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September 8, 2005

2003 SME Annual Meeting  
Cincinnati, OH, United States  
February 24, 2003 through February 26, 2003

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# Recovery of Minerals and Metals from Geothermal Fluids

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## ABSTRACT

Geothermal fluids are potentially significant sources of valuable minerals and metals. These fluids are water that is heated by the natural heat flow from the depths of the earth. Hotter fluids, typically with temperatures greater than 120°C, are used to generate electricity. Lower temperature fluids are directly used to supply thermal energy to applications such as agriculture, aquaculture and space heating. The geothermal waters have had intimate and lengthy contact with the layers of the earth's crust that they flow through, resulting in dissolution of minerals and metals from the rocks, and solution into the hot water. These aqueous solutions can be processed to recover minerals and metals. Potential products include silica, zinc, lithium, and other materials. Recovery of minerals and metals from geothermal fluids can be viewed as "solution mining by nature", followed by application of established or new hydrometallurgical techniques for isolation and purification. This paper discusses the opportunities, the processes, the challenges, the current status, the economics and the potential for recovery of minerals and metals from geothermal fluids.

## INTRODUCTION

Geothermal fluids contain significant concentrations of potentially valuable mineral resources. Although their mineral content was often considered more a nuisance than an asset, there is now increasing interest in improving the economics of geothermal energy by co-producing and marketing some of the dissolved constituents. Simple cost-effective methods are needed to extract mineral byproducts from geothermal fluids. Useful methods may have already been developed in the hydrometallurgical industry that could be modified for use with geothermal fluids. Although the enrichment of target elements in geothermal fluids is not as high as the enrichment in fluids commonly treated with hydrometallurgical methods, the costs associated with resource extraction from geothermal fluids are potentially low for several reasons:

- Plant costs are split between power and mineral production. Geothermal power plants already pump and process the fluids. Mineral extraction would consist of an additional treatment step added to existing plant facilities;
- There are no costs associated with mining and physical processing of the ore, and no negative environmental impacts;
- There are no costs associated with dissolution of ore minerals into an aqueous phase because they are already in solution;
- Geothermal systems process large volumes of water, commonly tens of millions of gallons per day, so that the mass of mineral resource is large in spite of relatively low concentrations.

This paper reports on previous and current research aimed at developing technologies for resource extraction from geothermal fluids, and provides a summary of the targeted mineral by-products, their potential value, and extraction methods being considered. It also summarizes zinc and silica extraction work at CalEnergy's Salton Sea, California field, silica extraction work in New Zealand geothermal plants, and current work to develop silica and other metals extraction at Dixie Valley, Nevada, and Mammoth Lakes, California.

## **CHEMISTRY OF GEOTHERMAL SYSTEMS**

Geothermal fluids are waters that percolate through and are heated by hot rocks. Most geothermal systems are therefore located in active volcanic areas such as the Pacific Rim and Iceland. Some are located in fractured areas that allow water circulation to great depths where the fluids are heated by the earth's natural heat, such as some Basin and Range fields in Nevada and Utah in the U.S. The source of the water may be meteoric, connate (filling the pores of the rocks), or a mixture, and in some cases a magmatic component is present from de-volatilization of hot magma. Fluid compositions are therefore variable. Acidities range from pH 5 to 9, and salinities from 1000 to over 300,000 ppm TDS. Most fluids have low oxidation states and may contain ferrous iron and reduced sulfur.

The chemical components of geothermal fluids are determined by their source (e.g. meteoric, seawater, magmatic), the rock types with which they have reacted along their flowpath, the temperature of those interactions, and the chemistry of the fluid. Reservoir processes such as mixing and boiling also impact fluid chemistry. The chemistry of fluids sampled at the surface therefore reflect their chemical and physical history. Certain elements may be especially indicative of their source. For example, lithium, cesium and rubidium are often enriched in fluids hosted by silica-rich volcanic rocks. Silica concentrations are generally controlled by strongly temperature dependent equilibration with silica polymorphs. Systems with more saline chloride-rich fluids are enriched in metals such as iron, zinc, and other base metals that form strong chloride complexes. Such fluids can be derived from reactions with evaporite-rich sedimentary rocks, as in the geothermal fluids from near the Salton Sea, or from seawater-basalt interactions.<sup>1</sup>

Geothermal fluids are produced from subsurface reservoirs at depths commonly between 500 and 3000 meters. Their heat is extracted and used to generate power. The fluids are then reinjected into the subsurface to replenish the fluid reservoir. Resource removal optimally takes place after or near the end of the energy extraction process, but prior to reinjection. The temperatures of reinjected fluids are commonly between 50 and 150°C and pressures at or slightly above steam saturation. In some cases, mineral extraction may allow further energy extraction that, without treatment, would be uneconomic due to scale formation. For example, the geothermal plants at Wairakei, New Zealand terminate energy extraction as the fluids cool to below 130°C because silica scaling becomes too difficult to control (Brown, 2000). Silica extraction would allow additional energy

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<sup>1</sup> Fossil basalt-seawater geothermal systems are the hosts of "massive sulfide" base metal ore deposits that are major sources of the world's lead, zinc, copper, silver, and barium.

extraction to lower temperatures. Mineral recovery also improves the economics of geothermal energy production by helping to minimize scaling both in the plant and in reinjection wells. Current geothermal electricity generation capacity worldwide is about 8000 megawatts. Individual geothermal plants produce between a few and a few hundred megawatts.

## **GEOHERMAL FLUID RESOURCES AND THEIR MARKETS**

Many constituents of geothermal fluids have value provided they can be separated and purified. The recovery of a valuable material from a geothermal resource is dependent on the state and chemistry of the feedstock; the recovery may be from the fluid, or from solid material such as sludge or scale that precipitates from the fluid. The process must be economically profitable and environmentally acceptable. Previous published work on extraction of resources from geothermal fluids has focused on a wide variety of materials including precious and platinum group metals, zinc, lead, copper, manganese, rare earths, silica, lithium, arsenic, antimony, boron, bromine, iodine, strontium and barium sulfate, precipitated calcium carbonate, calcium chloride, potash, table salt, sodium sulfate, and others (Gallup, 1998; Harper et al., 1992). Most of this work has focused on extraction of silica, lithium, and zinc, the resources that have the greatest potential to be economically extracted, and on which we focus our review.

In the early history of geothermal resource development, boric acid, sulfur, and ammonium salts were recovered commercially until they lost economic competitiveness to other mining processes. (Garbato 1961; Lenzi, 1961; Villa 1975). Recently, several processes have been reported for the recovery of other valuable materials from geothermal resources (Duyvesteyn 1992; Lin et al. 2000, 2001). Typical recovery methods are discussed below.

### *Recovery from solid geothermal residues (sludges and scales)*

Acid leaching: In geothermal power plants in the Salton Sea area, a solid waste separated as filter cake from the clarifier contains a mixture of iron-bearing silica, salts, and heavy metals. Hydrochloric acid has been employed to leach out the iron and other metals, such that the remaining silica becomes pure enough for uses as a pozzolanic additive for cements.

Biochemical leaching: Bioleaching used for mining low-grade copper, uranium and gold ores (Ehrlich and Brierley, 1990) has been modified to treat the solid waste separated as filter cake from the clarifiers at Salton Sea plants. In the process, acidophilic bacteria were used to leach out most of the toxic heavy metals, to make the treated solid safe for landfill disposal. In some cases the byproduct is pure enough to be used as feedstock for further processing (Premuzic et al. 1995b).

### *Recovery of metals and salts from geothermal fluids*

Sorption: Synthetic ion-exchange resins as well as bacteria are known to adsorb ions selectively from solution. The selectivity and capacity of the adsorption is pH, temperature and ionic strength dependent. Laboratory studies of the use of the adsorptive property of cell walls to recover U, Co, Zn, Mn, and Li ions in solution have been reported (Premuzic et al., 1995b). However, no biological process has yet been commercialized. Separation using commercial ion-exchange resins has been used to recover zinc from high salinity brines (see Salton Sea case history below).

Evaporation: Leslie Salt operated solar evaporation ponds to recover salt minerals from saline brines at Imperial Valley, CA in the early 1970's. Evaporation is an energy intensive process that can be employed under rare circumstances when energy costs and the need for reinjection water are of no concern. Additionally, reinjection of fluid after salt and potash removal could negatively impact the injection zone (Premuzic, 1995a).

Precipitation as sulfides: Hydrogen sulfide was added to geothermal fluids to precipitate out most heavy metals as insoluble metal sulfides (Schultze and Bauer, 1985). The advantage of this treatment is its near quantitative efficiency. However, if the geothermal brine is rich in many metals, quantitative precipitation gives rise to a complex metal sulfide mixture that requires further purification (SRI, 1980). Precipitation as hydroxides induced by raising the pH gives rise to similar problems (Hazen Research Inc., 1978).

#### *Recovery of silica from geothermal fluids*

Silica is an ubiquitous component of geothermal fluids and must be removed or reduced in concentration to allow other components to be removed. Most hydrothermal systems equilibrate with quartz ( $\text{SiO}_2$ ) causing the fluids to have silica concentrations that reflect the temperature of the reservoir - the hotter the reservoir, the higher the silica concentration of the fluid.

During energy production, the geothermal fluid cools and some water is extracted as steam. Both processes cause the silica to become increasingly supersaturated. Eventually the silica tends to precipitate and forms scale on various plant components or in reinjection wells. Silica will also tend to precipitate on mineral extraction processing equipment if not removed prior to mineral co-production. Thus a key need for mineral co-production is the elimination of silica scaling. This can be done by purposefully precipitating silica as a high surface area porous material with properties similar to those of commercially produced precipitated silicas. In this way the silica scaling problem is solved and at the same time a marketable silica by-product is produced. In addition, silica removal may allow additional energy extraction that would not be economic due to scaling problems. There is currently world-wide interest in silica production from geothermal fluids, including work in New Zealand (Brown and Bacon, 2000), Japan (Sugita et al., 1998), Russia (Kashpura and Potapov, 2000), and the U.S. (Bourcier et al., 2001; Lin et al., 2000). The commercial market for silica is currently about 6 million pounds per day, versus the total flux of silica through all of the world's geothermal plants of about 3 million pounds per day.

Silica is a very versatile material. Its price varies widely depending on its purity and physical properties. The majority of marketed high surface area silicas are “precipitated silicas” that have been industrially produced by dissolving clean quartz sand in alkali solution, and then precipitating colloidal silica by acidification. “Colloidal silica” generally refers to silicas produced by precipitation from acidic solution brought about by an increase in pH. By varying process conditions, silicas having a variety of textures can be produced. These silicas have surface areas of tens to hundreds of square meters per gram and uniform pore sizes. The silicas are used in applications in the rubber, plastics, paper, paint, cement, ceramics, pharmaceuticals, pesticides, and adhesive industries. Some specific uses include (USGS, 1999):

- Desiccants and anti-caking agents in human and animal food
- Abrasives in sandpaper and for use in silicon wafer polishing
- Filler in plastics, paper, paint and rubber tires
- Fiber optics and catalyst manufacturing
- Feedstock for making semiconductor silicon, fine chemicals, and chromatographic silica.

The current silica markets total about 190,000 ton/yr. for precipitated silica and 68,000 ton/yr. for colloidal silica, with a 4% annual rate of increase in demand. The wholesale prices for low-end silicas range from a few cents per pound for cement additives and desiccants, to around one dollar per pound for silica used as rubber and paper additives. Higher priced silica markets exist such as ultrapure uniform textured silica for chromatography, but these market sizes are small relative to the potentially large flux of geothermally produced silica.

The key to making marketable geothermally produced silica is to match the compositional and textural requirements of the targeted market. Of these, the textural requirements are most difficult. The useful properties of silica are high surface area, large pore volume, and a uniform pore size distribution. These properties give it the ability to bond or adsorb as needed for various applications. For example, silica to be used as a rubber binder must have a texture consisting of 30-50 nanometer sized silica colloids bunched together into tens of micron-sized aggregates that are mixed with the rubber precursors. If the aggregates are too firmly bound, they will not disperse well in the rubber and will fail to produce a favorable product. Conversely, if they disperse too readily, the silica particles will cause the tire formulation to have too high a viscosity and it will not mix well. In addition, the pore size of the dispersed silica particles must match the size of the rubber polymers so that the polymers can penetrate and link the silica particles.

The composition of the silica is of less importance than the texture for most applications. Most commercial silicas have as much as one weight percent other salts. Geothermal silicas that do not meet the compositional requirements for the intended market can be acid leached to remove unwanted contaminants such as iron and calcium.

Less pure geothermal silicas may have applications where their impurities are an asset. For example, high surface area materials that can adsorb toxic elements are needed for *in situ* reactive barriers used underground to trap migrating contaminants. Silicas that contain iron and sulfide contaminants may be ideal for these types of applications where toxic metals such as mercury, cadmium, and arsenic sorb to iron hydroxides or sulfides. The reactive barrier materials must be cheap and available in large quantities, as would be the case for geothermal silicas.

Many methods have been used to precipitate silica from geothermal fluids. One is to add salt such as magnesium chloride. Magnesium cations increase polymerization rates and facilitate agglomeration of silica. Synthetic polymer electrolytes can also be used, but are more costly. In geothermal systems that have been acidified to control silica scale formation, adding base to increase the pH will induce silica precipitation. Although silica solubility does not vary significantly at pH values less than about 8, the rate of silica polymerization does increase with increasing pH. By adding base, the rate of silica polymerization increases and leads to the formation of silica colloids, which then flocculate to form silica precipitates. Cooling can also be used to precipitate silica. A rapid drop in temperature increases the degree of silica supersaturation and leads to nucleation of silica colloids. Finally, seed silica can be added to geothermal fluids to act as nucleation sites for silica precipitation (Harper et al., 1995).

Silica particles can be removed from solution using filtration or centrifugation, depending on the particle size. Modern ultrafiltration membranes have been incorporated into silica extraction processes carried out at Wairakei, New Zealand (Brown and Bacon, 2000).

#### *Recovery of lithium and alkali metals from geothermal fluids*

Lithium is often enriched in geothermal fluids. The current market for lithium is estimated at about 350 million dollars per year. Lithium is used in the production of ceramics, glass, and aluminum, and also has a growing use in rechargeable lithium batteries. Chile is the largest lithium producer in the world, followed by Australia, China, Russia and the U.S. The price of lithium as lithium carbonate has increased 10% in the world market from 2000 to 2001 and currently remains stable at \$4.37/kg (USGS, 2001). The U.S. has remained the leading consumer of lithium minerals and leading producer of value-added lithium products. Lithium ore concentrate (as lithium) imports to the US for consumption have increased rapidly from 884 tons in 1996 to 3000 tons in 2000.

Lithium can be extracted from geothermal fluids by direct precipitation as lithium salts, or captured using ion exchange resins. Both methods are currently being used for commercial lithium extraction from saline (non-geothermal) brines (e.g. at Searles Lake California a dilithium sodium phosphate precipitate is made; FMC uses a proprietary ion exchange process to remove lithium from brines originating in Chile). Lithium removal from geothermal fluids at Hatchobaru, Japan was reported by Yanagase et al. (1982) and at Wairakei, New Zealand by Rothbaum and Buisson (1986) but neither site currently produces and markets extracted lithium.

Both cesium and rubidium can be enriched in geothermal fluids and because of their high value could be extracted at a profit. Both are specialty chemicals that sell for a few dollars per gram. The total U.S. market for these elements is estimated at a few thousand kilograms per year. Cesium and rubidium are used interchangeably in applications in thermionics, as oxygen getters in vacuum tubes, and alloys used in photocells. The hydroxides of cesium and rubidium are the strongest known bases. Additional applications for these elements may arise given a significant cost reduction. Cesium and rubidium can be separated using high cross-linkage ion exchange resins. Novel methods utilizing crown ethers have also been investigated (Harper et al., 1992).

#### *Other byproducts*

Geothermal fluids could be used to produce some inexpensive salts such as NaCl, Na<sub>2</sub>SO<sub>4</sub>·H<sub>2</sub>O, CaCl<sub>2</sub> and others. Although they are not of high value, they may be produced as by-products of the processes that produce other more valuable solids and may add to the profitability of geothermal co-production. Another potential by-product is high surface area precipitated calcium carbonate. Although calcium carbonate as limestone is inexpensive, freshly precipitated high surface area CaCO<sub>3</sub> has unique properties that make it useful in applications such as paper filler and allows it to command a much higher price.

Precious metals such as gold and silver are contained in geothermal scale, and extraction from the scale rather than the fluid has been attempted (Gallup, 1998). Base metals such as zinc, copper, and lead are generally not highly enriched in geothermal waters. One exception is the very saline geothermal system at the Salton Sea in southern California. CalEnergy Minerals has developed a commercial zinc extraction process at this site, and has plans to remove manganese as well (see below).

### **CASE HISTORIES**

#### *Colloidal silica extraction in New Zealand*

A pilot plant at the Wairakei geothermal system in New Zealand (Figure 1) was designed to produce colloidal silica -“silica sols”- from geothermal water (Brown and Bacon, 2000).

They used a two-step process: cooling to induce polymerization leading to colloid formation, and ultrafiltration to remove water and concentrate the silica colloids. They used the amount of undercooling to control particle size. The greater the amount of undercooling, the greater the amount of silica supersaturation, and the greater the number of silica nuclei. A large number of nuclei limit the size to which the particles can grow before depleting the available silica. As a result, cooling by 70°C results in a large number of smaller (10nm) particles, whereas cooling by 20°C results in a fewer number of larger (70 nm) particles. Both processes depend upon controlled slow cooling from that point on to produce monodisperse colloids. Too rapid cooling could generate another

round of nuclei formation and a bimodal colloid size distribution. Monodisperse silica colloids – colloids having a narrow size range - are more valuable.



**Figure 1.** Geothermal fluid drain at Wairakei, New Zealand geothermal site. Silica precipitates of orange-brown color line the channels. A bluish color indicates the presence of colloidal silica in the water.

After formation of silica colloids, a dispersant was added to retain the silica as individual colloids and not allow colloid agglomeration. The slurry consists of 30-50 wt. % silica colloids suspended in water.

Ultrafiltration was then used to concentrate the colloids. Membrane pore sizes of the filters were selected such that they would allow water passage but retain the colloids. The primary problem with ultrafilters in this application is silica fouling. Frequent membrane cleaning and flow reversal are needed for long-term success. The silica sols were then rinsed with local potable water. Chemical analysis of the rinsed silica colloids showed them to be enriched in calcium, aluminum, magnesium, cesium, rubidium, and antimony. Further rinsing with acid may effectively remove these contaminants. They also may be avoided by adding chelating agents that would tend to keep them from sorbing to the silica colloids. Major uses of colloidal silica in this form include silicon wafer polishing, photographic coatings, and as binders for catalysts.

The silica extraction process at Wairakei was piloted for about 11 months. The greatest operational cost appeared to be care and replacement of the ultrafilters. The process was never put into production mainly because there was no nearby buyer (in central New Zealand) for the colloidal silica concentrate. Shipping costs were significant for potential buyers overseas and negated the low production costs. However, negotiations continue with potential buyers and a successful full-scale operation is still a possibility (K. Brown, personal communication, 2001).

#### *Mineral extraction at the Salton Sea, California geothermal field*

One of the most metal-rich geothermal fluids in the world exists near the Salton Sea in the Imperial Valley of southern California (Figure 2). The geothermal fluid at this site is unique in having extremely high salinity and a high base metal content. The fluid is especially enriched in metals that form strong hydrothermal complexes with chloride, such as zinc, copper, lead and silver. The geothermal system is hosted by a thick sequence of sedimentary rocks into which volcanic rocks have recently been intruded. The volcanic rocks are associated with the northern extension of a rift zone that forms the Gulf of California. The geothermal field currently produces about 330 MW of electrical power.

The metal-rich geothermal fluids are being mined for their zinc content by CalEnergy Minerals. Their process utilizes 105°C “spent brine” downstream from the steam separation and energy extraction processes. The brine is passed over an anionic ion exchange bed (IX) to extract the zinc present in the fluid primarily as anionic  $\text{ZnCl}_4^{2-}$ . The resin is then eluted with an acidic solution that contains a reducing agent. Iron, arsenic and lead are also extracted in the process, but are subsequently removed by oxidation followed by solids removal. The zinc is then extracted from the eluate in a solvent extraction process (SX) utilizing a water immiscible cationic extractant. After removal of the zinc-depleted aqueous phase, the zinc-loaded SX extractant is rinsed and

then stripped with a sulfuric acid solution. After separation of the SX extractant, the zinc sulfate solution undergoes electrowinning to produce metallic zinc.

When operating at full output, CalEnergy will produce about 30,000 metric tons per year of 99.99% pure zinc to be sold under contract to Cominco Ltd. CalEnergy expects to make as much profit from zinc production as they do from energy sales.

Silica must be removed from the fluid for the zinc extraction process to be successful. If not, the ion exchange resins are quickly covered by silica precipitates and fail to efficiently extract zinc. The silica is currently removed upstream using a clarification process that combines lime addition and silica seeding. The pH increase accompanying lime addition accelerates silica polymerization, and silica seeds enhance precipitation. The silica is removed by flocculant-aided settling. The silica precipitated with this method has significant amounts of contaminants such as iron and calcium that make it unsuitable for many silica markets for which high purity is needed. Tests showed that it had some favorable properties for use as a cement additive. Currently the silica is being disposed of in a nearby landfill.



**Figure 2.** CalEnergy's geothermal power production facility near shore of Salton Sea in the Imperial Valley of southern California.

CalEnergy has investigated methods for extracting manganese from their brines. The targeted by-product is electrolytic manganese dioxide for use in batteries. The overall U.S. manganese market is expected to remain at the same level in the near future except for the electrolytic manganese dioxide market, which is expected to grow with the expanding use of alkaline batteries. Preliminary work shows that a solvent extraction method utilizing diethylhexyl phosphoric acid and a quaternary amine shows good selectivity for manganese over other metals present in the brine. More work on manganese extraction is anticipated subsequent to successful full-scale zinc extraction.

#### *Silica Extraction at Mammoth Lakes, California*

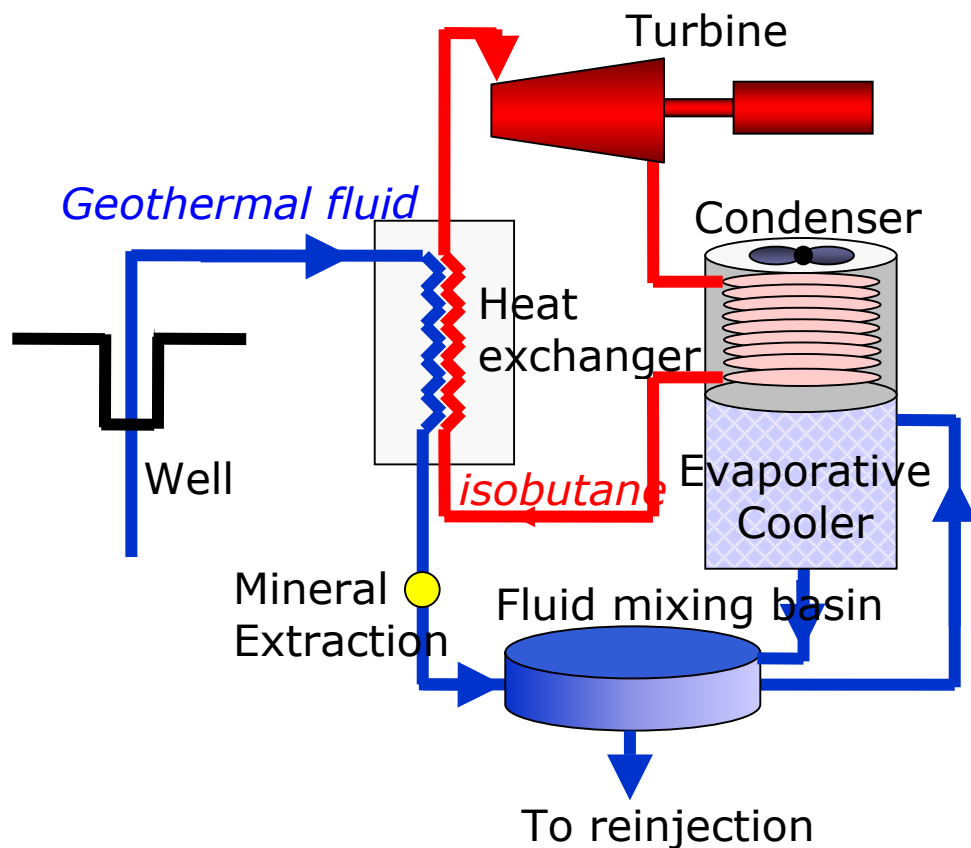
Current work is underway to extract silica at the Mammoth Lakes, California geothermal plant (Figure 3), with major R&D sponsorship by the U.S. Department of Energy Geothermal Technologies Program through Lawrence Livermore National Laboratory, the California Energy Commission, and Mammoth Pacific L.P. The geothermal fluid at Mammoth has one of the lowest salinities of any geothermal fluid (1200 ppm TDS), with very low calcium, and negligible iron and other metals content. For this reason, the co-produced silica is of very high purity, and therefore may be useful in markets where high purity is necessary, such as colloidal silica for silicon chip polishing.



**Figure 3.** Mammoth Pacific L.P.'s geothermal power production plant near Mammoth Lakes, California where silica extraction R&D is currently being carried out.

The power plant at Mammoth is a binary plant (see Figure 4) in which the geothermal fluid is used to heat a working fluid (isobutane) used to drive the turbine. In flash plants, separated steam is used to drive the turbine. A unique feature of the Mammoth geothermal site is the need for a low-salinity fluid to be used in an evaporative cooler to cool the isobutane downstream from the turbine. Because the geothermal plant is located near a resort area, a cooling tower was not permitted.

A problem with silica extraction at Mammoth is the relatively low silica content of 250 ppm in the fluid, as compared to most geothermal fluids from flash plants that contain 500 ppm or more silica. Conventional methods for extracting silica are not effective for the Mammoth fluids due primarily to slow kinetics of polymerization at low silica concentrations. A higher silica concentration is needed to allow efficient silica extraction.



**Figure 4.** Schematic of binary power plant at Mammoth Lakes site. The geothermal fluid is used to heat the isobutane “working fluid” that turns the turbine.

For this reason, current silica extraction work at Mammoth is done using geothermal fluid first processed through a reverse osmosis (RO) membrane. The RO unit provides a silica-enriched concentrate for silica and other metals removal, and a low TDS permeate for use in the evaporative cooler. The reverse osmosis unit can be used to concentrate the silica to any desired level; high enough to allow rapid extraction, but not so high that the reverse osmosis membranes foul with precipitated silica. Silica concentrations of between 600 and 700 ppm appear to satisfy both constraints.

The silica is precipitated using a commercial agglomerating agent and removed using a tangential flow ultrafilter. The silica is then characterized using a particle size analyzer and gas adsorption surface area measurements, and digested for chemical analysis. The most promising samples are sent to commercial laboratories for product testing. Comparison of these test results with properties of known commercial silicas and their products guides further extraction work that is aimed at specific uses.

Of additional interest at Mammoth are potentially economic concentrations of lithium, cesium, and rubidium that are enriched in the reverse osmosis concentrate. Work is underway to extract these alkali earth elements using commercial ion exchange resins, and special porous silicon membranes functionalized with crown ethers.

#### *Silica Extraction at Dixie Valley, Nevada, Coso, California, and Steamboat Springs, Nevada*

As part of the U.S. Geothermal Technologies Program, work is underway to develop economic and environmentally acceptable methods for extraction of silica from fluids at three geothermal sites owned by Caithness Operating Company. The work is being carried out by Brookhaven National Laboratory in collaboration with Caithness, industrial groups, and educational institutions. The work is focused both on production of marketable silica and silica scale prevention at three geothermal fields: Dixie Valley and Steamboat Springs in Nevada and Coso in California.

Current R&D includes the following tasks:

- Test reaction parameters such as temperature, pressure, pH, concentration of reagents, and aging for their effects on properties of silica products.
- Use data obtained from pilot plants for predicting full-scale silica production with economic analysis.
- Investigate and test silica surface modification process (e.g. silane coupling agents) on produced silica.
- Apply knowledge learned to other geothermal sites

### **ECONOMICS OF SILICA EXTRACTION**

The value of silica varies over a wide range and depends upon the quality and properties of the product. Both high and low value silica recovery processes are being explored and developed. Based on low, conservative pricing for geothermal silica, it is reasonable to assume that the co-production of silica is a practical step to realizing one of the three DOE programmatic goals: reducing geothermal power production costs down from the current level of 5-7 cents/kWh to 3-5 cents/kWh by 2010. Additionally, the synergistic effects of co-production revenue and cost savings from maintenance and repairs may assist in the expansion of geothermal power production to more states where the exploitation of geothermal power is only marginally profitable, which is another programmatic goal.

An economic analysis of silica production at the Dixie Valley geothermal site indicates the following. Capital costs including equipment and building are about \$7.8 million. Annual operating costs including labor, power and chemicals are estimated at \$3.1 million for a 6,000 ton/year plant. Annual sales at \$0.60/lb would yield \$7.2 million in sales. After amortization costs, the yield from this project would be equivalent to \$0.0094 per kWh produced. In addition, the savings from scale reduction are estimated to be \$0.0015 per kWh in terms of annual maintenance and repairs. The total benefit of silica production is equivalent to \$0.011 per kWh (1.1 cents/kWh). The pay back period will be less than 3 years based on a 10% interest rate. Market analysis (Moskovitz, 2002) assumes that this is a base case model and that silica sales would far exceed this estimate.



**Figure 5.** Geothermal power plant at Dixie Valley, Nevada, U.S. where a pilot-scale silica extraction process is in operation.

The attractive economics of geothermal silica derived from low salinity resources lie in part in the fact that the raw silica product that is produced after a simple acid wash of geothermal silica is a product that can compete directly with much higher priced silicas that are on the market. For example, geothermal silica may have an application for thin-layer chromatography (TLC). The retail price for this silica (15 micron, 60 angstrom pore diameter) is \$1000 per 25 kg lots. TLC prepared plates retail for \$2-\$4 per plate and contain a few grams of silica that is of similar quality to that produced by the current Brookhaven/Caithness geothermal silica process (Premuzic et al., 1999).

## SUMMARY

Significant interest currently exists on the recovery of materials from geothermal fluids. The most significant current operation is the recovery of zinc by CalEnergy at the Salton Sea in California. The U.S. Department of Energy, in partnership with U.S. industry, is sponsoring recovery R&D at Brookhaven National Laboratory and at Lawrence Livermore National Laboratory, with emphasis on recovery of various grades of silica. Based on results to date, mineral and metals recovery from geothermal fluids has the potential to significantly improve the economics of geothermal applications and to therefore increase the amount of geothermal energy production in the world.

## ACKNOWLEDGEMENTS

Financial support was provided by the DOE Geothermal Energy Technology Program and the California Energy Commission. We appreciate the advice and encouragement of our program managers, Ray LaSala of DOE and Pablo Gutierrez of the CEC. We thank staff at Mammoth Pacific Power LLP and Caithness Operating Company for their help in carrying out on-site work, and Kevin Brown of the Geothermal Institute at University of Auckland for helpful discussions of his work on silica colloid production. The paper benefited from a review by Carol Bruton of Lawrence Livermore National Laboratory.

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This work was performed under the auspices of the U.S. Department of Energy by University of California, Lawrence Livermore National Laboratory under Contract W-7405-Eng-48.