

Developing a Process for Commercial Silica Production from Geothermal Brines

W. Bourcier, S. Martin, B. Viani, and C. Bruton

*This article was submitted to
Geothermal Resources Council 2001 Annual Meeting, San Diego,
California, August 26-29, 2001*

U.S. Department of Energy

Lawrence
Livermore
National
Laboratory

April 11, 2001

DISCLAIMER

This document was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor the University of California nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or the University of California, and shall not be used for advertising or product endorsement purposes.

This is a preprint of a paper intended for publication in a journal or proceedings. Since changes may be made before publication, this preprint is made available with the understanding that it will not be cited or reproduced without the permission of the author.

This report has been reproduced directly from the best available copy.

Available electronically at <http://www.doc.gov/bridge>

Available for a processing fee to U.S. Department of Energy
And its contractors in paper from
U.S. Department of Energy
Office of Scientific and Technical Information
P.O. Box 62
Oak Ridge, TN 37831-0062
Telephone: (865) 576-8401
Facsimile: (865) 576-5728
E-mail: reports@adonis.osti.gov

Available for the sale to the public from
U.S. Department of Commerce
National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
Telephone: (800) 553-6847
Facsimile: (703) 605-6900
E-mail: orders@ntis.fedworld.gov
Online ordering: <http://www.ntis.gov/ordering.htm>

OR

Lawrence Livermore National Laboratory
Technical Information Department's Digital Library
<http://www.llnl.gov/tid/Library.html>

DEVELOPING A PROCESS FOR COMMERCIAL SILICA PRODUCTION FROM GEOTHERMAL BRINES

W. Bourcier, S. Martin, B. Viani, and C. Bruton
Lawrence Livermore National Laboratory
Livermore California 94550 USA

Abstract

Useful mineral by-products can be produced from geothermal brines. Although silica has many commercial uses, problems remain in producing a marketable product. We are conducting laboratory and modeling studies aimed at optimizing for rubber additive use, the properties of silica precipitates from Salton Sea and Coso-like geothermal fluids. Our goal is to develop a robust technique for producing silicas that have desirable physical and chemical properties for commercial use, while developing a generic understanding of silica precipitation that will allow extraction to be extended to additional fluid types, and to be easily modified to produce new types of marketable silica.

Our experiments start with an acidified geothermal fluid similar to those treated by pH modification technology. Silica precipitation is induced by adding base and/or adding Mg or Ca salts to affect the nature of the precipitate. For the analog Salton Sea fluids, adding base alone caused silica to precipitate fairly rapidly. To date, we have characterized precipitates from experiments in which the final pH varied from 4 to 8, where NaOH and Na₂CO₃ were added as bases, and CaCl₂ and MgCl₂ were added as salts.

SEM photos of the silica precipitates from the Salton Sea and Coso fluids show that the silica particles are clusters of smaller silica particles down to the resolution of the SEM (about 80-100 nm in diameter). The particle sizes and surface areas of silicas from the Salton Sea and Coso analog brines are similar to the properties of the Degussa silica commonly used as a rubber additive. An evaluation of the strength of the silica-organic bond as tested by dispersion in oil (polybutadiene) was inconclusive. Neither the Degussa materials nor our laboratory precipitates dispersed readily in nor dispersed down to the fundamental particle size. Preliminary NMR data indicates that the Degussa silica has a smaller degree of silica polymerization (a slightly smaller average number of Si-O bonds per silica tetrahedron) than the synthetic samples, but a comparable degree of hydrogen bonding of the surface silanol sites.

Introduction

The problem of silica scaling in geothermal plants is now being approached as an opportunity to encourage precipitation of a useful silica byproduct. A technology that turns a waste stream of silica scale into a marketable commodity will have a favorable impact on the economics of geothermal power use. Silica, and especially high-surface area amorphous silica, is widely used in industry. The bulk of these specialty silicas are currently being synthesized in acid/base aqueous precipitation processes that could easily be carried out using geothermal fluids before reinjection. Upstream silica removal would

also eliminate silica scaling problems during reinjection. For these reasons, there is currently a considerable effort by geothermal energy producers to develop the appropriate silica extraction technologies (Brown, 2000; Johnson, 1999).

In spite of this effort, there are currently no successful commercial demonstrations of extraction of specialty silicas from geothermal fluids in the U.S. Produced silicas generally have been sold as low-cost concrete additives (Escalante et al., 1999) or disposed of in landfills. Problems remain in generating high-purity silicas with surface areas, pore sizes, densities, and other properties that match the requirements for commercial silicas (Lin et al., 2000). Even when these problems seem to be solved, finding a commercial market has remained elusive (Brown and Bacon, 2000).

We report here results of laboratory and modeling studies aimed at optimizing for commercial use the properties of silica precipitates from fluids similar to those of two geothermal systems: high-salinity fluids from the Salton Sea geothermal field, and moderate salinity fluids from the Coso geothermal field. Our goal is to develop a simple robust technique for producing silicas having desirable physical and chemical properties for commercial use. We also hope to develop a basic understanding of how the chemical and physical properties of a fluid affect the properties of silica precipitates. This will allow us to extend the extraction technology to additional fluid types and silica markets.

Commercial Silica Markets

There are numerous industrial uses for silica. Among the largest are as refractory bricks and cement. However, the low costs of silica for these applications make them unattractive targets for geothermal silicas. Among specialty applications for silica, the largest markets exist for a rubber reinforcement binder (rubber used in shoes and tires), silicone adhesives and paints, dessicants, functional fillers for paper, raw material for zeolite synthesis, catalytic supports, polishing compounds, and odor and waste control products.

In order to select the best markets for geothermal silicas, several factors must be considered. We must be able to match the physical and chemical properties of silica used in a particular market, identify a market that is large enough to include the volume of geothermally produced silica without being overwhelmed, and also obtain a price for produced silica such that the silica extraction process is economic.

The silica through-put in geothermal plants is large. Currently, the available silica from geothermal plants worldwide is estimated at about 500,000 MT/year, or about 3 million pounds per day (Johnson, 1999). Compare this with the production of precipitated silicas (the silica used in tires and rubber shoe soles) that in 1995 was about 5.4 million pounds per day and was growing at about 5% per year. This precipitated silica product has the largest world usage of any type of synthetic amorphous silica.

A growing market for "green tires" that incorporate about 30 wt. % silica may significantly increase the market for precipitated silicas. Tires made with a silica

reinforcer are stronger, bond better to steel belts, have less rolling resistance (improve mileage), and can be produced in any desired color, unlike tires with added graphite reinforcer that give tires their black color. About 360 million tires are produced each year in North America. If green tires became favorable, this would more than double the current market for precipitated silicas to over 12 million pounds per day, even if only half the tires incorporated the silica additive. The current price for precipitated silicas is about 70 cents per pound. For these reasons, the rubber additive market is our primary target for geothermal produced silicas, although other markets will also be considered.

Silica as a Rubber Additive

Modern tire tread rubber is produced by mixing and curing a variety of organic and inorganic compounds, which commonly include as major constituents: polybutadiene, aromatic oils, and up to 30 wt. % silane coupled silica. The mixture is stirred vigorously and allowed to cure. The particle size of the silica additive is extremely important. The best rubber reinforcement occurs when the silica particles are less than about 50 nm in size. However, if 50 nm particles were added directly to the mixture, the viscosity would be so large as to prohibit mixing. Therefore the optimum silica additive is a larger agglomerate of the small particles which are so loosely held together that they disperse during mixing to give rise to the smaller particles. The surfaces of the 50 nm sized particles then bond to the tire constituents. The silica does not dissolve into the mixture as molecular silica.

A manufactured silica that is commonly used to make tire rubber is the Degussa product VN3. As discussed below, this material consists of 20-150 micron particles which themselves are agglomerates of sub-micron particles. The texture resembles that of a raspberry with the individual nodes on the berry corresponding to the particles having diameters of tens of nanometers. The measured gas adsorption surface areas of the Degussa silicas are in the range of 100-200 m²/g. This rather large value indicates there is significant internal surface area. The geometric surface area of the agglomerates (assuming a smooth surface) would be only 0.1-0.01 m²/g.

The goal of our laboratory experiments is to produce precipitated useful as a rubber additive. We have therefore characterized the Degussa VN3 material in detail and have tried to match its properties with our laboratory precipitates. With our characterization work we hope to identify the key molecular properties of the precipitated silicas in terms of number and types of silanol surface sites, degree of polymerization of the silica network, and amount of adsorbed water, which are favorable for its use as a rubber additive. Our experimental method will be adjusted to generate silicas that match the key physical properties of rubber additives, such as surface area, pore size and distribution, and dispersion in oil. We will develop an optimized precipitation methodology detailing the type of base and/or salt used to induce precipitation, the final pH of the precipitation process, and type of coagulant (if needed) added, to induce rapid precipitation of marketable precipitated silica.

Laboratory Experiments

Design

The pH modification (pH Mod) technology is one of the most successful methods for preventing silica scaling at geothermal sites (Gallup, 1996). The process involves adding acid to the geothermal fluid to lower the rate of silica precipitation. Our experiments therefore start with an acidified geothermal fluid. Silica precipitation is then induced by adding base and/or adding Mg or Ca salts. The type of base and salt, and the rate it is added, affect the nature of the precipitate. For the analog Salton Sea fluids, adding base alone caused silica to precipitate fairly rapidly, as desired. The lower salinity Coso analog fluids needed additional salt (CaCl_2 or MgCl_2) as well as base to stimulate silica precipitation. In both cases, the silica precipitate was then removed by filtration or centrifugation for characterization. Figure 1 shows a schematic of the silica extraction step in relation to energy and other metals extraction at a geothermal power plant.

Methods

We first performed laboratory simulations of the silica precipitation process in glassware at room temperature. This allowed us to develop procedures for preparing silica supersaturated solutions, for adding base to the solutions to promote silica precipitation, and for separating and examining the precipitate.

We are currently performing bench-top tests of the silica precipitation process in either an open 5 liter Teflon-coated stirred glass reaction vessel at 80°C , or a pressurized 20 liter stainless steel vessel for temperatures up to 120°C . We used simplified synthetic solutions at first but have been adding additional components so that we can examine the effect of each on the silica precipitate. The optimized process will later be performed on-site in a side stream of real geothermal fluid.

We start with brine containing 700 ppm silica, prepared from a known concentration of sodium metasilicate solution. Prior to the experiment, the alkaline sodium silicate solution is acidified to pH 2-3. Polymerization of silica begins at this point, and it is critical to begin the experiment immediately in order to obtain reproducible results. A base/salt is then added induce precipitation. To date, we have characterized precipitates from experiments in which the final pH varied from 4 to 8, where NaOH and Na_2CO_3 were added as bases, and CaCl_2 and MgCl_2 were added as salts.

Characterization of precipitates

A variety of characterization techniques are used to examine the silica precipitates. Textures and morphologies are examined using both optical and SEM microscopies. Surface area and pore size distribution are determined using the BET gas-absorption, and particle size distributions are determined using dynamic light scattering (DLS). Some samples are also characterized using nuclear magnetic resonance (NMR) in order to determine the number and types of surface silanol sites, the amounts of sorbed water, and

the degree of polymerization of the silica network. Samples are also silane coupled and dispersed in polybutadeine oil to test their suitability as rubber additives.

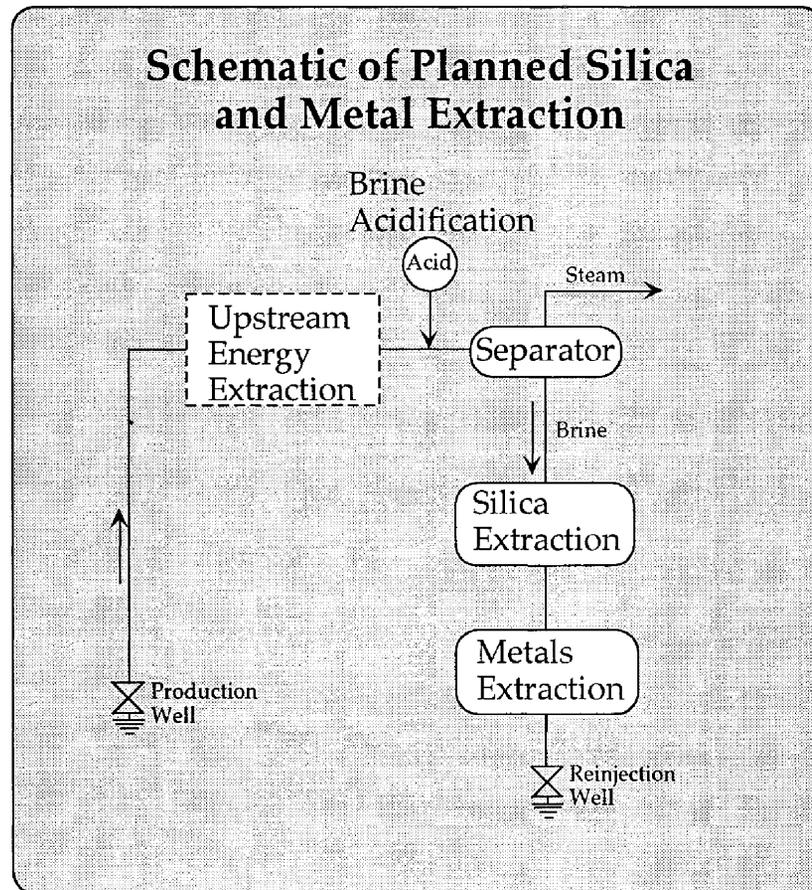


Figure 1. Schematic of silica and metals extraction processes in a geothermal power plant.

SEM Photos of Silicas

Figure 2 shows photomicrographs of DegussaVN-3 silica (a) and precipitates from our analog Salton Sea (b) and Coso fluids (c). SEM photos of all the silica precipitates show that the silica particles are always clusters of smaller silica particles down to the resolution of the SEM (the smallest resolvable particles are about 80-100 nm in diameter). The SEM photos in most cases confirm the particle sizes measured using DLS. Samples for SEM must be de-hydrated and placed in a hard vacuum, a process that may introduce changes in properties of the precipitated silicas. We also show a Salton Sea analog silica precipitate that has been silane coupled (d), a process that appears to increase the particle size.

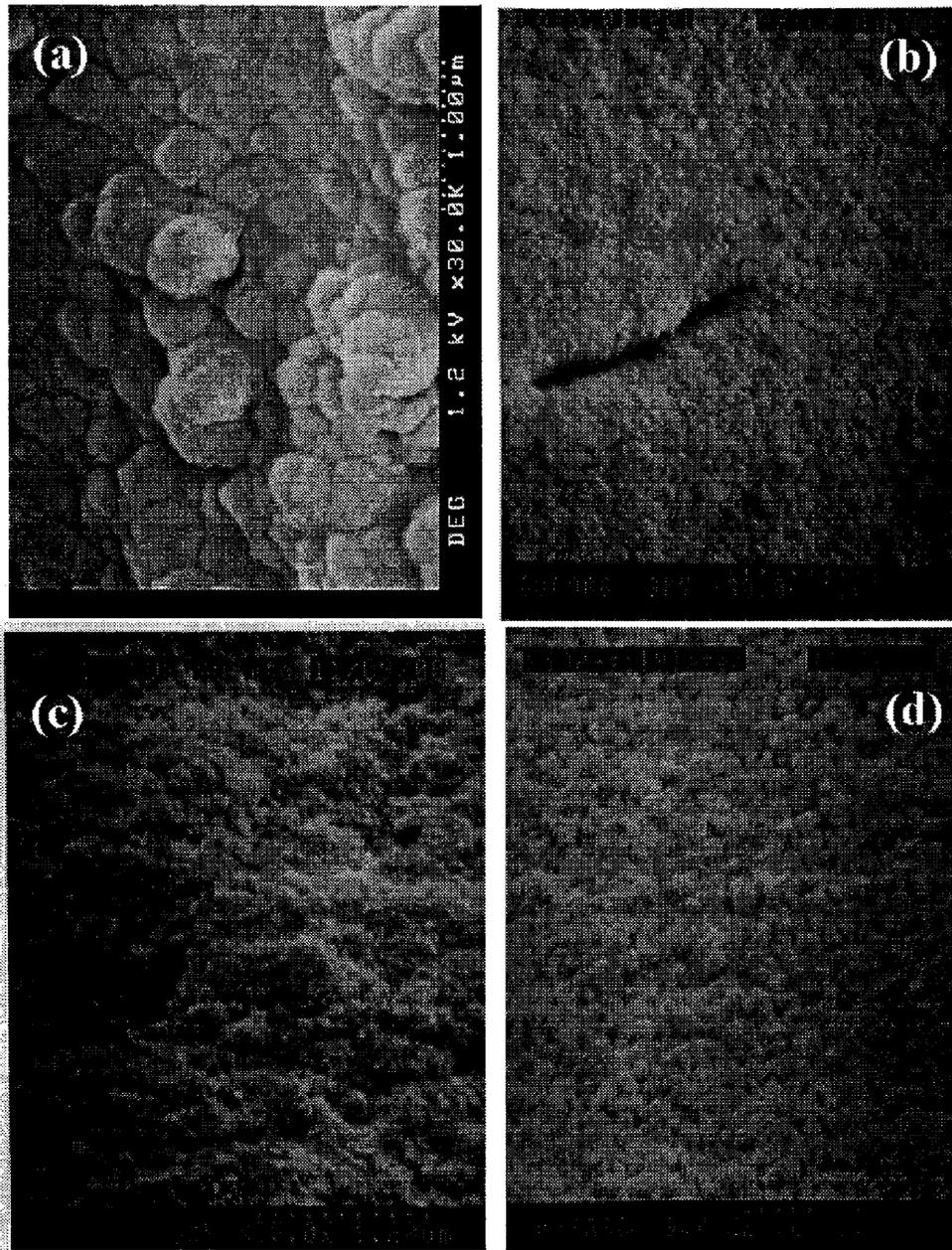


Figure 2. Comparison of SEM photomicrographs of (a) Degussa commercial precipitated silica, and laboratory-produced silica precipitates from (b) Coso analog fluids and (c) Salton Sea analog fluids. In addition, (d) shows silica (c) after silane coupling. Scale bars are about one micron in all photos.

Particle Size Analysis

Dynamic light scattering (DLS) provides particle size distributions of silica precipitates. With increasing time and pH, our laboratory silica precipitates show growth of larger particles at the expense of smaller particles. Particles appear to grow rapidly in seconds to minutes. Thus a very short residence time would be needed to keep particle sizes small.

The size distribution of the pH 5 experiments of the simulated Salton Sea fluid is similar to the measured distribution of the Degussa silica.

BET Surface Areas of Silica Precipitates

High surface areas are characteristic of small particles or particles with large amounts of internal surface area. The Degussa silicas commonly used as rubber additives have surface areas in the range of 100-200 m²/g. Our Degussa VN3 sample had a measured surface area of about 150m²/g. Our precipitated silicas had measured surface areas in this range or higher. Table 2 shows our measured surface areas for both simulated Salton Sea fluids and simulated Coso fluids. The Coso precipitate generated by base addition to pH 6 had the highest surface area of any of our laboratory silicas. The two Salton Sea analog fluid precipitates were both generated at pH 5. The two experiments differed only in that Si110300 used a more dilute NaOH solution and therefore the precipitation occurred over several hours. Sample Si120700 precipitated in less than 15 minutes and has a much smaller surface area.

Table 2. BET surface areas of silicas.

Sample ID	BET Surface Area, m²/g
Degussa Ultra VN3 SP	150
Si 110300 Salton Sea analog fluid	313
Si 120700 Salton Sea analog fluid	118
Si 011201 Coso analog fluid	509

Oil dispersion

Silicas are treated with a silane coupling agent prior to mixing with rubber precursors. The coupling agent bonds to the silica surface through silanol groups (Si-OH) and changes the silica surface from hydrophilic to hydrophobic. The hydrophobic surface bonds well with the rubber. The silane-coupled silicas must disperse readily in oil.

The effectiveness of the silica-organic bond is tested by dispersion in oil. We examined the tendency for silane-coupled silicas to disperse in polybutadiene by examining them using optical microscopy. A few milligrams of silica powder were placed into a few drops of oil and stirred. The results were inconclusive. Neither the Degussa materials nor our laboratory precipitates dispersed readily in oil. Vigorous mixing was needed in order to break the aggregates down into sub-micron particles. None of the samples appeared to disperse down to the fundamental particle size believed to be a few tens of nanometers.

We did observe that our precipitated silicas had much higher relief in oil than the Degussa silica. Apparently the refractive index of water is much closer to that of the Degussa silica than that of our precipitated samples. It may be that the water content of our precipitates is lower than the water content of the Degussa silica. Water contents of

the silica will be measured using differential thermal analysis (DTA) in order to resolve this issue.

Nuclear Magnetic Resonance Spectroscopy

Preliminary NMR data shows that the average silica-oxygen bond numbers, amounts of adsorbed water, and amounts of hydrogen bonding differ among the various solids. In general, the Degussa material has a smaller degree of silica polymerization (a slightly smaller average number of Si-O bonds per silica tetrahedron) than the synthetic samples, but a comparable degree of hydrogen bonding of the surface silanol sites. Although at this point we are uncertain how these observations affect bonding of the silica in rubber, we can use the observations in an empirical way to produce silicas with properties that match the silicas that bond well to rubber.

Computer Modeling Results

One of the major differences between commercial silicas and geothermally produced silicas is their purity. Commercial silicas are generally very pure, but geothermal silicas may have significant amounts of impurities such as Fe, Al, and Ca. These impurities can sometimes be leached out with acid (Lin et al., 2000). However, it may be possible to design the silica extraction process to selectively precipitate these impurities before or during silica precipitation. The metal precipitates can then be dissolved to leave behind a high purity silica precipitate. This process also has the potential for efficiently separating metals which themselves have economic value.

We performed modeling calculations aimed at determining a method for removing potential impurities, in particular iron. Our first calculation simulates the effect of adding soda ash (Na_2CO_3) to Salton Sea brine to increase the pH (Figure 3). Soda ash should react with the dissolved iron in the brine to precipitate iron carbonate (FeCO_3) and perhaps other carbonates as well. The results for the simplified Na-Ca-Mg-Fe-Zn-C-Si-Cl-H₂O system show favorable trends (Figure 3). Iron carbonate is the most insoluble carbonate and precipitates first as Na_2CO_3 is added, followed closely by CaCO_3 and then ZnO. In reality, the precipitate will probably be a single carbonate phase that contains varying amounts of Ca, Fe, Mg and Zn. These results suggest that it will be possible to selectively lower the iron content of the brine with soda ash addition. The model results are currently being tested with silica precipitation experiments in which the simulated Salton Sea brine contains representative amounts of Fe, Mn, Zn, Ba, and Sr in addition to Na and Ca chloride.

Summary and Conclusions

Silica production from geothermal brines can be used to limit scaling and reduce reinjection problems. The rubber additive market is lucrative primary target for silica produced from geothermal brines. Experimental results to date show that silica precipitates can be produced from Salton Sea and Coso brines that possess surface areas and particle size distributions similar to commercial silica used as tire additives.

However, key questions remain. For example, how important is the pore size and pore size distribution in the agglomerates, and what is the optimum size of silica particles for use in tires? Although a size of about 50 nm has been provided, we need to confirm that number with microscopic (SEM, TEM) analysis of actual silica-reinforced tire rubber. It would also be helpful to examine how well the silica particles disperse in rubber. In addition, the observations of differences in refractive index between Degussa and synthetic silica suggest that we should analyze their water contents to determine if there is an ideal amount of water in the silica that is best for rubber synthesis.

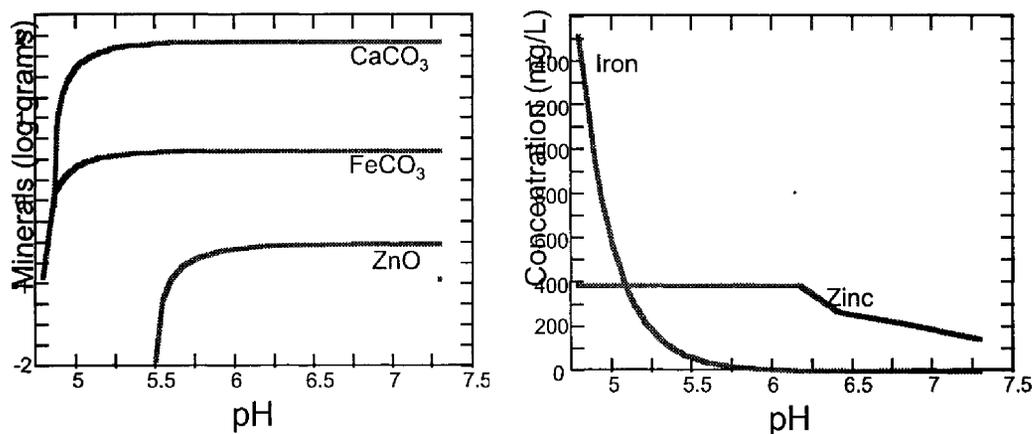


Figure 3. Results of modeling calculation of the effects of adding Na_2CO_3 to Salton Sea brine to raise pH and induce metal precipitation. The concentration of iron is selectively lowered due to iron carbonate precipitation until just above pH 5.5 where zinc oxide begins to precipitate. Calcite also precipitates as the pH rises. Calculations performed using the React code (Bethke, 1996).

When impurities reduce the value and/or performance of the silica product, it may be possible, given results of computer modeling and experiments in progress, to design the extraction process to selectively precipitate these impurities as a separate phase. This phase can then be efficiently separated from the silica and used as a feedstock for additional metal extraction.

Acknowledgements

The authors wish to thank the Office of Geothermal and Wind Technologies, U.S. Department of Energy, and Raymond LaSala, DOE Program Manager for research on geothermal drilling and energy conversion technology, for support of this research. This work was performed under the auspices of the U.S. Department of Energy by University of California Lawrence Livermore National Laboratory under contract No. W-7405-Eng-48.

References

Bethke C. M. (1996) *Geochemical Reaction Modeling*. Oxford University Press, Oxford 396 p.

- Brown, K. L. (2000) Geochemistry of cascaded development and mineral extraction. In "Advances in Geochemical methods for Geothermal Applications", GRC Short Course Notes, Oct. 15-16 2000, Reno Nevada.
- Brown K. L. and Bacon L. G. (2000) Manufacture of silica sols from separated geothermal water. *World Geothermal Congress*.(in press).
- Escalante J. I., Mendoza G., Mancha H., Lopez J., and Vargas G. (1999) Pozzolanic properties of a geothermal silica waste material. *Cement and Concrete Research* 29(4), 623-625.
- Gallup D. L. (1996) Brine pH modification scale control technology. *Geothermal Resources Council Transactions*, 749-755.
- Johnson J. H. (1999) High performance natural amorphous silicas and silicates for the paper industry, pp. 10 pages. University of Wellington. (unpublished report)
- Lin M., Bohenek M., Premuzic E., and Johnson S. D. (2000) Silica production from low-salinity geothermal brines. *Geothermal Resources Council Transactions*, p. 671-674.