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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. 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 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 resource extraction (Li, Cs, Rb). Preliminary results suggest that silica recovery at Mammoth Lakes could reduce the cost of geothermal electricity production by 1.0¢/kWh.

Summary of Work
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 Lakes has one of the lowest salinities of any geothermal fluid (1200-1500 ppm salt), with very low calcium, and negligible iron and other metals. 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

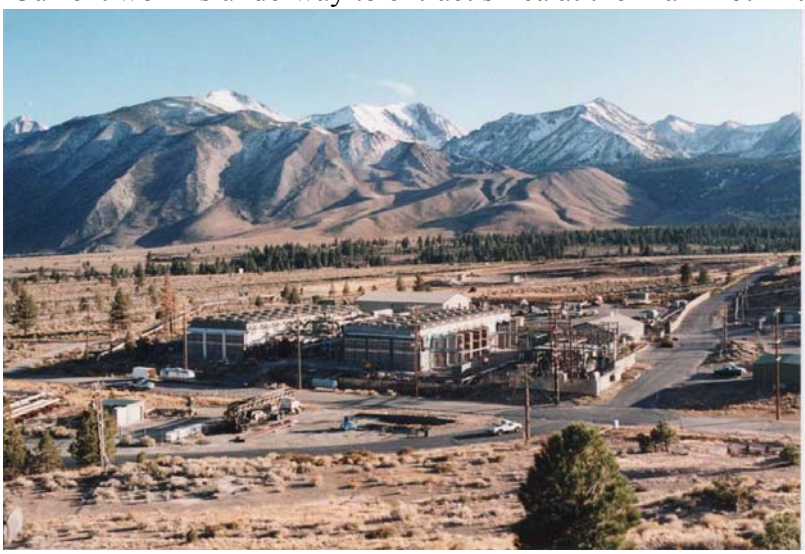

Figure 1. Mammoth Pacific L.P.'s geothermal power production plant near Mammoth Lakers, California where silica extraction R&D is currently being carried out.

polishing, precision casting, paper coatings, and raw silica for photovoltaics.

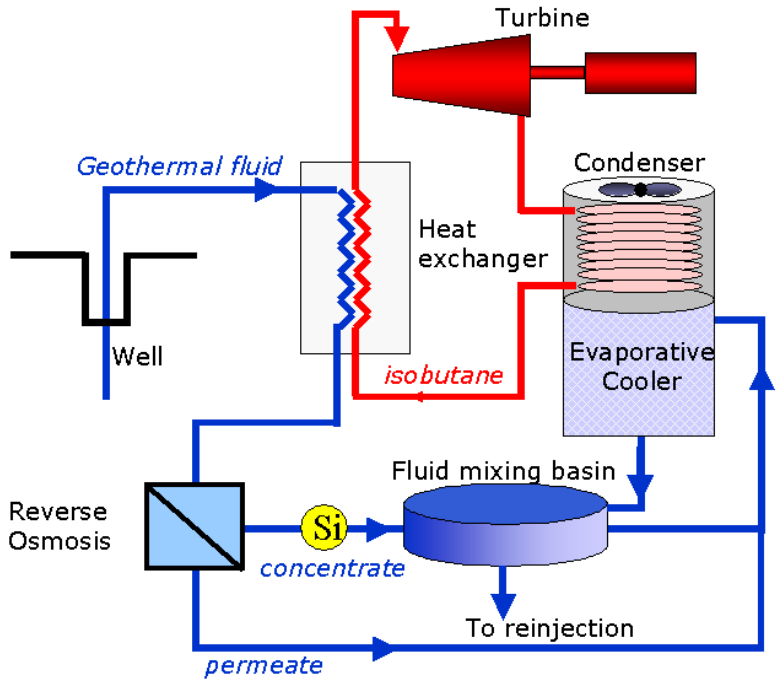

Figure 2. Schematic of binary power plant at Mammoth Lakes showing location of reverse osmosis unit and silica extraction process ('Si').

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 reverse osmosis (RO). The RO unit provides a silica-enriched concentrate for silica and other metals removal, and a low TDS permeate (Fig. 2). Mammoth Pacific is currently considering using low-salinity fluids for evaporative cooling during the warm summer months, and the RO permeate is being considered for this use. 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.

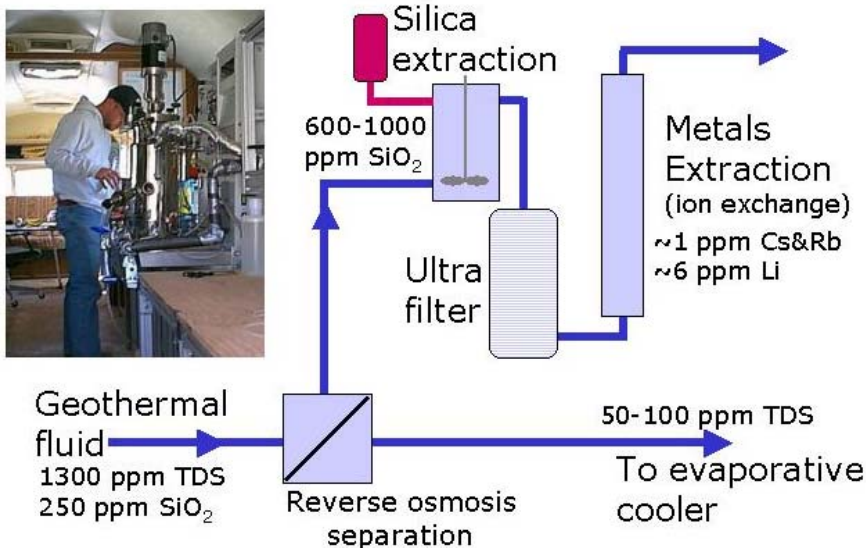

Figure 3. Schematic of the mineral extraction process.

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°C (Fig. 3). We extracted silica in two forms for different markets: precipitated solid silica, and a colloidal silica slurry (Fig 4). 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. 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

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.

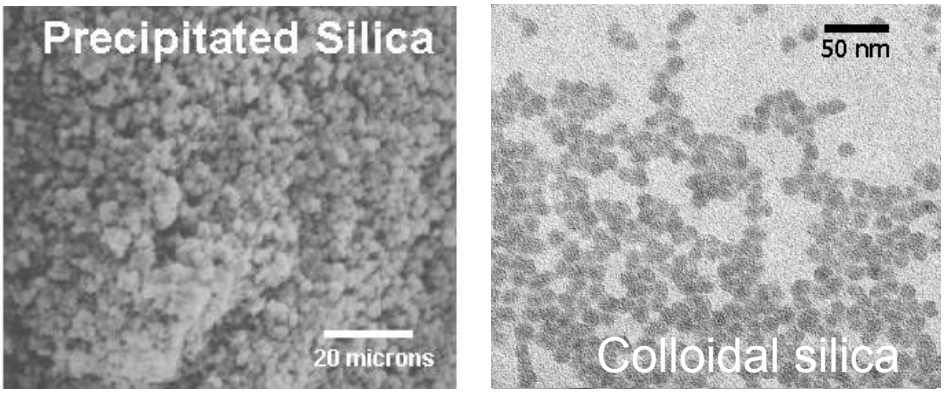

Figure 4. Images of precipitated and colloidal silica extracted from geothermal fluids at Mammoth Lakes. The precipitated silica had surface areas of 40-130 m^2/g. The consistent size of silica colloids makes it favorable for marketing.

The goal of our current work is to carry out pilot-scale (10-20 GPM) tests of silica recovery. These pilot tests are designed to optimize the three stages of the silica extraction process: (1) reverse osmosis (RO) treatment of the geothermal extraction fluid; (2) silica precipitation or colloid formation in a stirred reactor; and (3) silica separation through cross-flow filtration.

We will carry out the silica extraction tests with a 20 gpm reverse osmosis unit, an 80 liter PPS-coated stirred reactor, a separation and filtration system, and a mobile field laboratory. Our results should provide us with the process data needed for full-scale design calculations. 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. The overall goal is to generate a detailed optimized silica extraction process that has been validated by long-term testing.

Economics of silica production at Mammoth Lakes

We have shown that we can produce two marketable silica by-products, a solid precipitate and a colloidal slurry. For a process that treats and extracts silica from a 1.5 MGD fluid stream, sufficient to provide a permeate for evaporative cooling, the estimated capital costs are $2,300,000 and estimated operating costs are $700,000 per year. These estimates are based on cost data from the water treatment industry, embodied in a cost estimation program (WTCOST, I. Moch and Associates). The annual value of silica produced is $950,000, and low-salt water could be purchased for $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

Table 1. Composition of silica precipitates.

Major components wt %	Raw	DI Rinse	Dilute Acid Rinse
SiO2	98.09	99.13	99.63
Al2O3	0.33	0.31	0.31
Fe2O3	0.22	0.22	0.20
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
Total	100.24	99.94	100.22

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

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 could lower the cost of producing electrical energy by about 1.0¢/kWh.

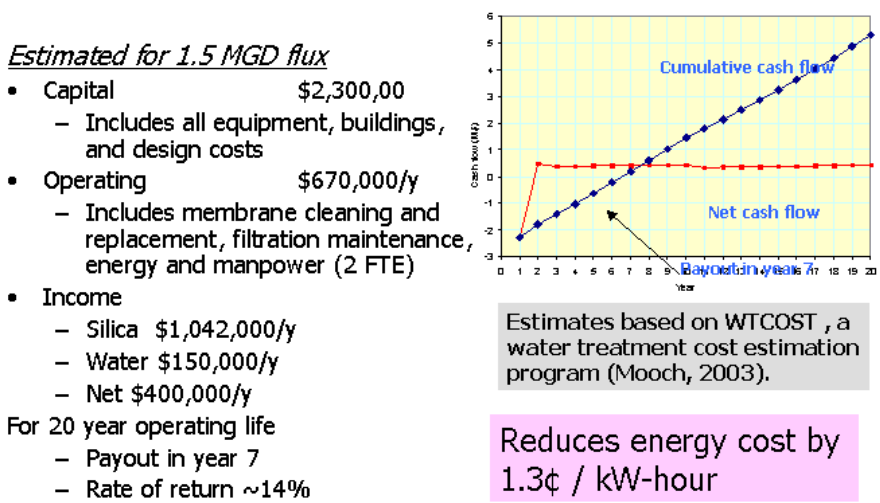

Figure 5. Key components of preliminary economic analysis of silica extraction at Mammoth Lakes.

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.