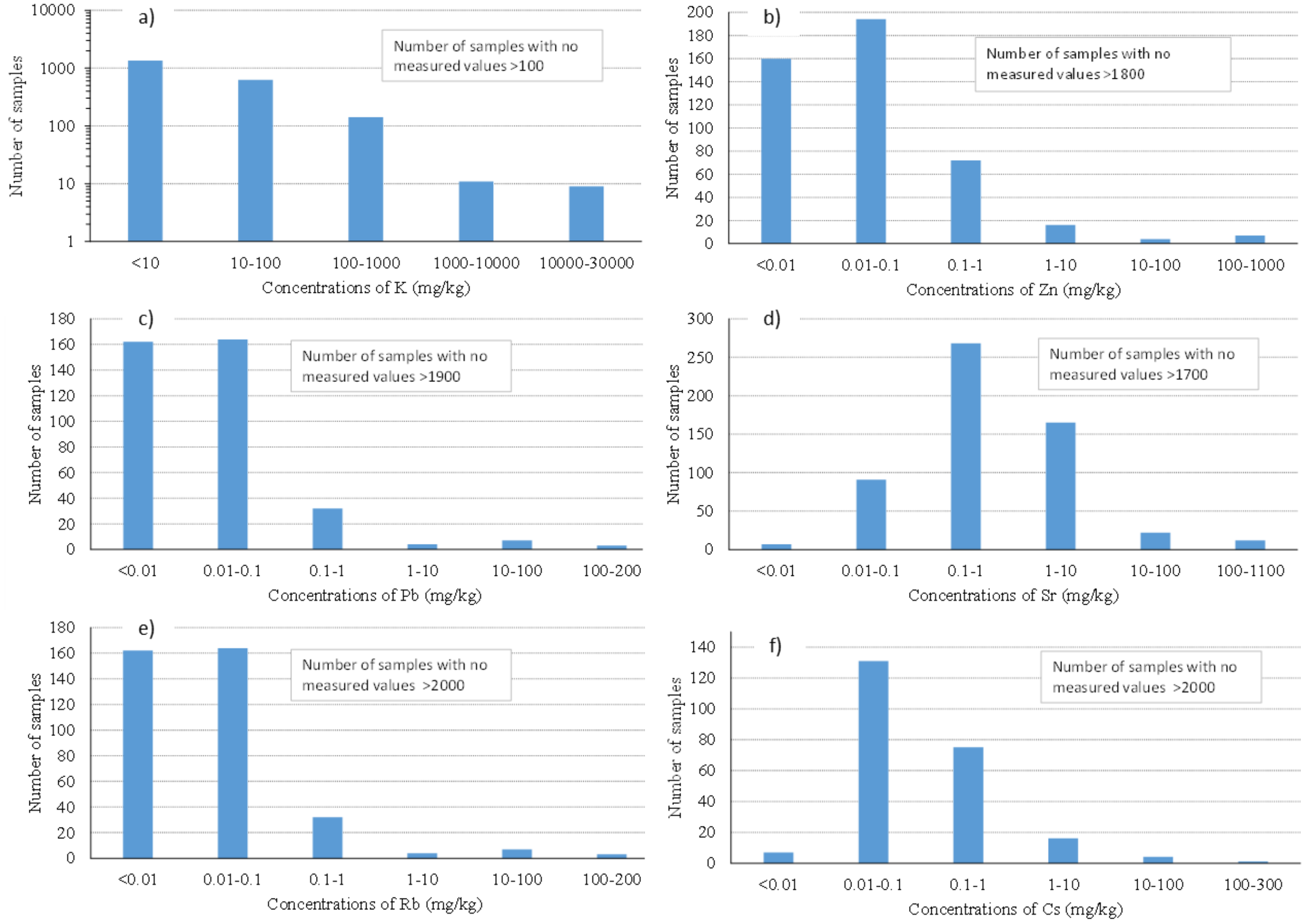

Figure 10. Number of brine samples with various concentrations of K (a), Zn (b), Pb (c), Sr (d), Rb (e), and Cs (f).

4.8 Other minerals in the US geothermal brines

In our database, over 450 (20%), 350 (16%), 550 (24%), 250 (11%), and 230 (10) samples in the database have the measured concentrations of Zn, Pb, Rb, Sr, and Cs, respectively. Figures 10b through 10f illustrate the concentration ranges of these minerals in the geothermal brines represented in the database. Most of the brines with measured concentrations have very low values of these elements. For example, only ca. 10 brines samples have the Zn and Pb concentrations >10 mg/kg. Similarly, ca. 35 samples have Sr concentrations in excess of 10 mg/kg. Only five samples have Rb and Cs concentrations >10 mg/kg. Moreover, all the samples with higher levels of these minerals are reported from the Salton Sea area geothermal fields (Salton Sea, East Mesa, Heber, etc.).

5. TARGET MINERALS IN THE US GEOTHERMAL BRINES

An effort was made to identify a list of target minerals that could have the greatest potential for recovery. For this, the brine samples were grouped according to their locations on a map of the US geographic subdivisions (Fenneman, 1917). Specifically, we focused our mineral assessments on several geographic provinces in the western US because the majority of the geothermal features (and available data) are located in this part of the country (Figure 1b). These provinces are: 1) Basin and Range, 2) Columbia Plateau, 3) Colorado Plateau, 4) Northern Rocky, 5) Middle Rocky, 6) Wyoming Bain, 7) Southern Rocky, 8) Cascade-Sierra, and 9) Pacific Border.

Table 2 presents a list of minerals with potential for recovery in each of the province in the western US (Figure 1b). The Basin and Range Province has the greatest promise for recovering various minerals. The Great Basin Section of this province offers the best sites for extraction of SiO_2. Very few sites in other provinces have suitable water chemistry for SiO_2 extraction. The geothermal features in the Salton Trough Section of the Basin and Range Province have distinct brine compositions such as having very high TDS. These high TDS brines also contain various economic minerals of interest (e.g., Li, Mn, Cs etc.) at higher concentrations. Several geothermal brines in the Columbia Plateau Province (Walla Walla, Harney, and Blue Mountains Sections) contain parts-per-billion levels of Ag and Au. Several geothermal brines likely to be good candidates for Li extraction have been identified in various provinces. With the exception of a few geothermal features characterized by acidic brines [e.g., in the Middle Rocky Province (Yellowstone National Park) and Southern Rocky Province (Valles Caldera National Preserve)], all other geothermal features produce brines with extremely low (ppt to low ppb) levels of REEs. The available data indicate that the extraction of REEs from the US geothermal brines could be economically prohibitive with the current market forces.

Table 2. List of minerals with potential of recovery from brines of various geographic provinces.

Geographic Provinces	Potential Minerals	Remarks
Basin and Range	SiO_2, Ag, B, Cs, Cu, Li, K, Mn, Pb, Rb, and Zn	SiO_2 and K can be recovered from numerous brines; Ag, Cu, Li, Mn, Pb, Zn have recovery potential from Salton Trough Section of this province; Li could be recovered from some brines in the Great Bain Section in Utah and Nevada; B, Cs, and Rb could be recovered from some brines in the Great Basin and Salton Trough Sections.
Columbia Plateau	SiO_2, Ag, Au	Some brines from Walla Walla, Harney, and Blue Mountains Sections have Ag and Au in µg/kg (ppb) levels of concentration. Several brines in this province are identified with positive attributes for SiO_2 recovery.
Northern Rocky	SiO_2	SiO_2 concentrations are relatively low (<125 mg/kg) in most of the brines. One sample is identified with SiO_2 and TDS level suitable for recovery (Figure 9b).
Middle Rocky	SiO_2, Ag, Li	The geothermal features with some recovery potential of these minerals are located in Yellowstone National Park, Wyoming.
Wyoming Basin	Ag	A small number of samples are reported to have about 50 µg/kg (ppb) silver content.
Southern Rocky	SiO_2, Li	Li could be recovered from brines around Vales Caldera National Preserve. Only two brine samples are identified with good attributes for SiO_2 recovery.
Colorado Plateau	Li, K	Li can be recovered from brines located in the Datil and Navajo Sections; K has higher recovery potential from brines in the Canyon Lands Section
Cascade-Sierra	SiO_2, B, Li	A small number of sites have SiO_2 recovery potential; a small number of geothermal waters in the Northern Cascade have B and Li concentrations up to 40 mg/kg and 10 mg/kg, respectively.
Pacific Border	SiO_2, Li,	A small number of sites have SiO_2 recovery potential; a small number of sites have Li concentrations between 10-33 mg/kg.

6. TECHNOLOGIES FOR MINERAL RECOVERY FROM BRINES

Since the 1940s, the possibility of extracting minerals from large-volume of produced geothermal fluids and creating a new revenue stream has been enticing to geothermal communities including private industries and geothermal program at DOE (Kimura, 1953; Kennedy, 1961; Werner, 1970; Blake, 1974; Maimoni, 1982; Thomas et al., 2015; Thomas et al., 2016). Early research on mineral recovery from geothermal fluids was conducted in Japan and New Zealand (e.g., Kimura, 1953; Kennedy, 1961). Since then numerous studies and works, ranging from chemical characterization of geothermal fluids (e.g., Cosner and Apps, 1978; Wood, 2001) to operation of pilot-scale onsite extraction facilities (e.g., Bourcier et al., 2009; Harrison, 2014) have been conducted over the years. Table 3 summarizes several technologies suggested for extraction of various minerals from geothermal brines.

In the US, the Salton Sea geothermal brines are known for having high concentrations of metals and other minerals. Initially, these hyper saline brines got attention because of the problems they created such as fouling (scaling) of the wells and waste disposal (Austin, 1966). Eventually, several studies were carried out aiming to extract minerals from these brines. Werner (1970) suggested a serial approach involving sorption of aminated metal complexes on activated charcoal/coke followed by leaching and sequential evaporations in multiple ponds to precipitate chloride salts of Na, K, Ca, Mg, Li, and others from the Salton Sea geothermal brines. Later researchers associated with Hazen Research, Inc. in Golden, Colorado published a series of works on Li recovery from Salton Sea brines for the US Bureau of Mines. Specifically, Berthold and Baker (1976) put forward a method for recovering Li from the brines by chemical precipitation and ion-exchange. Their extraction method involved cleaning up post-flash brines (from the Salton Sea Sinclair No. 4) for removal of SiO_2, Fe, Mn, Zn, and Pb prior to Li recovery. In their work, the “clean up” was achieved by adjusting pH to 7.5-8.0. Then the “cleaned up” brine was treated with aluminum chloride (Al:Li ratio 3) to precipitate Li aluminate complex at pH 7.5. Besides suggesting the Li recovery method, Berthold and Baker (1976) also identified two important constraints to be considered while developing mineral recovery infrastructure at power producing geothermal sites. These two constraints are: 1) the post-flash brine need to be re-injected regardless of whether or not mineral recovery is performed to sustain the reservoir for a long time, and 2) the post-flash brine should not be chemically altered to the point that it becomes unsuitable for re-injection (left over resin or other chemicals used during recovery).

Maimoni (1982) conducted an extensive study on mineral recovery from Salton Sea geothermal brines. Chemical compositions of brines and scales were found to have promising levels of concentrations for several precious and economic metals that could be extracted as value-added commodities. Maimoni (1982) notes that for a 1000 MWe geothermal power plant at Salton Sea, the potential revenue from the extraction of metals could exceed the revenue from power production. As an extraction technique, Maimoni (1982) suggested a fluidized-bed cementation reaction with metallic iron to recover precious metals, lead, and tin. The post-extraction brines could be injected back to the reservoir through injection wells.

Table 3. Technologies of mineral recovery from geothermal brines

Minerals	Technologies	Remarks	Ref.
Ag	a. Sulphidization using H_2S, NaHS, or Na_2S	Technologies tailored for Salton Sea area brines. Extraction efficiency ca. 100%.	1
	b. Metallic iron induced precipitation as sulfide from acidified post-flash brine, magnetic separator/thickener/centrifugation		2
	c. Ag recovery/deposition by passing brines through mild steel collection vessel	Extraction in the range of 0.096-0.84 mg/tonne (brine)	3
	d. Ag recovery from geothermal scales		4
Au	a. Au deposits in scale		5,6
	b. Au recovery/deposition by passing brines through mild steel collection vessel (plates)	Extraction in the range of 0.007-0.24 mg/tonne (brine)	3
	c. Biochemical leaching of geothermal sludge/scales		7
B	a. Evaporation of brines, steam heated system (extracted borax salt)	First mineral recovered (Larderello, Italy); facility was run for decades.	8,9
	b. B removal by resin	Developed environmental purposes (not intended for B recovery).	10-12
	c. B recovery by sorption on resin	Vionit AS-116 resin tested with brine containing 59-100 mg/kg B for recovery	13
	d. B removal by electrocoagulation	Developed for environmental purposes. Removal efficiency ca. 95%.	14
Ba (as $BaSO_4$)	a. Gypsum-induced precipitation of Ba-salt, non-evaporative	Achieved partial success.	15
Cs and Rb	a. Fractional precipitation	Extraction efficiency ca. 70-80%.	16
	b. Ion-exchange (e.g., sorption on zeolites)	Extraction efficiency ca. 92%.	16
	c. Solvent extraction	Extraction efficiency ca. 96-99%.	16
	d. Removal of Cs and Rb (along with K) with tetrafluroborate from desilicated and deferricated brines		17
Cu	a. Metallic iron induced precipitation as sulfide from acidified post-flash brine, magnetic separator/thickener/centrifugation		2
Li	a. Precipitation of Li as aluminate, non-evaporative	Good recovery (99%), no further refinement process suggested.	15
	b. Precipitation as Li-Al by addition of $AlCl_3$ and raising pH to 7.5 with lime slurry, precipitate dissolved in HCl and evaporated at 100ºC to obtain a mixture of chlorides	Further processing include leaching with tetrahydrofuran, evaporation, and re-dissolution in water and treatment with oxalic acid. Extraction efficiency ca. 97%.	18
	c. Li co-precipitation with aluminum hydroxide at pH 10±0.5	For Al recycling, desilicate prior to Li extraction. Extraction of ca. 50% (at 64 ºC) and 95% (at 30 ºC).	19
	d. LiCl-alumina pellets used to recover (sorb) Li, process can be repeated by unloading (water washing) and loading (reacting with brine)		20, 21
	e. Li sorption on improved sorbents from post-flash and SiO_2 removed brine	Demonstrated in a pilot plant. Extraction efficiency ca. 95%.	22
	f. Li sorption on Li-Mn or Li-Fe-Mn oxides (spinel)	Extraction efficiency ca. 20 to 96%.	23-26
	g. Electrodialysis of desilicated brine (13 ppm Li)	Experimentally verified, pilot-test ready. Extraction efficiency ca. 87%.	27
	h. Evaporation and extraction of LiCl along with others		28
K (as K_2O)	a. Evaporation and extraction of KCl along with others	Extraction efficiency ca. 80%	28, 29
	b. Cation exchange uptake of K by zeolites	Targeted for 50% recovery, process cost found to be unfavorable.	30
Mn	a. Lime-induced selective precipitation of Mn-oxides	Desilication advantageous, mixed precipitates (Fe, Pb, Zn oxides) create difficulty in separation.	17
	b. Precipitation from post-flash and desilicated brine		22
	c. Precipitation as hydroxides at pH about 8-9	95% extraction, could be economic and competitive with the other commercial operations.	30
Pb	a. Lime-induced selective precipitation of Pb-oxides		15
	b Sulphidization using H_2S, NaHS, or Na_2S	Targeted for 100% extraction.	1
	c. Metallic iron induced precipitation as sulfide from acidified post-flash brine, magnetic separator/thickener/centrifugation		2

	d. Precipitation by treating pH-stabilized (with lime) brine with H_2S	Extraction efficiency ca. 99%.	31
Pt	a. Recovery of Pt by contacting geothermal brine with carbon	Technology refers to Salton Sea brines	32
SiO_2 (col.)	a. SiO_2 pre-concentrated to 1250 ppm (by reverse osmosis) and aged to grow SiO_2 colloids and filtered	Demonstrated with a 20 gpm pilot plant at the Mammoth Lake site.	33
	b. Precipitation of SiO_2 as calcium silicates by lime treatment		34-36
Sn	a. Metallic iron induced precipitation as sulfide from acidified post-flash brine, magnetic separator/thickner/centrifugation		2
Sr	a. Evaporative extraction		15
Zn	a. Lime-induced selective precipitation Zn-oxides	Used aqueous ammonia and ammonium chloride solutions to separate Zn. Extraction efficiency ca. 50%.	15
	b Sulphidization using H_2S, NaHS, or Na_2S	H_2S at about 1 atm led to precipitate 50% of Zn. With Na_2S treatment, 85% Zn recovered, precipitates contain 31% ZnS, 5% PbS, 14% MnS, and 41% SiO_2.	1
	c. Zn precipitation from post-Ag, Cu, Pb, Sn, and Fe (added) recovery brines.		2, 15
	d. Precipitation from post-flash, desilicated brine		22
	e. Precipitation as hydroxides at pH about 8-9	95% extraction, could be economic and competitive with the other commercial operations.	30
	f. Precipitation by treating pH-stabilized (with lime) brine with H_2S	Extraction efficiency ca. 99%.	31
REEs	a. Pre-concentration of REEs on the specialized resin and recovery by acid elution		37- 39
	b. Capturing REEs in geothermal fluids by highly-selective engineered microbes		38-40
	c. Recovery of REEs from brines using functionalized magnetic-core nanoparticles	Extraction efficiency up to ca. 95%.	38, 39, 41
	d. Sequestration of REEs from geothermal brines on proprietary media		38, 39, 42
	e. Recovery of REEs from geothermal waters with advanced sorbet structures		38, 39, 43
	f. Magnetic segregation of REEs from hydrothermal products		44
Ref.: 1. Farley et al. (1980); 2. Maimoni (1982); 3. Brown and Roberts (1988); 4. Gallup (1992); 5. Brown (1986); 6. Gallup (1998); 7. Premuzic et al. (1997); 8. Allegrini et al., (1992); 9. Hodgson (2013); 10. Recepoglu and Beker (1991); 11. Badruk et al. 1999; 12. Yan et al. (2008); 13. Gilau and Stanasel (2010); 14. Yilmaz et al. (2008); 15. Christopher et al. (1975); 16. Zhang et al (2014); 17. Harrison et al. (2014); 18. Shultze and Bauer (1984); 19. Rothbaum and Middendorf (1986); 20. Bauman and Burba (1997); 21. Bauman and Burba (2001); 22. Harrison (2011); 23. Iwanaga et al. (2007); 24. Park et al. (2012); 25. Matsushita et al. (2013); 26. Chitrakar et al. (2014); 27. Mroczek et al. (2015a); 28. Mercado et al. (1979); 29. Mercado and Hurtado (1992); 30. Harrison, 2014; 31.Shultze and Bauer (1985); 32. Gallup and Ririe (1994); 33. Bourcier et al. (2009); 34. Rothbaum and Anderton (1976); 35. Shannon et al. (1982); 36. Kato et al. (2003); 37. Noack et al (2015); 38. Thomas et al. (2015); 39. Thomas et al. (2016); 40. Ajo-Franklin (2015); 41. McGrail (2015); 42. Stull (2015); 43. Addleman (2015); 44. O'Brien (2013).			

Gallup et al. (1992 and 1995) described an electrochemical method to recover Ag and other precious metals from the Salton Sea geothermal brines. Their method involves passing the pH adjusted (to 5) brine through a conduit packed with metal higher in the electromotive series than Ag to precipitate Ag and other precious metals. The suggested packed material is Zn-galvanized steel chicken wire mesh which facilitates precipitation of iron silicate and heavy metal scales. The mesh also acts as a filter where the suspended particles are trapped. The precipitate is then dissolved with acid that leaves precious metal residue. The post-extraction water, which has much less dissolved/suspended load, would extend (x3) the useful life of injection wells. A US patent was granted for this technology. However, no production plant is built employing this technology.

A few years ago, Simbol Materials Inc. operated a pilot-scale Li extraction plant at the Salton Sea (Harrison, 2014). The extraction technology used in the pilot-plant likely involved the co-precipitation of Li with aluminate complex as described in a series of US patents by company employees (e.g., Bauman et al. 1996; 2001; Harrison et al., 2014). Although it was claimed that the pilot-plant successfully extracted the battery-grade Li, a plan to build a full-fledged extraction facility was suddenly stopped because of lack of investors (Roth, 2015). Recently, it has been reported that a new company (Alger Alternative Energy, LLC.) has acquired Simbol's assets at the Salton Sea site, and is trying to attract new investors to build a full-fledged Li extraction plant (Roth, 2016). However, it is too early to see how this new effort pans out in enticing new investors for this endeavor.

Bourcier et al. (2009) reported a pilot-scale SiO_2 extraction demonstration facility at the Mammoth Lakes geothermal power plant in California. For this technology demonstration pilot plant, about 20 gpm post-production brines (at 50-80 ºC) was routed to the recovery system, which consisted of a two-step process: 1) reverse osmosis, and 2) ultrafiltration. Reverse osmosis concentrated SiO_2 (initial concentration of 250 ppm) to 1250 ppm without SiO_2 fouling, the concentrate was aged to grow SiO_2 colloids and then passed through a cross-flow ultra-filter to extract the SiO_2 colloids. This pilot-scale work demonstrated that the extraction of colloidal SiO_2 with specifications comparable to known commercial colloidal SiO_2 products is possible from geothermal brines.

Currently, DOE is funding several projects to develop technology to extract REEs, Li, and Mn from geothermal brines (Thomas et al., 2015 and 2016). In the case of REEs, it is not yet fully understood whether there exist economic levels of concentrations of these elements in geothermal brines. Available data (Figure 8) show very low levels of REEs in geothermal brines. An ongoing research project led by the University of Wyoming (e.g., Nye et al., 2017) is measuring REEs in produced waters from oil and gas wells.

Besides the ongoing and previous mineral recovery work in the US, there have been several mineral extraction studies performed in other countries. Particularly, researchers in New Zealand and Japan have conducted several mineral recovery studies and developed extraction technologies (e.g., Kimura, 1953; Kennedy, 1961; Mroczek et al., 2015b). For example, researchers worked on developing technologies such as co-precipitation of Li-aluminate complex (Rothbaum and Middendorf, 1986) as well as adsorbing Li on manganese oxide and resins (Park et al., 2012). Similarly, some other technologies (e.g., electrochemical, evaporation, etc.) were also included for Li extraction in some studies conducted in New Zealand (e.g., Kennedy, 1961). In Mexico, Mercado et al. (1979) came up with a recommendation for recovering K and Li minerals from Cerro Prieto geothermal brines. They suggested that by recovering salt by evaporating geothermal brines in disposal ponds, the Cerro Prieto geothermal plant could have solved two problems: 1) disposal of a large volume of brine, and 2) developing a domestic source of K and Li for Mexico. However, evaporating a large volume of brines could jeopardize the longevity of a geothermal reservoir by depriving the water to inject back into the formations. Furthermore, the creation of massive evaporating ponds could also be environmentally problematic.

There has also been research performed for extracting B, Mn, Rb, and Cs from geothermal brines (Table 3). These technologies range from absorption of target metals on metal oxides, clays, and resins to electrochemical extractions. Several of these technologies are reported to be effective in test cases; however, further tests mimicking natural scenarios (such as natural brines and T) need to be completed before deploying them for mineral recovery.

7. ECONOMIC VALUES OF MINERALS IN BRINES OF SOME GEOTHERMAL PLANTS

For some operational geothermal plants in the US, we assembled both the chemistry and total mass flow rates of brines produced for power generation to assess the revenue that could potentially be generated from the recovery of various minerals. Table 4 includes brines mass flow rates, concentrations, recoverable masses, and market values of Ag, Au, Cu, Li, and Mn. Several assumptions were made to generate the recoverable masses and market values of these minerals. The most important assumptions are that the concentrations of minerals in the brine will not change significantly over time, all of production volume will be available for extraction of minerals, plant outages will be limited (operating 90% of the time), the extraction technology operates at a certain efficiency (80% extraction from brines), there will be minimum market pricing volatility for the minerals of interest, and so on. Similarly, no specific capital and operating costs for any of the potential extraction plants are considered. Data included in Table 4 show that geothermal brines produced in southern California areas have the highest levels of recoverable masses of Ag, Au, Cu, Li, and Mn. Specifically, geothermal plants in the Salton Sea area produce brines rich in these minerals. As with the previous estimates (e.g., Maimoni, 1982), our general estimates show that the Salton Sea area brines could generate substantial revenue from recovery of minerals. However, all past attempts to recover Li and Mn from these brines has been limited to pilot-scale activities, and fully commercial mineral recovery plants have yet to be realized.

8. CAPITAL COSTS, OPERATING COSTS, AND MARKET VALUES OF RECOVERED MINERALS

Information related to the costs for deployment of mineral extraction technologies is scarce in the literature. Only a few studies with pilot-scale demonstration facilities (e.g., Bourcier et al., 2009) provide some detailed economics for the deployment of mineral recovery technologies. Simbol's economic analysis for Li and Mn recovery was not accessible to us. Some recent reports (e.g., Stull, 2016; Addleman et al., 2016; Ventura et al., 2016) submitted to DOE by various research groups working on developing new mineral extraction technologies include some preliminary economic analysis. Here we first summarize the results presented by Bourcier et al. (2009) as a guide for the potential upfront costs related to a SiO_2 extraction facility. Bourcier et al. (2009) did their cost calculations for a facility that would involve both a reverse osmosis process for increasing the brine SiO_2 concentrations and a SiO_2 seeding process for actual SiO_2 extraction. One of the tools they used for estimating the capital and operating costs is used for estimating costs for water treatment facilities (WTCOST, Moch, 2005). With this tool, they reported a total capital costs of about 25 million dollars and a total operating cost of about 16 million dollars for the SiO_2 extraction plant at a geothermal site producing a brine volumes of 18 million gallon-per-day. Bourcier et al. (2009) noted that the calculations they presented have several assumptions and uncertainties, and the cost associated with staffing was considered one of the major uncertainties. Overall, Bourcier et al. (2009) show positive economic impacts to the geothermal operator from SiO_2 recovery. Their analysis indicated that SiO_2 extraction could offset the cost of geothermal power by more than \$0.01 kWh and extraction of other metals could generate about \$0.005 kWh per metal.

Table 4. Concentrations, recoverable mass, and market values of some minerals in brines of some US geothermal plants

Geothermal Plants	Brine x 1000 (kg/day)[1]	Concentrations (mg/kg)				
		Ag	Au	Cu	Li	Mn
Beowawe	22,960	0.02		0.01-0.1	2.1-2.6	0.014-0.1
Desert Peak-1	10,230				1.4-5.6	
Dixie	52,610		0.002	0.002-0.016	0.38-2.65	0.003-0.02
Salton Sea	273,130	0.5-1.4	0.1	0.8-12	90-440	448-1560
Brady	43,190				0.19-3.3	0.5-0.5
East Mesa	190,640	0.01-0.06	.01-0.08	0.03-0.89	0.8-40	0.02-0.95
Heber	133,760	0.04		0.2-0.8	2.8-6.6	0.9-1.9
Soda Lake	23,150			0.01	0.05-1.7	0.02-0.07
Desert Peak-2	860				1.4-5.6	
Steamboat Com.	20,830			0.01	6.4-10	0.02
Stillwater	28,030				1.5-2.1	
Casa Diablo	65,660	0.002-0.04	0.1	0.004-0.07	0.3-4	0.002-0.24
Wabuska	14,150	0.00001	0.00005	0.00062-0.01	0.26-0.53	0.02
Raft River	34,400		0.000082	0.08	1.2-3	0.06-0.08
Tuscarora	31,300				0.6-0.7	
San Emidio	23,130	0.00001	0.00008	0.00084-0.01	2.2-2.5	0.13-0.15
Neal[2]	51,060	0.02	0.1	0.02-0.02	0.3	0.06
Roosevelt	24,490	0.09		0.03	16-27	0.15
Recoverable masses of some minerals [in troy ounce (31.1 g) per year for Ag and Au, and in metric ton per year for Cu, Li and Mn][3]						
Beowawe		3880		0.06-0.6	13-16	0.08-1
Desert Peak-1					4-15	
Dixie			890	0.028-0.22	5-37	0.04-0.3
Salton Sea		1,154,000-3,231,000	230,800	57-860	6,460-31,580	32,000-112,000
Brady					2-37	6
East Mesa		16,100-96,600	16,100-128,900	1.5-45	41-2000	1-48
Heber		45,200		7-18	98-230	32-67
Soda Lake				0.06	0-10	0.12-0.43
Desert Peak-2					0-1	
Steamboat Com.				0.5	350-550	1.1
Stillwater					11-15	
Casa Diablo		1,110-2,2200	55,500	0.07-1.2	5-69	0.3-4.1
Wabuska		1	6	0.002-0.037	1-2	0.1
Raft River			24	0.723	11-27	0.5-0.7
Tuscarora					5-6	
San Emidio		2	16	0.005-0.06	13-15	0.8-0.9
Neal		8630	43,100	0.27	4-4	0.8
Roosevelt		18,630		0.19	100-170	1
Market values of some recoverable minerals (in $/year @market prices given in Table 1)						
Beowawe		78,000		430-4,280	445,000-551,000	1-6
Desert Peak-1					132,000-529,000	
Dixie			1,187,000	200-1,600	185,000-1,287,000	0.4-3
Salton Sea		23,262,000-65,133,000	308,079,000	408,000-6,115,000	226,908,000-1,109,000,000	322,000-1,122,000
Brady					75,800-1,316,000	60
East Mesa		325,000-1,948,000	21,504,000-172,029,000	10,700-317,000	1,443,000-70,391,000	10-500
Heber		911,000		50,000-125,000	3,457,000-8,149,000	320-700
Soda Lake				430	10,700-363,000	1-4
Desert Peak-2					11,100-45,000	
Steamboat Com.				3,900	12,305,000-19,227,000	11
Stillwater					388,000-543,000	
Casa Diablo		22,400-447,000	74,061,000	490-8,600	182,000-2,424,000	0.3-41
Wabuska		20	8,000	16-260	33,000-69,000	1
Raft River			32,000	5,100	381,000-953,000	5-7
Tuscarora					173,000-202,000	
San Emidio		40	20,900	36-430	470,000-534,000	8-9
Neal		174,000	57,596,790	1,900	141,000	8
Roosevelt		375,000		1,400	3,618,000-5,992,000	10

[1] Brine masses [tentatively (without considering TDS effect) converted from volumes to mass] are obtained from Clark et al. (2011) and other open source documents.

[2] Concentrations are reported for the Neal Hot Spring (Mariner et al., 1974). Available production wells' water chemistry data do not include concentrations for these elements.

[3] Recovery mass calculated assuming 80% efficiency of recovery method(s) and 90% operation time

Ventura et al. (2016) presented a preliminary process cost assessment for the recovery of Li and production of Li_2CO_3 from geothermal brines. Their general estimates for a Li plant capable of processing 6000 gallons of brine per minute (containing 400 mg/kg of Li) would have total capital and annual (running for 300 days/year) operating costs of about $20.5 million and $11.1 million, respectively. With a production rate of 49 kg/min of Li_2CO_3 and a very conservative market price ($2000/ton; USGS market price in Table 1 is $6,600/metric ton), Ventura et al. (2016) conclude that the Li extraction plant would generate a revenue over $40 million per year. Stull (2016) also provides a preliminary cost estimate for recovering REEs from geothermal brines. His study showed the total cost of recovering REEs could be about $89.90/kg whereas the current market price for a blended REEs was reported to be $15.90/kg. Stull (2016) concludes that without the improvement in market economics, the extraction of REEs from geothermal brines could be economically prohibitive. Addleman et al. (2016) also provide a similarly unfavorable conclusion for the recovery of REEs from geothermal brines. However, they show very optimistic economics for the recovery of precious and base metals. Their preliminary techno-economic analysis estimates a total capital cost of about $43.8 million and an annual operating costs of about $17.2 million for a mineral extraction plant with a processing capacity of 6000 gallons of brine per minute (having “average” mineral contents) generating a gross revenue of about $27.4 million and a net revenue of about $10.2 million with a rate of 23% return on investment (ROI).

9. BARRIERS AND CHALLENGES IN MINERAL RECOVERY

Review of available literature indicates that the geothermal community has long ago identified that recovery of minerals could be a new and net positive stream of revenue. Some previous studies, for example, Maimoni (1982), suggested that the Salton Sea geothermal site could generate more revenue from minerals recovered from the brines than from electricity. Such optimism led industry as well as the US DOE to fund numerous research projects aiming to develop and field test recovery technologies. Outcomes from previous efforts indicate that mineral extraction from the geothermal brines is possible. Specifically, technologies for the extraction of commercial grade SiO_2 and Li have been successfully demonstrated in pilot-scale plants in the US. Nevertheless, the deployment of these extraction technologies at a large scale at any geothermal site has not yet been realized. Therefore, it is equally important to recognize the outstanding issues that may have hindered the construction and operation of extraction facilities alongside geothermal power production.

Major barriers for the large-scale mineral extraction from geothermal brines can range from the lack of deployable technologies to the presence of very low mineral contents in brines. As noted earlier by Berthold and Baker (1976), the extraction process should keep the post-mining brines chemically acceptable for reinjection back into the formations for a sustainable operation of power plants. The industrial scale mineral recovery technologies need to be successfully verified for the target brines with onsite pilot plants. Aside from Li and SiO_2 extraction technologies, the other extraction technologies have not been tested in pilot-scale plants in the US. Several mineral recovery technologies presented in Table 3 seem very promising (showing high recovery efficiency); however, most of the performance results were based on laboratory bench-scale experiments that used simple brines with far less chemical complexity than real brines. Even for the field-tested technologies, full-fledged recovery plant have not yet materialized. Specifically, the early optimism generated by Simbol’s plan for Li extraction from the Salton Sea geothermal brines decreased over time due to a lack of investors to build an extraction plant (Roth, 2015). The general hesitancy of investors to invest in such plants could have stemmed from the fear that the expected economic benefits may soon vanish because of market forces such as competition from traditional miners/producers. Roth (2016) noted that the Simbol’s plan was likely failed to entice new investors because the currently dominant Li mining companies might have discouraged them for investing in a new approach of Li recovery from geothermal brine. Therefore, it is likely that the risk-averse geothermal power operators and hesitant investors will remain one of the greatest challenges for future industrial scale brine mining from geothermal brines.

Other issues such as the presence of low mineral content in the brine could be prohibitive for extraction. For example, the concentrations of REEs in near-neutral to alkaline geothermal brines tend to be very low, and economical extraction of these elements may not be possible. Both Stull (2016) and Addleman et al. (2016) show that the recovery of REEs from geothermal brines is not economic with current market prices.

10. CONCLUSIONS

In this study, we assembled over 2250 compositions of geothermal brines representing numerous hot springs and thermal wells in the US and assessed them for their contents of economic minerals. The mineral loadings in geothermal brines vary, ranging from extremely low levels for some minerals to high levels for others. In general, our resource assessment shows that numerous geothermal brines in the US contain concentrations for some minerals that could, if successfully recovered, potentially provide a new value-adding revenue streams to the geothermal industry.

Brine contents of precious metals (Ag and Au) stand out in their potential for positive economic impact to the geothermal operators in the Salton Sea geothermal areas. Furthermore, the Salton Sea geothermal brines also contain economic levels of Li, Mn, and K among others. Some brine samples from the Columbia Plateau Province (Walla Walla, Harney, and Blue Mountains Sections) also contain parts-per-billion levels of Ag and Au. The Middle Rocky Province and Wyoming Basin Province are other areas with geothermal brines having detectable levels of Ag.

Most of the geographic provinces in the western US have geothermal brines with positive attributes for SiO_2 recovery. Particularly, several geothermal systems in the Basin and Range Province produce brines suitable for SiO_2 recovery.

Recovery of Li could be done from brines from the Basin and Range (besides the brines of the Salton Trough Section), Middle Rocky, Southern Rocky, Colorado Plateau, Cascade-Sierra, and Pacific Boarder Provinces. Similarly, the recovery of K could be done from geothermal brines in the Basin and Range and Colorado Plateau Provinces.

The concentrations of REEs in (filtered) geothermal brines are very low. Available REEs data for the US geothermal brines with potential for high volume production do not appear promising for economic recovery of these elements.

Despite extraction technologies having been verified for economic recovery of some minerals (e.g., Li, and SiO_2) the commercial extraction of minerals have yet to be started in the US. Even though the Salton Sea geothermal brines show very profitable mineral recovery scenarios, the latest effort to recover industrial scale Li from these brines by Simbol Materials Inc. did not come to fruition. For other minerals, the recovery technologies are limited to laboratory bench-scale experiments/performance tests. For these low technical readiness level (TRL) technologies, it is important to perform pilot-scale testing prior to commercial-scale deployment. For sustainable recovery, the extraction technology needs to be designed for the mineral types, contents, overall chemistry of the target brines, and likely future market conditions for the mineral commodities.

ACKNOWLEDGEMENTS

This work was supported by funding by the Assistant Secretary for Energy Efficiency and Renewable Energy, Geothermal Technologies Office of the U.S. Department of Energy under the U.S. Department of Energy Contract Nos. DE-AC07-05ID14517 with Idaho National Laboratory.

REFERENCES

Addleman, R.S., 2015. Recovery of rare earths, precious metals and other critical materials from geothermal waters with advanced sorbent structures. Geothermal Technologies Office 2015 Peer Review, US Department of Energy, Energy Efficiency & Renewable Energy, May 11-14, 2015.

Addleman, R.S., Chouyyok, W., Palo, D., Dunn, B.M., Brann, M., Billingsley, G., Johnson, and Nell, K.M., 2016. Evaluation of advanced sorbent structures for recovery of rare earth, precious metals, and other critical materials from geothermal waters-preliminary results. Technical Report, Pacific Northwest National Laboratory, Richland, WA 99352, p. 31.

Ajo-Franklin, C.M., 2015. Engineering thermophilic microorganisms to selectively extract strategic minerals. Geothermal Technologies Office 2015 Peer Review, US Department of Energy, Energy Efficiency & Renewable Energy, May 11-14, 2015.

Allegrini, G., Luccioli, F., & Trivella, A., 1992. Industrial uses of geothermal fluids at Larderello. Geothermics, 21(5), 623-630.

Austin, C.F., 1966. Undersea geothermal deposits – their selection and potential use. US Naval Ordance Test Station, China Lake, California, p. 75.

Badruk, M., Kabay, N., Demircioglu, M., Mordogan, H., and Ipekoglu, U., 1999. Removal of boron from wastewater of geothermal power plant by selective ion-exchange resins. I. Batch sorption–elution studies. Separation Science and Technology, 34, 2553-2569.

Bauman, W.C. and Burba, J.L., 1997. Recovery of lithium values from brines. US Patent No. 5,599,516.

Bauman, W.C. and Burba, J.L., 2001. Composition for the recovery of lithium values from brine and process of making/using said composition. US Patent No. 6,280,693 B1.

Berthold C.E. and Baker, D.H., 1976. Lithium recovery from geothermal fluids. In: Lithium Resources and requirements by the year 2000, Editor Vine, J.D. Geological Survey Professional Paper 1005, USGS, Washington, 61-66.

Blake, R.L., 1974. Extracting minerals from geothermal brines: a literature study. US Bureau of Mines, Information circular 8638, p. 25.

Bourcier, W., Bruton, C., Roberts, S., Viani, B., Scott, S., Martin, S., 2009. Pilot-scale geothermal silica recovery at Mammoth Lakes. Public interest Energy Research (PIER) Program Final Project Report, Lawrence Livermore national Laboratory, p. 94.

Brown, K. L., 1986. Gold deposition from geothermal discharges in New Zealand. Economic Geology, 81, 979-983.

Brown, K. L., & Roberts, P. J. C., 1988. Extraction of gold and silver from geothermal fluid. In Proceedings 10th New Zealand Geothermal Workshop, 161-163.

Chitrakar, R., Makita, Y., Ooi, K., and Sonoda, A., 2014. Synthesis of iron-doped manganese oxides with an ion-sieve property: lithium adsorption from Bolivian brine. Industrial & Engineering Chemistry Research, 53(9), 3682-3688.

Christopher, D. H. and Stewart, M., 1975. The recovery and separation of mineral values from geothermal brines. Hazen Research, Inc., for the US Bureau of Mines, OFR 81-75.

Christopher, D. H., Stewart, M., and Rice, J., 1975. The recovery and separation of mineral values from geothermal brines. Research report, 1974--1975 (No. PB-245686). Hazen Research, Inc., Golden, Colo. (USA).

Cosner, S.R. and Apps, J.A., 1978. A compilation of data on fluids from geothermal resources in the United States. Earth Sciences Division, Lawrence Berkeley Laboratory, University of California, Berkeley, California 94720, 116 p.

Dickson, J.S., 2015. Rare earth elements: Global market overview. In: Simandl, G.J. and Neetz, M., (Eds.), Symposium on Strategic and Critical Materials Proceedings, November 13-14, 2015, Victoria, British Columbia. British Columbia Ministry of Energy and Mines, British Columbia Geological Survey Paper 2015-3, pp. 5-11.

Farley, E.P., Watson, E.L., MacDonald, D.D., Bartlett, R.W., and Krishnan, G.N., 1980. Recovery of heavy metals from high salinity geothermal brine. SRI International, open file report, U.S. Bureau of Mines, Reno, Nevada.

Fenneman, N.M., 1917, Physiographic subdivision of the United States. Proceedings of the National Academy of Sciences, 3, 17-22.

Gallup, D.L., Featherstone, L., Reverente, J.P., Messer, P.H., 1992. Recovery of metals from aqueous media. US Patent No. 5082492.

Gallup, D.L., Featherstone, L., Reverente, J.P., Messer, P.H., 1995. Line mine: A process for mitigating injection well damage at the Salton Sea, California (USA) geothermal field. Proceedings World Geothermal Congress.

Gallup, D.L. and Ririe, G.T., 1994. Platinum recovery. US Patent Number 5,290,339.

Gallup, D. L., 1998. Geochemistry of geothermal fluids and well scales, and potential for mineral recovery. Ore Geology Reviews, 12(4), 225-236.

Gilău, L. and Stănăşel, O., 2010. Experimental study of boron recovery from geothermal water on ion exchange. Proceedings World Geothermal Congress 2010, Bali, Indonesia, 25-29 April 2010.

Harrison, S., 2011. Technologies for extracting valuable metals and compounds from geothermal fluids. Geothermal Technologies Program 2011 Peer Review, US Department of Energy, Energy Efficiency & Renewable Energy, June 9, 2011.

Harrison, S., 2014. Technologies for extracting valuable metals and compounds from geothermal fluids. California Energy Commission, Publication Number: CEC-500-2015-023.

Harrison, S., Sharma, C.K., Bhakta, R., and Lan, P.Y., 2014. Methods for Removing Potassium, Rubidium, and Cesium, Selectively or in Combination, From Brines and Resulting Compositions Thereof. US Patent No. 14/188,293.

Hodgson, S.F., 2013. Larderello to Las Vegas: 1818, 1944, 2013. GRC Bulletin, September/October 2013, 26-31.

Humphries, M., 2013 Rare earth elements: the global supply chain. Congressional Research Service, 7-5700, R41347, p. 31.

Iwanaga, T., Watanabe, E., Mroczek, E. and Graham, D., 2007. Lithium extraction from geothermal brines using an adsorption method after removal is silica using electrocoagulation. Proceedings of the New Zealand Geothermal Workshop 29.

Kato, K., Ueda, A., Mogi, K., Nakazawa, H., and Shimizu, K., 2003. Silica recovery from Sumikawa and Ohnuma geothermal brines (Japan) by addition of CaO and cationic precipitants in a newly developed seed circulation device. Geothermics, 32, 239-273.

Kennedy, A.M., 1961. The recovery of lithium and other minerals from geothermal water at Wairakei. Proceedings of the United Nations Conference on New Sources of Energy: Solar Energy, Wind Power and Geothermal Energy, Rome, G/56, 502-511.

Kimura, K., 1953. On the utilization of hot springs in Japan. Proceeding of the Seventh Pacific Science Congress, New Zealand 1949, 2, p. 500.

Maimoni, A., 1982. Minerals recovery from Salton Sea geothermal brines: a literature review and proposed cementation process. Geothermics, 11, 239-258.

Matsushita, T., Yonezu, K., Inoue, Y., Watanabe, K., Yokoyama, T., 2013. Adsorption characteristics of lithium adsorbent aimed at recovery of lithium from geothermal fluid. Proceedings of 35th New Zealand Geothermal Workshop, 2013.

McGrail, P.B., 2015. Magnetic partitioning nanofluid for rare earth extraction from geothermal fluids. Geothermal Technologies Office 2015 Peer Review, US Department of Energy, Energy Efficiency & Renewable Energy, May 11-14, 2015.

Mercado, S., Lopez, J.A., and Angulo, R., 1979. Chemical recovery as alternative of environmental solution by geothermal brines in Cerro Prieto. GRC Transactions 3, 449-452.

Mercado, S. and Hurtado, R., 1992. Potash extraction from Cerro Prieto geothermal brine. Geothermics, 21, 759-764.

Mroczek, E., Graham, D., Dedual, D., and Bacon, L., 2015a. Lithium extraction from Wairakei geothermal fluid using electrodialysis. In Proceedings World Geothermal Congress 2015, Melbourne, Australia, 19-25 April 2015.

Mroczek, E., Carey, B., Climo, M., and Li, Y., 2015b. Technology review of mineral extraction from separated geothermal water. GNS Science Report 2015/25, p. 32.

Nelson, B. J., Wood, S. A., and Osiensky, J. L., 2004. Rare earth element geochemistry of groundwater in the Palouse Basin, northern Idaho–eastern Washington. Geochemistry: Exploration, Environment, Analysis, 4(3), 227-241.

Noack, C.W., Perkins, K., Washburn, N., Dzombak, D.A., and Karamalidis, A.K., 2015. Screening the effects of ligand chemistry and geometry on rare earth element partitioning from saline solutions to functionalized adsorbents. GRC Transactions 39, 1023-1024.

Norman, A., Zou, X., and Barnett, J., 2014. Critical minerals: Rare earths and the US economy. National Center for Policy Analysis, Backgrounder No. 175, p.16.

Nye, C.W., Quillinan, S., Neupane, G., McLing, T., 2017. Aqueous rare earth element patterns, concentrations, and stable isotopes in thermal brines associated with oil and gas production. PROCEEDINGS, 42nd Workshop on Geothermal Reservoir Engineering Stanford University, Stanford, California, February 13-15, 2017, SGP-TR-212.

O'Brien, T.B., 2013. Recovery of elements from hydrothermal products. US Patent No. 8,377,165B2.

Park, J., Sato, H., Nishihama, S., and Yoshizuka, K., 2012. Lithium Recovery from Geothermal Water by Combined Adsorption Methods. Solvent Extraction and Ion Exchange, 30(4), 398-404.

Premuzie, E. T., Lin, M. S, Bohnek, M., Bajsarowicz, V., and McCloud, M., 1997. Advanced Biochemical Processes for Geothermal Brines Current Developments. GRC Transactions, 21, 145-149.

Recepoglu, O. and Beker, U., 1991. A preliminary study on boron removal from Kizildere/Turkey geothermal waste water. Geothermics, 20, 83-89.

Roth, S., 2015. Lithium plans in doubt as Simbol Materials fires dozens. The Desert Sun, February 4, 2015.

Roth, S., 2016. Tesla offered $325 million for Salton Sea startup. The Desert Sun, June 8, 2016.

Rothbaum, H.P., and Anderton, B.H., 1975. Removal of silica and arsenic from geothermal discharge waters by precipitation of useful calcium silicates. In United Nations 2nd Symposium on the development and use of geothermal resources, San Francisco, Proceedings (Vol. 2, pp. 1417-1425).

Rothbaum, H.P. and Middendorf, K (1986). Lithium extraction from Wairakei geothermal waters. New Zealand Journal of Technology, 2, 231-235.

Schultze, L.E., and Bauer, D.J., 1984. Recovering lithium chloride from a geothermal brine. Report of investigations/1984 (No. PB-84-224500; BM-RI-8883). Bureau of Mines, Reno, NV (USA). Reno Research Center.

Schultze, L.E., and Bauer, D.J., 1985. Recovering zinc-lead sulfide from a geothermal brine. Report of Investigations/1985 (No. PB-85-185254/XAB; BM-RI-8922). Bureau of Mines, Reno, NV (USA). Reno Research Center.

Shannon, W.T., Owers, W.R., and Rothbaum, H.P., 1982. Pilot scale solids/liquid separation in hot geothermal discharge waters using dissolved air flotation. Geothermics, 11, 43-58.

Stull, D.P., 2015. Environmentally friendly economical sequestration of rare earth metals from geothermal waters. Geothermal Technologies Office 2015 Peer Review, US Department of Energy, Energy Efficiency & Renewable Energy, May 11-14, 2015.

Stull, D.P., 2016. Environmentally friendly economical sequestration of rare earth metals from geothermal waters. Final Report, DE-EE006751, Tussar Corp, Lafayette, CO 80026, p. 17.

Thomas, H., Reinhardt, T.P., and Segneri, B., 2015. Low temperature geothermal mineral recovery program. PROCEEDINGS, Fortieth Workshop on Geothermal Reservoir Engineering Stanford University, Stanford, California, January 26-28, 2015 SGP-TR-204.

Thomas, H., Reinhardt, T.P., Anderson, A., and Segneri, B., 2016. Critical and strategic materials and potential importance for geothermal projects. PROCEEDINGS, 41st Workshop on Geothermal Reservoir Engineering Stanford University, Stanford, California, February 22-24, 2016 SGP-TR-209.

USGS (2015). Mineral commodity summaries 2015: U.S. Geological Survey, 196 p., http://dx.doi.org/10.3133/70140094.

Ventura, S., Bhamidi, S., Hornbostel, M., Nagar, A., and Perea, E., 2016. Selective recovery of metals from geothermal brines. Final Report, SRI International, Menlo Park, CA 94025, p. 34.

Werner, H.H., 1970. Contribution to the mineral extraction from supersaturated geothermal brines, Salton Sea area, California. Geothermics, 2, 1651-1655.

Wood, S.A., 2001. Behavior of rare earth elements in geothermal systems: a new exploration/exploitation tool? Report No. DOE/ID13575, University of Idaho, Moscow, Idaho, pp. 94.

Wood, S. A., and Shannon, W. M., 2003. Rare-earth elements in geothermal waters from Oregon, Nevada, and California. Journal of Solid State Chemistry, 171(1), 246-253.

Yan, C., Yi, W., Ma, P., Deng, X., & Li, F., 2008. Removal of boron from refined brine by using selective ion exchange resins. Journal of Hazardous Materials, 154, 564-571.

Yilmaz, A. E., Boncukcuoğlu, R., Kocakerim, M. M., Yilmaz, M. T., & Paluluoğlu, C., 2008. Boron removal from geothermal waters by electrocoagulation. Journal of Hazardous Materials, 153, 146-151.

Zhang, N., Gao, D. L., Liu, M. M., & Deng, T. L., 2014. Rubidium and Cesium Recovery from Brine Resources. Advanced Materials Research, 1015, 417-420.