Silica Extraction at Mammoth Lakes, California

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Abstract

The purpose of this project is to develop a cost-effective method to extract marketable silica (SiO_2) from fluids at the Mammoth Lakes, California geothermal power plant. Marketable silica provides an additional revenue source for the geothermal power industry and therefore lowers the costs of geothermal power production. The use of this type of 'solution mining' to extract resources from geothermal fluids eliminates the need for acquiring these resources through energy intensive and environmentally damaging mining technologies. We have demonstrated that both precipitated and colloidal silica can be produced from the geothermal fluids at Mammoth Lakes by first concentrating the silica to over 600 ppm using reverse osmosis (RO). The RO permeate can be used in evaporative cooling at the plant; the RO concentrate is used for silica and potentially other (Li, Cs, Rb) resource extraction. Preliminary results suggest that silica recovery at Mammoth Lakes could reduce the cost of geothermal electricity production by 1.0¢/kWh.

Introduction

Current work is underway to extract silica at the Mammoth Lakes, California geothermal plant funded by the U. S. DOE Geothermal Technologies Program, the California Energy Commission, and Mammoth Pacific L.P (Fig. 1). The geothermal fluid at Mammoth has one of the lowest salinities of any geothermal fluid (1200-1500 ppm salt), 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, precision casting,

Figure 1. Mammoth Pacific L.P.'s geothermal power production plant near Mammoth Lakers, California where silica extraction R&D is currently being carried out.

paper coatings, and raw silica for photovoltaics.

The power plant at Mammoth is a binary plant (Fig. 2) in which the geothermal fluid is used to heat a working fluid (isobutane) used to drive the turbine. This differs from flash plants where 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 evaporative cooling panels to cool the isobutene downstream from the turbine during the warm summer months.

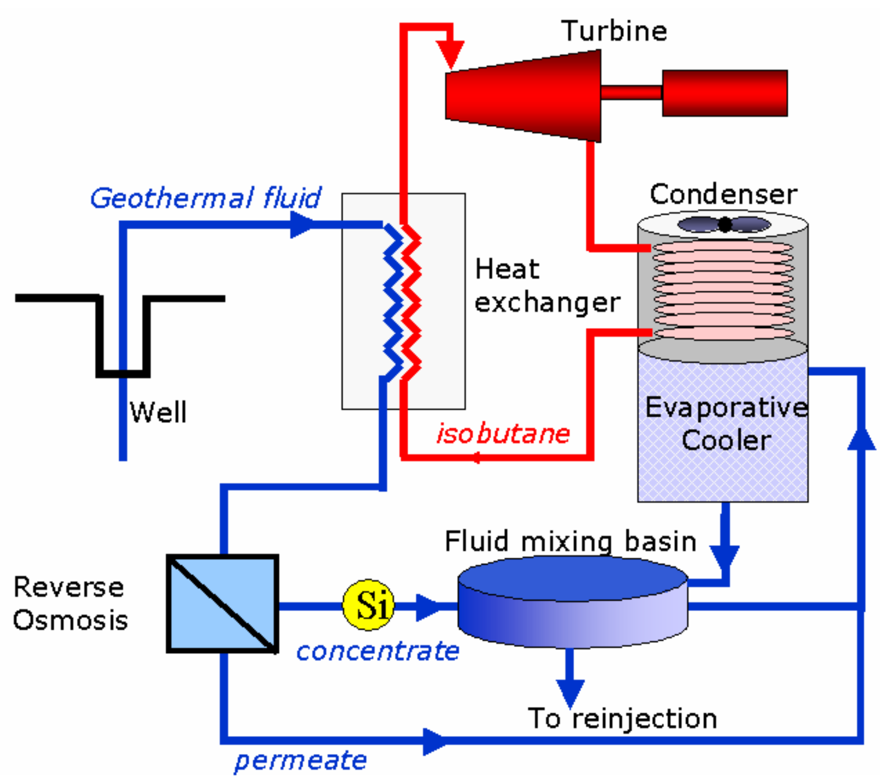


Figure 2. Schematic of binary power plant at Mammoth Lakes showing location of reverse osmosis unit and silica extraction process ('Si').

A problem with silica extraction at Mammoth is the relatively low silica content of 250 mg/L silica compared to most geothermal fluids having 500 ppm or more silica. Conventional methods for extracting silica are not effective for the Mammoth fluids due primarily to slow silica polymerization kinetics. A higher silica concentration is needed to allow efficient silica extraction.

For this reason, silica extraction work at Mammoth was carried out by first processing the fluid using using reverse osmosis (RO). 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 900 ppm appear to satisfy both constraints.

We tested silica extraction processes at Mammoth in a mobile laboratory using geothermal fluid obtained downstream from the power plant heat exchanger at 50-70^{o}C (Fig. 3). We extracted silica in two forms for different markets: precipitated solid silica, and a colloidal silica slurry. When our goal was to precipitate silica, the concentrated fluid flowed through our continuously stirred reactor where chemicals, such as salts and polyelectrolytes, were added to induce silica precipitation. Dissolved silica polymerized to form colloids, which agglomerated to form particles. When our goal was to produce a colloidal silica slurry, colloids were concentrated from the fluids without inducing agglomeration. In both cases, the particles or unagglomerated colloids were removed downstream from the reactor in cross-flow ultrafilters

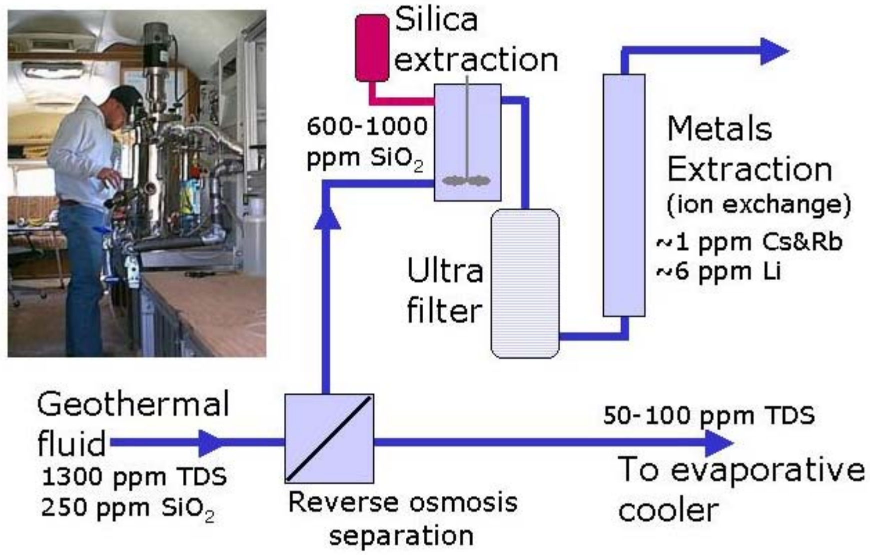


Figure 3. Schematic of the mineral extraction process.

The degree of concentration in the RO unit was tuned to provide the optimum silica concentration for extraction. The flow rate through the reactor was adjusted to optimize the fluid residence time. Process variables used to tune silica properties included the concentration and type of additive, residence time of the fluid in the reactor, pH, and filtration method. The silica was characterized using a particle size analyzer, gas adsorption surface area measurements, digested for chemical analysis (Table 1), and some samples sent to commercial laboratories for real product testing i.e. as a rubber binder for tires. Comparison of these test results with properties of known commercial silica guided further extraction work.

We developed two processes, one to generate high purity (>99%) silica with properties similar to those of commercially marketed precipitated silicas (surface areas of 40-130 m^2/g), and another to produce solutions of concentrated dispersed silica colloids (Fig. 4).

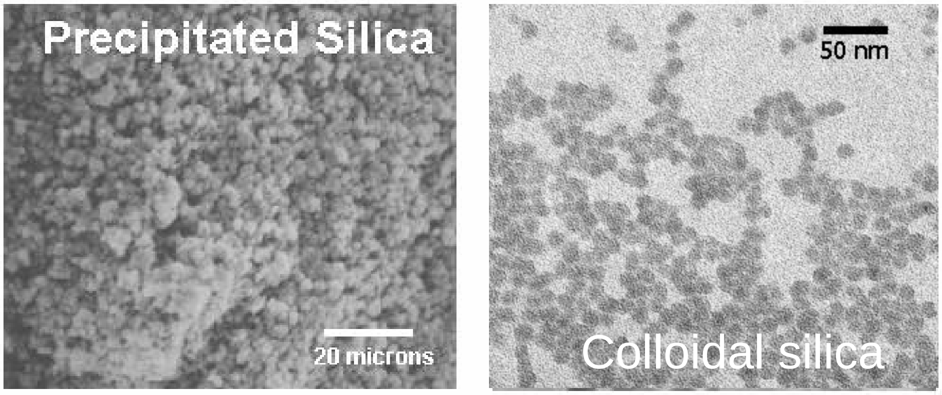


Figure 4. Images of precipitated and colloidal silica extracted from geothermal fluids at Mammoth Lakes. The colloidal silica is very monodisperse in size, a favorable property for marketing.

Table 1. Composition of silica precipitates.

	Raw	DI Rinse	Dilute Acid Rinse
Major components in wt %			
SiO2	98.09	99.13	99.63
Al2O3	0.33	0.31	0.31
Fe2O3	0.22	0.22	0.20
MnO	0.01	0.01	0.01
MgO	0.13	0.12	0.04
CaO	0.17	0.15	0.02
Na2O	1.15	0.08	0.02
K2O	0.15	0.05	0.00
TiO2	0.01	0.00	0.00
P2O5	0.03	0.03	0.02
Total	100.28	100.11	100.26

Minor components in ppm	Raw	DI Rinse	Dilute Acid Rinse
As	450	304	162
Au	0.07	0.06	0.05
Cs	21	18	5
Hg	4	4	1
Mo	20	18	10
Sb	350	332	200
Sc	0.3	0.3	0.2
W	31	26	15
Cu	14	13	10
Zn	126	175	46

Pilot testing of silica extraction

Piloting is needed prior to full-scale commercialization of silica extraction for many reasons. Previous attempts to develop geothermal silica extraction processes have not reached a mature stage and as a result uncertainties in the economic analyses have prevented plant owners from further investment in silica extraction. We believe that a critical need exists to show progress in process development to the point where a detailed economic assessment can be produced that allows full-scale commercial development of the silica extraction process. Once the favorable economics are demonstrated, additional sites will follow by developing their own processes for silica and other resource extraction. We believe that uncertainty in the economics of silica extraction is primarily due to a lack of pilot-scale test data. This uncertainty has been the major impediment to commercialization of silica co-production.

The goal of our current work is to carry out pilot-scale (10-20 gallons per minute) tests of silica recovery. These pilot tests are designed to evaluate and optimize the three stages of the silica extraction process we have previously developed: (1) reverse osmosis (RO) treatment of the geothermal extraction fluid; (2) silica precipitation (or colloid formation) in a stirred reactor containing the RO concentrate; and (3) silica separation through cross-flow. The overall goal is to generate a detailed optimized silica extraction system that has been validated by long-term testing. We will then use the process information to generate a detailed plant design for full-scale production that includes cost estimates that can be used by geothermal plant operators on which to base their investments in silica co-production.

We will carry out the silica extraction tests with our previously purchased 20 gpm reverse osmosis unit, an 80 liter PPS-coated stirred reactor, a separation and filtration system, and a mobile field laboratory that houses the equipment for necessary on-site chemical analyses. Our results should provide us with the process data needed for full-scale design calculations. The exception is the stirred reactor for which the process data will need to be adjusted to account for the differences in fluid mixing properties (additive to geothermal fluid) in order to simulate full-scale operation. We estimate we will produce about 50 pounds per day of silica in our pilot process, and produce at least one metric ton of silica over the duration of the project.

Economics of silica production at Mammoth Lakes

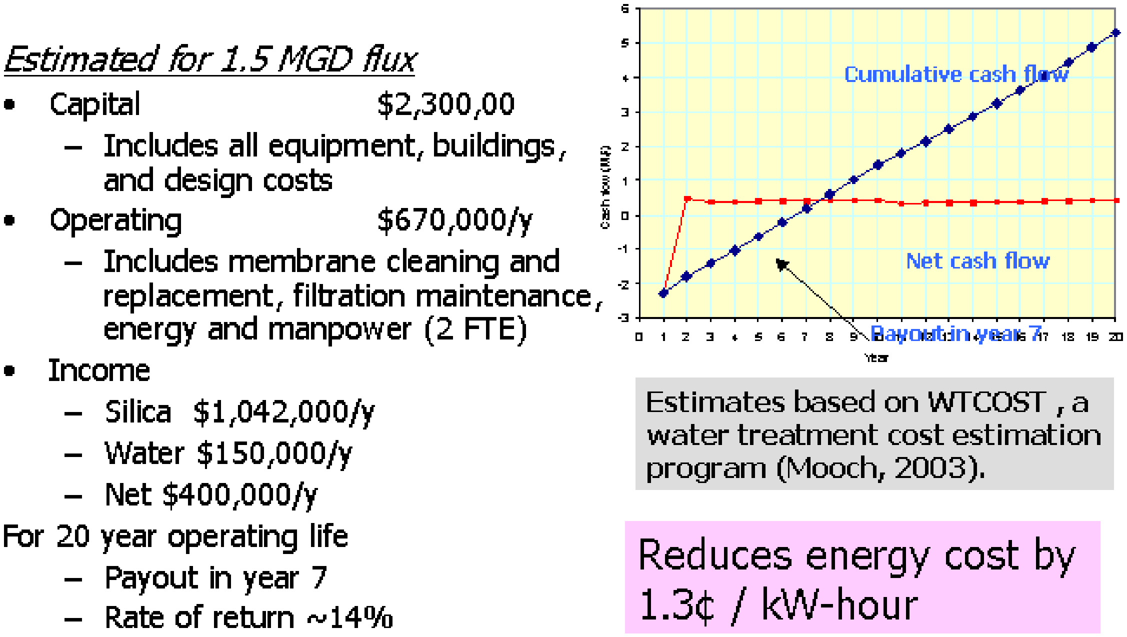
We have shown that we can produce marketable silica by-products, both as a solid precipitate useful in rubber binder applications, and a colloidal slurry useful in precision casting and paper applications. The market value of silica that could potentially be produced from the Mammoth Lakes site if the entire fluid stream is used for silica extraction is about $11,000,000/year based on a typical market price of $0.75/lb. for precipitated silica used in rubber manufacture and a silica recovery of 7200 tons per year.

For a process that treats and extracts silica from a volume of fluid stream sufficient only to provide a low-salt fluid for use in evaporative cooling panels (~1.1 mgd), the estimated capital cost for the extraction technology we have identified is about $2,300,000, and operating costs of about $700,000 per year. These estimates were obtained based on cost data from the water treatment industry, embodied in a cost estimation computer program (WTCOST, I. Moch and Associates). The annual value of silica produced is $950,000, and low-salt water is $150,000. The process thus provides about $400,000 net profit per year for the 1.5 MGD stream. These preliminary estimates suggest a rate of return of 14% and payout in 7 years (see Fig 5).

When normalized to a process that produces silica from the entire fluid flux at Mammoth Lakes of 18 MGPD, silica extraction lowers the cost of producing electrical energy by about 1.0¢/kWh. Note that this value agrees well with economic estimates for silica extraction at Dixie Valley of about 1¢/kWh provided by Stu Johnson (pers. com.).

Recovery of lithium and alkali metals at Mammoth Lakes

Of additional interest at Mammoth are potentially economic concentrations of lithium, cesium, rubidium and tungsten that are enriched in the RO concentrate. Technologies are needed for efficient extraction of these resources. We plan to test a novel ion exchanger resin for cesium and rubidium that has been developed for cesium removal from DOE nuclear waste sites. We also hope to test a reverse osmosis/softening process to remove lithium. These extraction tests will be carried out downstream from the silica extraction, where silica precipitation will not be a problem



Estimated for 1.5 MGD flux

- Capital $2,300,00
  - Includes all equipment, buildings, and design costs
- Operating $670,000/y
  - Includes membrane cleaning and replacement, filtration maintenance, energy and manpower (2 FTE)
- Income
  - Silica $1,042,000/y
  - Water $150,000/y
  - Net $400,000/y

For 20 year operating life
  - Payout in year 7
  - Rate of return ~14%

Estimates based on WTCOST , a water treatment cost estimation program (Mooch, 2003).

Reduces energy cost by 1.3¢ / kW-hour

Figure 5. Key components of preliminary economic analysis of silica extraction at Mammoth Lakes.

Summary

We have developed processes for extraction of precipitated and colloidal silica from geothermal fluids at Mammoth Lakes, California. We are currently beginning a pilot-test phase of this work in order to better define the economics of our silica process. Preliminary data suggest the silica removal could lower the electricity generation costs by as much as one cent per kilowatt hour.