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Silica Production from Low-Salinity Geothermal Brines

Mow S. Lin[1], Michael Bohenek[1], Eugene T. Premuzic[1], and Stuart D. Johnson[2]

[1]Energy Resources Division, Brookhaven National Laboratory, Upton, NY
[2]Oxbow Geothermal Corporation, Reno, Nevada

ABSTRACT

Earlier studies have shown that the extraction of valuable products from geothermal resources could offset the overall cost of power generation. Silica extraction is of special interest because it may reduce or prevent silica scaling, which is detrimental to plant operations. At the same time, silica extraction can produce a valuable commodity for other industries. Based on these studies, a pilot plant has been designed and constructed for the extraction of silica from low-salinity brines at Dixie Valley, Nevada. Some results dealing with the properties of silica recovered from the preliminary field tests and the commercial usage of such products will be discussed.

Background

Depending on the geologic source, geothermal brines may be a source of minerals as well as a source of energy. An early example of mineral recovery is the 18th century use of geothermal steam to aid the recovery of boric acid from fumaroles in Larderello, Italy long before the steam was used for power generation (Bowen and Groh, 1977). Since then, geothermal resources have been used for power generation, space heating, agricultural drying and therapeutic spa resorts. Current power deregulation policies have forced geothermal power generation to compete more directly with other energy sources used for power production. This has stimulated a return to mineral recovery as a consideration to reduce the direct costs of power production from geothermal sources.

Although production of power has been the primary use of geothermal resources, methods to recover minerals have been proposed and studied in order to offset geothermal power production costs. For example, the recovery of zinc, manganese, and silica has been reported and a commercial facility for the recovery of zinc from high salinity sources is under construction at the Salton Sea where brines contain zinc at a concentration of a few hundred ppm.

However, silica is of special interest to the geothermal industry since silica exists in all geothermal brines, and during heat extraction and steam loss the brine becomes supersaturated to the point of precipitation. These precipitates are a major cause of scaling in some systems and are detrimental to the process of geothermal power production. Thus, the benefits of learning how to remove silica from geothermal brines are twofold: 1) By reducing or preventing scale, power production becomes more efficient, and 2) A refined silica product may be recovered for sale to end users in the silica industry.

Silica recovered from high-salinity geothermal brines contains up to a few percent of iron as well as other colored metal salts such as Zn, Mn, Sr, and Ba at ppm levels. These impurities have to be removed in order to produce high-grade silica products, and removal may be both process-and energy-intensive. The cost to produce high-grade silica from such resources reduces the value of the end product. In contrast, silica recovered from low-salinity brines contains remarkably few impurities and the value of the primary silica precipitate is significantly higher than the product obtained from high-salinity resources. The silica content in the Dixie Valley brines reinjected into injection wells is shown in Table 1. It is within the range of 300 to 700 ppm, which is typical for low-salinity geothermal brines. The kinetics of silica precipitation and the properties of the silica product are likely to be dependent on the chemistry of the individual brine sources. High-salinity brines will produce large amounts of low-grade silica; low-salinity brines will produce lesser amounts of high-grade silica.

Table 1. Typical data of low-salinity brine from Dixie Valley with species concentration in (ppm) on 9/9/1999.

Na (578)	K (87.3)	Ca (10.15)	Mg (0.028)
SiO_2 (591)	B (14.1)	Li (2.95)	HCO_3 (97)
CO_3^{-2} (64)	Cl (617)	F (15.7)	SO_4 (265)
Lab EC (2590)	Field (3000)	Calc. TDS (2380)	Meas. TDS (2295.11)
Lab pH (9.44)	Field pH (9.20)	P (142 psig)	

Preliminary studies have identified several parameters that affect the optimization of production of quality geothermal silica. These include adjustment of pH and the addition of salt to induce silica precipitation from low-salinity geothermal brines. Ultra-filtration can be used to facilitate the separation of the silica colloid precipitates from the primary, super-saturated brines.

Based on preliminary results, a laboratory pilot plane has been designed and constructed to process Dixie Valley geothermal brines. The results from experimental operation of this pilot plant will now be discussed.

Experimental Laboratory Test: Flow diagram for the test units as shown in Figure 1:

1. Reaction (Reactor) tank and reagent (Reagent) tanks at a volume of 10 to 50 gallons each. Each is equipped with valves and pressure gauges.

2. Metering pumps (P1-P4) with temperature controls are used to transfer the fluids.

3. The spent brine is mixed with acids or divalent salts in the reaction vessel. Salt is added at ppm concentration to induce silica precipitation.

4. The precipitated silica is aged for the particles to grow in size, then filtered through a membrane filter.

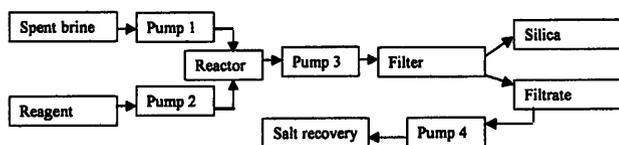5. Collected silica (Silica ppt) is washed with acid to yield pure silica.

Figure 1. Flow diagram of the laboratory processes.

Field Pilot Plant Operations: Based upon the results of the experimental studies conducted at Brookhaven National Laboratory, Oxbow Geothermal Corporation designed and constructed a pilot silica extraction plant to process Dixie Valley brines under field conditions. This pilot plant was designed to process a 5-gpm side stream flow of spent brine from the Dixie Valley power plant. Brine was obtained from the primary injection lines at a pressure of 140 psig and temperature of 230°F. The brine was cooled through a heat exchanger to 190°F prior to entering the silica extraction plant. The primary reason for cooling the brine was to prevent

flashing within the process stream and to avoid pressured vessels in the preliminary testing. This heat exchanger could conceivably provide process power and heat in a commercial plant.

Actual operation of the plant for sustained periods of time ranging from two to eight hours per run was at flows of 2 to 4 gpm and temperatures of 160 to 190°F. The chemistry of the brine entering the pilot plant is summarized in Table 1. The purpose of operating this initial pilot plant included:

1. Produce sufficient quantities of silica for characterization of properties such as purity and surface area.

2. Evaluate the effects of process temperature on produced silica properties and recovery.

3. Evaluate the effects of brine aging on produced silica properties and recovery.

4. Evaluate the effects of pH manipulation on silica properties and recovery.

Sample preparation: The purified samples were dried in a vacuum oven at 120°C under 5 torr for 16 hours. Representative commercial samples were prepared under the same conditions for use as standards.

Scanning Electron Microscopy (SEM) analyses were conducted with a JEOL 6400 using the secondary Electron Image method.

Major element analysis: The dried samples were analyzed using Energy Dispersive X-ray Spectroscopy (EDS).

Trace element analysis: Equal volumes of hydrofluoric and nitric acid were added to dried samples in a sealed Teflon tube. The samples were digested at a constant temperature (120°C) for 16 hours. The digested samples were diluted to 1% in nitric acid with 50 ppb of indium as an internal standard. Samples were then analyzed by VG PQ-2 ICP-MS spectroscopy. The instrument was tuned and calibrated according to company specifications. For quality control, the instrument was assured to reach a sensitivity over 2,000,000 counts/sec per 50 ppb internal standard and better than 99.5% correlation for the measured elements.

BET surface area, pore volume and pore diameter determination: These variables were determined from adsorption isotherms with nitrogen, which covers the accessible surfaces with a monolayer of gas. Gas adsorption, data acquisition and computation were performed using a Micromeritics Tristar instrument.

Results and Discussion

(A) **Initial laboratory test:** Conducted between 70 to 80°C, the precipitated silica reaction is completed in seconds. The filtering and washing processes, carried out at 25°C, produced pure silica at a 60% overall yield. Alternatively to prepare precipitated silica or silica gel, the geothermal brine had to be evaporated to produce crude silica. The crude silica was fused with sodium carbonate at 1000-1100°C, then treated with sodium hydroxide to form sodium silicate.

(B) **Silicate:** The purified sodium silicate can then be acidified to form silica products by conventional methods.

(C) **Field Pilot Plant Operations:** The results from this testing were very encouraging and provided results which will allow for design and construction of a more advanced recovery system. Significant results of this testing include the following:

1. The silica products were very similar to those produced in the laboratory. Table 2 summarizes the characteristics of typical field-precipitated silica.

2. The purity of the recovered silica product was very high and duplicated laboratory results.

3. Induction by seed crystal is essential for an efficient extraction of within a reasonable period of brine aging. Colloidal silica can be introduced to the precipitation tank through recycling of undersized silica, which is not removed by polishing filters.

4. Over the temperature range tested, the quantity of silica recovered is little affected. The size of the silica particles formed was not grossly affected by temperature.

5. Silica produced under basic conditions was readily recovered due to formation of particles greater than 1-micron diameter. Raising the pH of seeded silica-saturated brines resulted in voluminous silica precipitation, which is readily recovered.

6. Silica produced under acid conditions tended to show poor recoveries due to slower precipitation rates and due to production of a large fraction of under-sized particles, which bypassed the 1-micron polishing filter.

Figure 2. X-ray spectroscopy analysis for major elements.

Table 2. Physical Properties of the Silica Products.

	Leading commercial product	Dixie Valley silica 1	Dixie Valley silica 2
BET* surface area (m²/g)	237	487	396
Total pore volume (ml/g)	1.3	1.0	0.9
Pore diameter at which pore volume is at maximum (nm)	100 or greater	30	30

*Branuer-Emmet-Teller

(D)   Product characterization: The value of silica is related to its purity. The produced silica was analyzed by x-ray spectroscopy. The results shown in Figure 2 indicate that only peaks for the element silicon and oxygen appear. This indicates that the product is >99.9% pure. Analysis of the hydrofluoric acid digested samples by ICP-MS further support the purity of the product. Typical results given in Table 3 show that the purity is comparable to a leading commercial product. Colored impurities, e.g., iron and manganese, interfere with the quality of the product. This is particularly important if the product is to be used as filler in paper pulps and paints. This silica can be incorporated and tested in paint or paper for reflectance, sheen, stability, ease of dispersion and application and other properties relevant for commercial applications.(2)
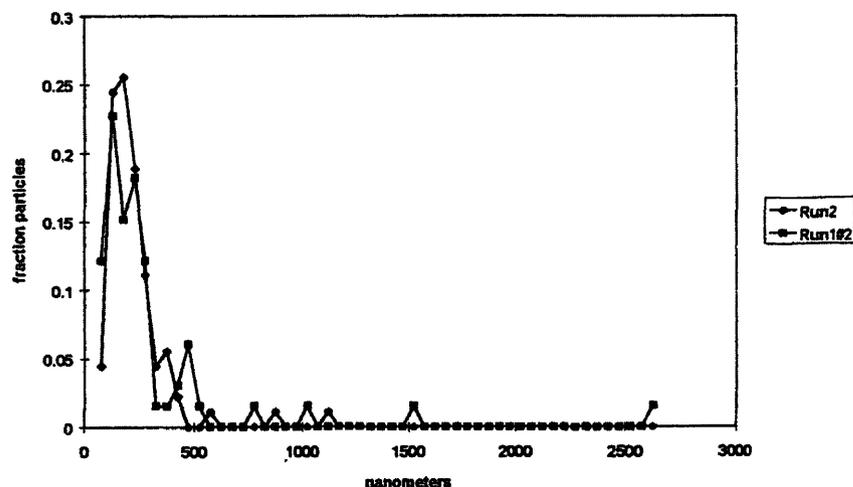
Table 3. Trace Elements Analyzed by ICP-MS with concentration in ppm.

Concentration (ppm)→	Mg	Al	Ca	Ti	Sb	Cs	Ba	Hg
Commercial ppt silica	45	65	970	53	0.2	0.02	21	48
Dixie Valley Run1#2	8400	760	988	17	84	86	6	16
Dixie Valley Run 1#2 washed	180	87	166	14	95	18	5	6
Dixie Valley Run 2	6094	559	700	11	66	97	9	18
Dixie Valley Run 2 washed	1554	560	514	21	71	25	5	4

Further, when used in fine chemical preparations, the properties of silica are highly dependent on the specific surface area, pore volume and pore diameter. The results shown in Table 2 compare the current product with a leading commercial product. The total surface area of the silica is higher which indicates it consists of smaller primary particle. Also the silica has a consistent peak in pore volume in pores around 30 nm in size.

Silica with a high surface area may be suitable for making thin layer chromatography (TLC) plates. In addition to surface area, the pore size of silica is important in chromatographic separation. Silica with large hole traps, results in broad-band molecular separations. Silica with a smaller pore will reduce this effect and improve resolution. (4)

A scanning electron microscope (SEM) was used to analyze the silica products. Figure 3 shows the silica at low and high resolutions. The results shown in Figure 4 show most particles lay between 20-30 microns, with a small amount of larger aggregates of 100 microns. The results of Figure 4 were computed using SigmaPlot image processing software. The particles shown are aggregates of the much smaller primary particles. Based upon the magnitude of the surface area the primary particles are of the order of 10 nm. The current particle size was achieved with a modest but carefully controlled amount of grind-

ing. The silica aggregates are soft enough to grind further or can be left at a fairly large size. Higher resolution photographs begin to show the very finely porous nature of the silica.

Conclusions

The recovery of minerals from geothermal resources to offset power generation costs warrant furthers consideration and R&D efforts. The initial pilot plant testing has generated the following conclusions. More tests are planned to gather data needed for an economic evaluation of the process.

1. Directly induced silica precipitation has been demonstrated in field tests.

2. Preliminary results show that the product is very pure, has a high surface area, and a small primary particle size.
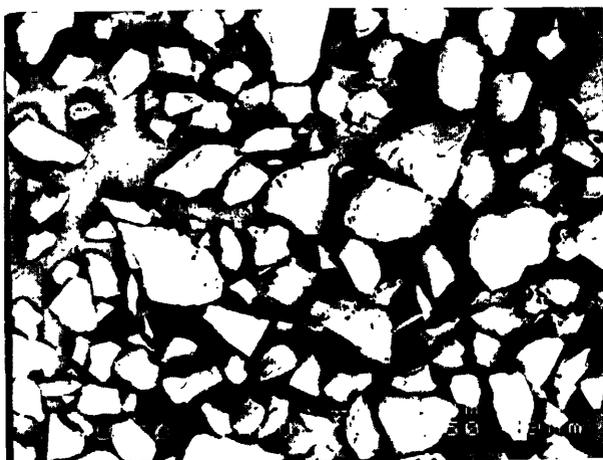

Figure 3a. Scanning Electro Microscopy at 50x for particle size analysis.
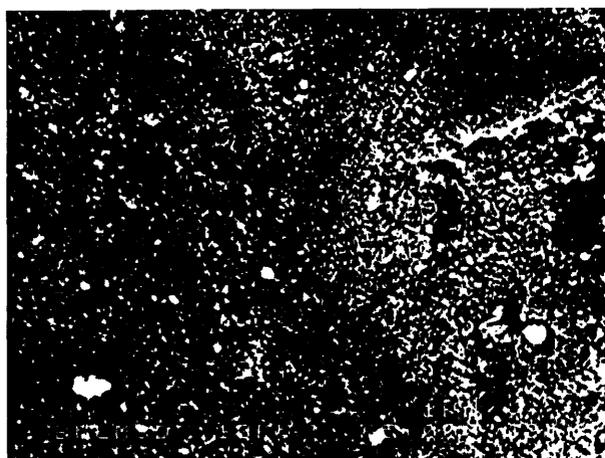

Figure 3b. Scanning Electro Microscopy at 5000x for particle size analysis.
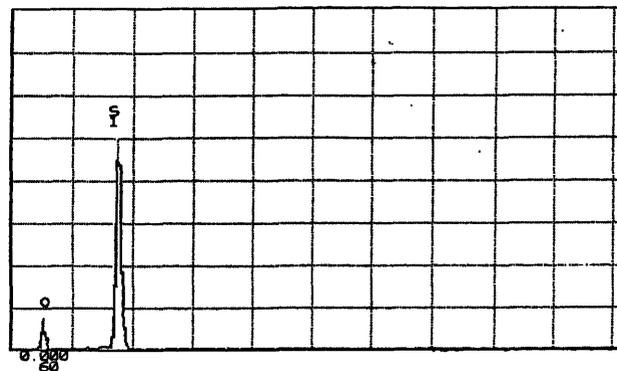

Figure 4. Size distribution of Oxbow silica samples.

3. Commercial silicas vary in their quality and expense to produce. Typical precipitated silicas cost on the order of $1.00 per pound for production costs. At this early stage of development, the cost for expendables used in the production of geothermal silica is estimated to cost $0.25 per pound or is equivalent to the approximately 5 kwhr in geothermal electricity sales.

4. The process is a promising commercial outgrowth of geothermal power production. Further tests of process control and optimization of product quality and yield are in progress.

The high quality of the silica produced so far bodes well for the development of high-valued silica products such as chromatographic materials and catalyst carriers.

Acknowledgements

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