Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Separation off Silica from Spent Geothermal Fluids by Adsorptive Bubble Techniques

Eric Heinen De Carlo[a]; Christina Ronay[a]
[a] DEPARTMENT OF CHEMISTRY, AND HAWAII INSTITUTE OF GEOPHYSICS UNIVERSITY OF HAWAII, HONOLULU, HAWAII

To cite this Article De Carlo, Eric Heinen and Ronay, Christina(1987) 'Separation off Silica from Spent Geothermal Fluids by Adsorptive Bubble Techniques', Separation Science and Technology, 22: 4, 1293 — 1311
To link to this Article: DOI: 10.1080/01496398708057181
URL: http://dx.doi.org/10.1080/01496398708057181

SEPARATION SCIENCE AND TECHNOLOGY, **22**(4), pp. 1293-1311, 1987

Separation of Silica from Spent Geothermal Fluids by Adsorptive Bubble Techniques

ERIC HEINEN DE CARLO* and CHRISTINA RONAY

DEPARTMENT OF CHEMISTRY AND HAWAII INSTITUTE OF GEOPHYSICS
UNIVERSITY OF HAWAII
HONOLULU, HAWAII 96822

Abstract

A method is described for the separation of amorphous silica from supersaturated high ionic strength geothermal fluids produced by the Hawaii Geothermal Project Well-A. A bench-scale technique which makes use of adsorptive bubble flotation is employed to remove silica after flocculation by the addition of polyvalent metal ions to hot (60–90°C) spent brine discharge. Ferric and aluminum salts are evaluated as flocculants under varying conditions. The anionic surfactant sodium lauryl sulfate and the cationic surfactant lauryl amine hydrochloride (LA) are utilized as the collectors below and above the isoelectric point, respectively. Efficiency of removal of the silica is pH, metal concentration, and surfactant-type dependent. Best results are achieved under slightly alkaline conditions (pH = 8), using $3.75 \times 10E^{-4}$ *M* ferric ion present as its sulfate, LA as the collector, and with a gas flow of 15 ± 3 mL/min. Under these conditions, approximately 70 ± 2% of the total silica is separated from the brine discharge; this value, although not quantitative, represents more than 85% removal of the silica present above its amorphous solubility at the operating temperature. After the separation process, fluids contain residual concentrations of silica which are not expected to result in scale deposition and which can then be passed through heat exchangers to extract further energy for secondary uses.

INTRODUCTION

Geothermal fluids discharged by the Hawaii Geothermal Project Well-A (HGP-A) on the island of Hawaii consist of a mixture of meteoric water

---

*To whom correspondence should be addressed.

and seawater that has reacted at depth under high-pressure and high-temperature (350°C) conditions with basalts of the Kilauea Volcano east rift zone (*1*). The geothermal test well, completed in 1976, penetrates basalt to a depth of 1966 m. The well site is 182 m above sea level, so most of the well bore is below sea level (*1*–*3*). The bottom hole temperature of the well, measured under shut-in conditions, reached a maximum of 358°C, thus making it one of the hottest geothermal wells on the planet. The test facility is presently capable of producing 49,000 kg/h of a geothermal fluid mixture composed of approximately 43% steam and 57% liquid. The separated brine produced is approximately 0.22 *M* in NaCl and is highly enriched over its seawater component in Ca, K, Li, and $SiO_2(aq)$ (*4*). A variety of other species of environmental interest such as oxyanions of arsenic, and selenium, $H_2S(aq)$, HS^-, Pb^{2+}, and Cd^{2+} are also present in the fluid and steam phase at differing concentrations. The speciation is governed by the overall chemistry of the fluids emanating from the well (*4*).

The seawater component of the geothermal fluids has increased steadily over the 4 years during which the well has been under nearly continuous production. Although the total dissolved solids (TDS) reflect this increase in seawater recharge (i.e., Cl^-, Na^+, K^+, Mg^{2+}, Ca^{2+}), the $SiO_2(aq)$ content of the brine has not changed significantly (see Table 1). The concentration of silica in the fluids is governed by its amorphous solubility and is indicative of the water–basalt interaction temperature in the geothermal reservoir (*5, 6*).

TABLE 1
Chemical Composition of HGP-A Unflashed Brine[a]

Date	Li	Na	K	Ca	Mg	Cl	SiO_2
06/20/81	0.38	1,280	220	30	0.008	2,320	—
08/03/81	0.49	1,710	265	55	0.027	2,940	844
12/22/81[b]	0.58	1,820	295	56	0.016	3,210	—
06/07/82	0.94	3,120	525	122	0.051	5,670	832
10/18/82	1.03	3,650	610	182	0.084	6,660	802
06/09/83	1.16	4,480	660	269	0.140	8,275	745
01/12/84	1.26	4,930	756	358	0.260	8,970	825
06/26/84	1.13	4,840	702	489	0.302	9,000	900
11/28/84	1.12	5,420	733	399	0.201	9,514	873
06/13/85	1.11	5,400	664	493	0.241	10,035	853
11/14/85	—	5,130	616	464	0.220	10,100	887

[a] All concentrations expressed in mg/L.

[b] Well started up again after shutdown from September to December 1981.

Presently, well production results in the generation of 3 MWE through a steam-driven turbine and represents nearly 5% of the electricity consumed on the island of Hawaii (*1*). Other wells in the vicinity are being tested and may be brought into commercial production soon. Commercial production of geothermal energy in the area will necessitate the inception of appropriate wastewater disposal methods should the wells be liquid-producing rather than dry steam reservoirs. The present method employed at HGP-A involves dumping the spent brine flow into an atmospheric flash tank (or rock muffler) where the fluids flash to atmospheric pressure and 100°C. The brine flow is then discharged into holding ponds and percolates into the ground. Although this method is environmentally acceptable on the small scale of HGP-A, it is by no means satisfactory for larger operations. Upon cooling, the fluids become supersaturated in SiO_2, which then slowly polymerizes and precipitates out of solution. The silica content of approximately 1.1 g/L in the spent brine results in the deposition of large amounts of scale in pipes as well as in the settling ponds; these deposits eventually cause serious clogging. Alternative brine disposal methods such as reinjection at depth under pressure or secondary use of the fluids such as in heat exchangers are not presently feasible at HGP-A, primarily because of the silica scaling. To make these processes viable, an effective method for silica removal or the selective inhibition of scale formation must be developed.

In this paper we evaluate a bench scale technique utilizing adsorptive bubble flotation for the removal of colloidal silica from the hot (60–90°C) spent brine discharge. Flocculation of the silica is achieved by the addition of small amounts of ferric or aluminum salts in slightly alkaline media and collection of the floc with long-chain alkyl surfactants. This technique was derived from an analytical method developed in our laboratory in order to separate the oxyanions of arsenic from cooled unflashed geothermal brine selectively (*4*). The method in the referenced study was also found to result in the separation of most of the silica from solution under certain conditions. The present study seemed a logical extension to attempt to solve a troublesome by-product disposal problem.

Adsorptive bubble separations have been in use since the early 1900s and have been extensively employed in the mineral processing industry for ore beneficiation (*7–9*). More recently, flotation methods have been successfully applied to the removal of heavy metals from wastewaters (*10–12*). Modern analytical applications of the methods were pioneered by Zeitlin and coworkers a few years after adsorbing colloid flotation (ACF) was first described by Sebba (*13*). Other applications of flotation technology have been extensively reviewed (*9, 14–16*).

Adsorptive bubble techniques are based on interactions between (ionic) surface-active agents and (residually charged) nonsurface-active species in liquid suspensions. Concentration of the nonsurface-active species of interest at the air/water interface of gas bubbles rising through the water column and their subsequent removal from solution are achieved because of the hydrophobic nature of the uncharged hydrocarbon tails of surfactant/floc entities. The effectiveness of these methods, which make use of the properties of the electrical double layer, is a function of a number of parameters such as ionic strength, pH, analyte concentration range, type and concentration of surfactant, and precipitating agent (*7, 8, 10, 16*). Physical characteristics of the cell, gas bubble size, and flow rate can also affect flotation behavior (*4, 8, 10, 17, 18*).

EXPERIMENTAL

Apparatus and Equipment

The flotation apparatus used in this investigation is shown in Fig. 1. The cell is the same as that used in previous work in our laboratory (*4, 17–20*). All silica determinations were carried out by atomic spectroscopy with a Leeman Labs Plasma Spec I inductively coupled argon plasma atomic emission spectrometer (ICAP/AES) or a Perkin-Elmer Model 603 atomic absorption (AA) spectrometer with the N_2O–C_2H_2 flame. The pH of solutions was measured with an Orion Model 404-A ionalyzer and a combination pH electrode. Calibration of the pH meter was checked several times daily by using standard reference buffer solutions (pH 4.01, 7.00, and 10.0) obtained commercially. Electrophoretic mobility was measured with a Zeta Meter Corporation Zeta Meter equipped with a Zeiss stereomicroscope and a Plexiglas UVA Type II electrophoresis cell.

Reagents

All chemicals used were analytical reagent grade or better. Aqueous solutions of reagents were prepared in water purified through a Barnstead 4 L glass still and Nanopure cartridge system. Resistivity of the water used was always greater than 15 MΩ·cm. Deionized water was used on site to rinse the apparatus after acid washing between experiments (at HGP-A). Aqueous surfactant solutions were prepared in the following concentrations: Lauryl ammonium chloride (LA), 0.011 *M* (2.5 mg/mL); sodium lauryl sulfate (SLS), 0.0017 *M* (0.5 mg/mL). Freshly

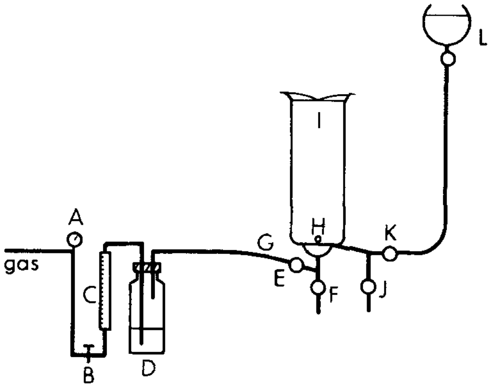


FIG. 1. Flotation cell and associated apparatus. After De Carlo et al. (*17*).

prepared solutions of 0.1 *M* $FeCl_3 \cdot 6H_2O$, 0.053 *M* $Fe_2(SO_4)_3 \cdot xH_2O$, 0.1 *M* $Al(NO_3)_3$, and 0.05 *M* $Al_2(SO_4)_3$ were used as a source of metal ion for flocculation of the silica in the brine. Commercially obtained spectroscopic standards of 1000 μg/mL and in-house prepared 600 μg/mL of Si as Na_2SiF_6 were diluted appropriately to prepare working standards for atomic spectroscopy.

Analytical Procedure

Spent geothermal brine was collected in a Dewar flask from the inlet of the atmospheric flash tank or at the rock muffler immediately prior to flotation runs. The temperature was measured *in situ* during collection and found to be 92 ± 2°C; the temperature was a few degrees lower when measurements were taken near the rock muffler rather than the inlet to the flash tank. Flotations were always carried out on brine that had not cooled to temperatures below 60°C. When the fluid temperature dropped below this value, a new sample was collected from the flash tank. The 200-mL aliquots of brine used in all experiments were spiked with varying amounts of Fe(III) and Al(III) salts, and the pH was adjusted with NaOH to the desired value. This procedure resulted in the hydrolysis of the metal cations and the formation of a colloidal suspension that clouded the brine and coagulated rapidly under certain experimental conditions. After stabilization of the pH (but prior to a temperature drop below 60°C) the suspension was transferred to the flotation cell, and N_2 gas flow was initiated at 15 ± 3 mL/min. An appropriate amount of the surfactant solution was then injected into the cell with a hypodermic syringe. The foam was allowed to collect at the top of the cell for 3 to 5 min (sometimes up to 10 min). The underlying mother liquor was then sampled and diluted tenfold in a volumetric flask for subsequent residual silica determinations. Tenfold dilutions were utilized to prevent polymerization should the remaining silica be present above its amorphous solubility at room temperature. The foam layer overlying the mother liquor was manually removed and stored in plastic containers for subsequent analyses. A minimum of three replicate flotations was undertaken for each set of experimental conditions in order to evaluate the reproducibility of the technique. Flotation studies were carried out as a function of pH, concentration of flocculant (metal ion), surfactant type, and in the presence of several surface altering ions (SO_4^{2-}, Cl^-, NO_3^-).

Electrophoretic mobility was measured on selected sample runs under a variety of conditions. Great difficulty was encountered in the measurement of the electrophoretic mobility of colloids at elevated temperature because of thermal overturn in the electrophoresis cell. Reliable data could only be obtained for samples that had been rapidly cooled to ambient temperature. The data obtained at low temperatures, however, may not be representative of the behavior of the floc particles at higher temperature. These problems are discussed below.

RESULTS AND DISCUSSION

Effect of pH and Surfactant Type

A series of flotations to evaluate the effect of pH and surfactant type on the removal of SiO_2 from hot spent brine was carried out with a fixed concentration of Fe^{3+} used as the precipitating agent. The concentration of ferric ion (2.65×10^{-4} *M*) present as the sulfate salt was chosen empirically from results of preliminary tests.

The anionic surfactant SLS was employed as the collector in the range pH 3–5, as the insoluble hydrolysis products of Fe^{3+} generally bear a positive residual surface charge at low to near-neutral pH (*4, 17, 18, 21, 22*). At higher pH a cationic surfactant (LA) is necessary because of the negative surface charge characteristics of ferric hydroxide flocs (*4, 17, 18, 21, 22*). In this study flotations were attempted using LA as the collector in the range pH 3.5–9. The studies between pH 3.5 and 5 were carried out with both surfactant types in order to compare the efficiency of each in circumstances where minimal surface charge was anticipated to exist on the flocs.

Figure 2 shows the relative removal of $SiO_2(s)$ from the spent brine as a function of pH for SLS and LA flotations. The initial concentration of silica present was 1.1 mg/mL or 1.8×10^{-2} *M*. Surfactant concentrations in the cell were 1.3×10^{-4} *M* and 1.6×10^{-4} *M* for SLS and LA,

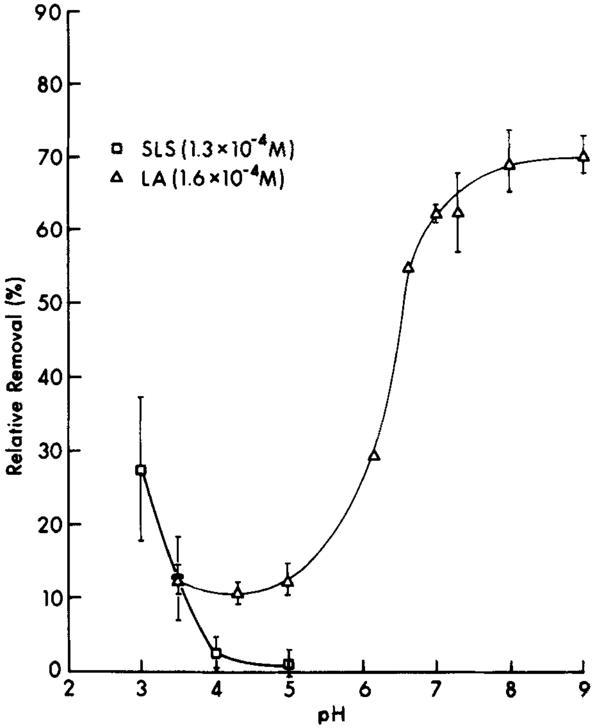


FIG. 2. Relative removal of SiO_2 from spent geothermal fluids as a function of pH with anionic and cationic surfactants.

respectively. The concentration of silica in the fluids represents approximately a 1.4-fold supersaturation at the plant operating temperature of 180°C and pH 7.8 and a 5.5-fold supersaturation with respect to amorphous silica at 50°C (a representative fluid temperature at the end of flotation experiments as well as in the settling ponds) (*6*).

As anticipated from theoretical considerations and the results of previous work, flotations at low pH with SLS as the collector were mostly ineffective. The poor recovery of silica under these conditions may be attributed to several factors: (a) at low pH the hydrolysis of Fe^{3+} has proceeded to a limited extent and results in the availability of only a small amount of floc to adsorb or coprecipitate SiO_2; (b) collection efficiency of the floc by SLS decreases rapidly with increasing pH because of the reduced positive surface charge in the ferric hydroxide; (c) since the isoelectric point (iep) of SiO_2 lies near pH 2, collection of the floc is inhibited by the presence of an increasingly negatively charged SiO_2(s) surface as the pH increases (*22*). A combination of all three effects rather than any one individual effect is more likely to lead to the observed behavior when SLS is used as the collector. The poor, yet significant, removal of close to 30% of the SiO_2 at pH 3 exemplifies the complex nature of the interactions occurring in the flotation cell. At pH 3 the iron hydroxide fraction of the floc will have a relatively large positive surface charge that can then readily adsorb negatively charged SiO_2(s) colloids as well as attach to the negatively charged SLS moiety. Another factor that may contribute to the removal of silica is the formation of polysilicic acid, which reacts strongly with Fe^{3+} in the range pH 2–3 (*23*). As the pH is increased from pH 3.5–5, however, the silica colloids become more negatively charged, the iron hydroxide less positively charged, and the reaction of polysilicic acid with Fe^{3+} less favored. Each of these effects may then contribute to a reduction in the efficiency of removal of SiO_2 from the brine as compared to that observed at pH 3.0.

From the above observations we believe that the mechansim governing the removal of SiO_2 at low pH with SLS as the collector is primarily the electrostatic attraction of negatively charged silica colloids onto a positively charged (ferric hydroxide) surface. The process is termed adsorbing colloid flotation (ACF) (*8*). We also believe that reaction with polysilicic acid and coprecipitation of SiO_2 catalyzed by the presence of Fe^{3+} hydrolysis products contribute to the removal process.

Below pH 6, LA proves to be an ineffective collector for the floc primarily because of incompatible surface charge characteristics. The nonzero recovery in this range is probably a result of the electrostatic attraction between negatively charged silica and LA as well as of entrainment of the mixed iron–silica floc into the surfactant foam, although it appears odd that the latter was not observed with SLS. Above pH 6 the flotation efficiency improves vastly and rises steadily to pH 7. Previous work in our laboratory (*4, 17, 18*) and at other institutions (*7, 21, 22*) has shown the iep of hydrous iron oxide, natural goethite (α-FeOOH), and iron hydroxide to lie near pH 6.3. Thus, the behavior observed in this study is not unexpected. The further increase in the recovery of silica with increasing pH up to pH = 8 is probably the result of enhanced silica polymerization and precipitation in the presence of Fe^{3+} hydroxy complexes as well as OH^-, both of which are known to catalyze this process (*6*). The effective removal of the flocs in the neutral to slightly alkaline pH range arises because of the large negative surface charge on both the ferric hydroxide and the silica components of the mixture; this large negative charge enables the floc to attach readily to the positively charged head of the LA moiety. In this range the mechanism controlling the removal of silica from solution is believed to be one of coprecipitation (catalyzed by the hydrolysis of polyvalent metal ions and the presence of increasing amounts of hydroxide ions) followed by adsorption onto an oppositely charged surfactant entity. This process is termed precipitate flotation (*8*).

It is interesting to note that the range pH 4–5 appears to be that in which the flocs have the least affinity for either surfactant. This effect is reflected in the extremely poor recoveries observed. The floc generated in this pH range, however, bears little difference in physical appearance to that generated at pH 6 or 7. Although surface charge was not measured on these samples, we suggest that the iep of the floc lies in this range. This would appear to be in contrast with observations in previous studies dealing with ferric hydroxide flocs (*4, 17, 18*); however, the presence of significant amounts of $SiO_2(s)$ present in a polymeric form, evident by the rapid increase in recovery above pH 5 and the twofold increase in ionic strength, both may contribute to a shifting of the iep toward lower pH. Such behavior has been documented by Parks, who noted that mixed flocs generally exhibit shifts in iep toward that of the admixed phase (*21*). In our study very little $SiO_2(s)$ need be present to alter significantly the charge characteristics of the floc, as the initial SiO_2 concentration is two orders of magnitude greater than that of the iron used as a precipitating agent.

Effect of Concentration of Fe^{3+} in the Presence of Cl^- and SO_4^{2-}

The removal of SiO_2 from solution by flocculation with ferric salts was studied as a function of iron concentration using $FeCl_3$ and $Fe_2(SO_4)_3 \cdot$

xH_2O as a source of ferric ion. This study was conducted at fixed pH and with 1.6×10^{-4} *M* LA as the collector. Flotations were carried out at pH 8 for two reasons. The natural pH of the spent brine is approximately pH 7.7; thus runs at pH 8 do not change the pH of the brine significantly during treatment. Additionally pH 8 marks the beginning of the plateau region where recovery of silica does not improve significantly with further increases in pH. Although these considerations may be minor for bench-scale tests, should the method be expanded to a larger-scale continuous operation, minimizing changes to the natural brine conditions might become more important in terms of reagent costs and the environmental suitability of residual fluids. The concentration of iron used in this phase of the investigation was systematically varied from 6.25×10^{-5} to 7.9×10^{-4} *M*.

The results of flotations with $FeCl_3$ and $Fe_2(SO_4)_3$ are presented in Fig. 3. With $FeCl_3$ the recovery of silica initially increases with increased iron concentration but quickly levels off above 2.5×10^{-4} *M* Fe^{3+} to approximately 70 ± 2% removal. Although this percentage represents far less than a quantitative separation of the silica from the brine, the natural solubility of amorphous silica must be considered. At 50°C and pH = 8 the solubility of amorphous silica is approximately 0.2 mg/mL *(6)*. As most flotations resulted in a final brine temperature near this value, the

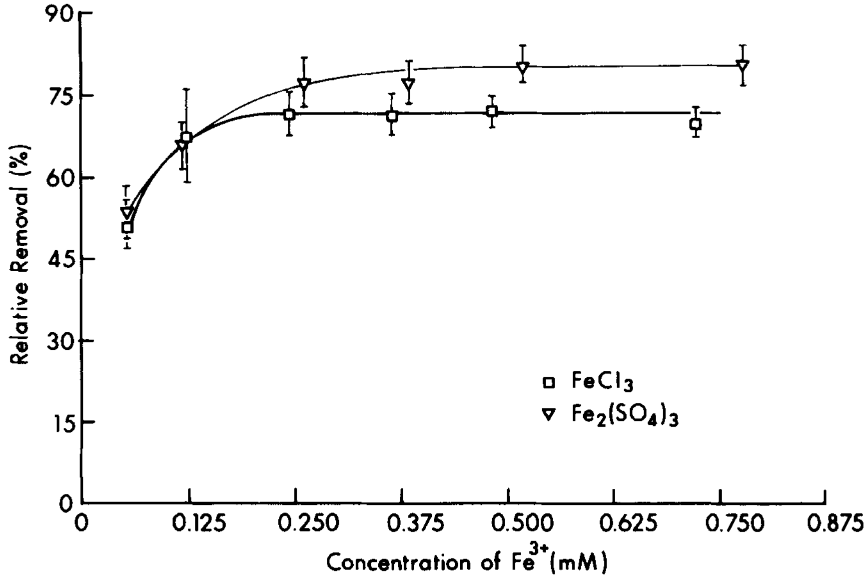


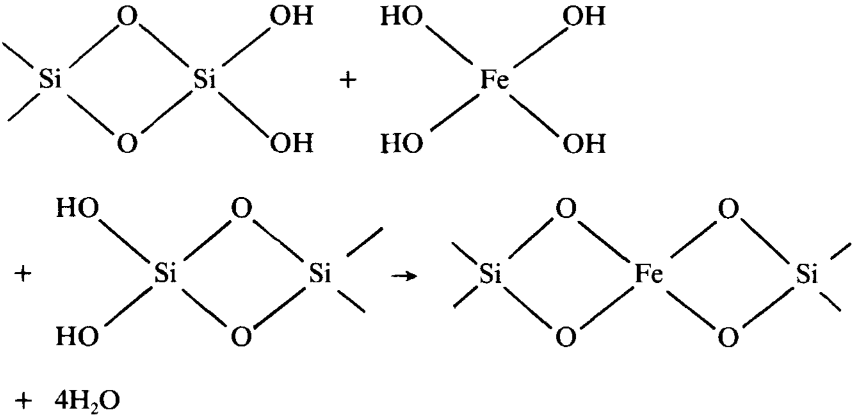
FIG. 3. Relative removal of SiO_2 from spent geothermal fluids as a function of Fe^{3+} concentration at pH 8.

amount of "insoluble" silica originally present in the brine at this temperature would be approximately 0.9 mg/mL. When removal efficiency is calculated on the basis of the supersaturation level of the silica in the brine, a 70% removal of total SiO_2 translates into an 85% removal of insoluble SiO_2.

The flotation behavior when $Fe_2(SO_4)_3$ is used as the source of ferric ion follows the same general pattern as that observed with $FeCl_3$. There appears, however, to be a small yet statistically significant overall improvement in the efficiency of removal. In addition, a leveling off in the removal occurs only above 5×10^{-4} *M*—twice the concentration at which this behavior was observed with $FeCl_3$. The enhanced removal of silica in the presence of SO_4^{2-} follows trends observed in previous work (*4*) where oxyanions of arsenic were floated from unflashed geothermal fluids by a similar technique. In that study, arsenic recovery improved slightly in the presence of SO_4^{2-}, but more important, the surface charge of the flocs was approximately 15 mV more negative in the presence of SO_4^{2-} than in the presence of Cl^-. Furthermore, coprecipitation of SiO_2 occurred when both $FeCl_3$ and $Fe_2(SO_4)_3$ were used as sources of ferric ion. Mechanisms proposed to explain the zeta potential depression were somewhat speculative and invoked the effect of specific adsorption of SO_4^{2-} onto the silica component of the floc in a manner analogous to that of the specific adsorption of $HAsO_4^{2-}$ onto ferric and aluminum hydroxides above their iep (*24*). The result in the present investigation is an improvement in the silica removal by nearly 10%. The 80% removal of total silica (i.e., dissolved plus colloidal SiO_2 arising from supersaturation) achieved with concentrations greater than 5.0×10^{-4} *M* Fe^{3+} corresponds to approximately 98% of the silica present above the solubility of amorphous silica at 50°C. Hence, the method can be considered quantitative for the removal of colloidal silica from spent brines at temperatures exceeding 50°C.

The mechanism of silica removal from the brines can be considered one of precipitate flotation. A number of characteristics of this system, however, make it unique. Most precipitate flotation techniques utilize to advantage the underlying principles of coprecipitation as a method for scavenging trace constituents. Such a method generally involves the use of a high concentration of precipitating agent relative to the concentration of the species to be recovered. In the present study the concentration of Fe^{3+} used is nearly two orders of magnitude less than that of the SiO_2 to be removed. The mechanism governing removal here cannot be that of bulk scavenging of SiO_2 by Fe^{3+} hydrolysis products, although the process is the flotation of a precipitate formed upon addition of particular reagents to the geothermal fluids.

At this point a discussion of the possible mechanism of formation of the mixed Fe–SiO_2 flocs is in order. Past experience with the fluids from HGP-A has shown that upon cooling, the SiO_2 slowly begins to polymerize yet requires extremely long standing times (from hours to days) in order to flocculate and deposit in the settling ponds (*25*). It is known from research on various silica systems that the stability is a result of the development of a negative surface charge on the colloidal silica polymers, which then leads to strong repulsive forces and prevents further growth of the polymers (*6*). Rees has shown that under conditions of low attraction, chainlike aggregates are preferentially formed (*26*), probably because a given particle approaching a pair or a short chain of particles is much more likely to overcome repulsive forces if contact is along the longitudinal axis of the chain rather than alongside of the chain (i.e., repulsive force due to only one "particle" as opposed to multiple "particles") (*27*). The presence of a high concentration of salts (0.3 to 0.4 *N*) or the addition of small amounts of polyvalent metal ions, however, results in coagulation or flocculation of the SiO_2 and precipitation primarily through the neutralization of repulsive forces (*6*). We now suggest that the flocculation of the silica in this study may be a result of the attachment of iron hydrolysis products to short chains by specific chemical forces followed by condensation as follows:



The slightly alkaline environment (pH 8) of the solution and the presence of ~0.22 *N* NaCl from the seawater component of the brine are both believed to enhance this process.

Iler has suggested a bridging mechanism between silica and single metal cations, polycations, or polyvalent basic (poly)cations. The process is believed to involve the neutralization of the negative surface charges on the silica as well as entrapment of the metal-bearing species in the precipitate (*6*). Furthermore, there is evidence that polymeric iron hydroxide complexes are more strongly adsorbed than the trivalent metal ion and are more effective flocculants at lower concentration (*28*). Although these arguments would appear to differ from the mechanism suggested in this paper in that our work deals primarily with ferric hydroxide complexes above the iep (i.e., bearing a negative surface charge), such behavior has also been observed by O'Meila and Stumm (*28*), who attributed the effective flocculation to specific chemical forces of sufficient magnitude to overcome electrostatic repulsive forces. As we also suggest, adsorption of negatively charged iron species on silica would necessitate the formation of Fe–O–Si linkages where actual chemical bonds represent the attractive forces between particles. With such a mechanism, flocculation of the silica is achieved through the growth of a three-dimensional network of short silica chains held together by Fe–O–Si bonds. Considering the concentration ratio of Si to Fe of approximately 100 used in this study, other mechanisms based on a stoichiometric neutralization of charges to permit attachment seem rather unlikely.

Use of Al^{3+} Salts

The removal of SiO_2 from solution by flocculation with aluminum salts was studied as a function of aluminum concentration using $Al(NO_3)_3$ and $Al_2(SO_4)_3$ as a source of Al^{3+} ion, and the results are presented in Table 2. Flotations were attempted at both fixed pH and varying pH. Except for the runs with 1.25×10^{-4} *M* Al^{3+}, serious difficulties were encountered with the flotations. In the runs with higher Al^{3+} concentrations the floc did not collect readily with LA nor was the performance any better at lower pH (i.e., pH 7.5) with SLS. These problems are primarily attributed to the incompatibility of the surface charge of the hydrolyzed aluminum species with that of the surfactants in the pH range investigated. The iep of hydrous aluminum oxides, aluminum hydroxides, and aluminum oxides are reported to lie between pH 5.0 and 9.0 (*21, 22*). In addition, the mode of preparation and sample history can also influence the iep of aqueous oxides and hydroxides, thus enlarging even further the possible range of iep. As mentioned above, only the attempts using 1.25×10^{-4} *M* Al^{3+} were successful although the gas flow rate had to be lowered to 10 ± 2 mL/min. Lower gas flow rates allowed a more efficient, albeit slower, collection of the floc at the top of the cell, whereas higher flow rates readily overcame the weak attraction between the floc and

TABLE 2

Efficiency of SiO_2 Removal Using Aluminum Salts under Selected Conditions

Metal salt	pH	$[Al^{3+}]$ ($\times 10^{-4}$ *M*)	Relative removal (%)	
$Al(NO_3)_3$	8.0	1.25	71.8 ± 1.5[a]	87.8 ± 1.8[b]
$Al(NO_3)_3$	8.0	2.50	74.0 ± 1.8	90.4 ± 2.2
$Al(NO_3)_3$	8.1	3.75	72.4 ± 3.0	88.5 ± 3.7
$Al(NO_3)_3$	8.0	5.00	71.5 ± 1.6	87.4 ± 2.0
$Al(NO_3)_3$	8.0	7.50	78.0 ± 7.9	95.3 ± 9.6
$Al(NO_3)_3$	8.5	3.75	65.9 ± 2.8	80.5 ± 3.4
$Al(NO_3)_3$	8.6	5.00	70.5 ± 2.8	86.2 ± 3.4
$Al(NO_3)_3$	8.5	7.50	81.4 ± 1.2	99.5 ± 1.5
$Al(NO_3)_3$	9.0	7.50	79.4 ± 0.4	97.0 ± 0.5
$Al(NO_3)_3$	9.5	7.50	75.4 ± 2.2	92.2 ± 2.7
$Al_2(SO_4)_3$	8.0	1.25	66.2 ± 1.9	80.9 ± 2.3
$Al_2(SO_4)_3$	8.2	2.50	72.9 ± 7.1	89.1 ± 8.7
$Al_2(SO_4)_3$	8.0	3.75	71.9 ± 2.7	87.9 ± 3.3
$Al_2(SO_4)_3$	8.5	3.75	71.2 ± 3.6	87.0 ± 4.4

[a] Relative to total SiO_2 in brine.

[b] Relative to SiO_2 present above amorphous solubility at 50°C.

surfactant and led to particle redistribution throughout the cell. Once redistributed into the mother liquor, the particles remained suspended and would not collect (even upon further addition of surfactant). The slow but effective collection of the floc with the lowest concentration of Al^{3+} may be attributed to the overwhelming amount of SiO_2 bearing a negative surface charge, thus enabling attachment of the positively charged head of the LA molecule in solution. Such a process is also consistent with the nonzero recovery of SiO_2 at the low end of the LA-Fe^{3+} experiments described above. Flocculation of the silica is expected to have proceeded by a mechanism analogous to that presented in the previous section of this paper. At the other extreme, flotation was possible (with greatly reduced gas flow rate) at pH 9.5. This particular experiment was carried out with 7.5×10^{-4} *M* Al^{3+}. In light of the iep data from Parks (*21, 22*), one would have expected flotation to be possible as a result of the electrostatic attraction between the negatively charged floc and the positively charged surfactant head. Again, higher gas flow rates led to the irreversible redistribution of the floc. Between the two extremes, flotation was never effective without some sort of unconventional procedure such as temporarily shutting off the gas to allow the floc to collect slowly. The poor behavior in terms of flotation is then attributed to the increased amount of Al^{3+} present, which is hydrolyzed to form a mixed floc with Si—O—Al linkages yet bears sufficient positive charge to repel the LA moiety over the pH range 7.5-9.0.

Electrophoretic Mobility

Electrophoretic mobility measurements were initially attempted on treated and untreated brine samples at elevated temperature in the Zeta Meter Plexiglas UVA Type II electrophoresis cell. Immediate thermal overturn in the cell precluded determination of the zeta potential, as the ensuing vertical motion was as great as any horizontal motion of the colloid in the electric field. This problem had not been previously encountered, as past studies have always dealt with suspensions in fluids at ambient temperature (*4, 20*).

A sample of flashed brine that had cooled and had been left undisturbed overnight was found to contain a suspension of finely dispersed SiO_2 colloids (that could not be resolved with the naked eye but that resulted in a cloudy appearance in the fluids). Repetitive determinations of the zeta potential were undertaken by using 67 and 100 V of applied potential between the electrodes. The average of eight independent measurements tracking 5–8 colloids each resulted in the calculation of a surface charge of -45 ± 3 mV at pH 7.7. The reasonable agreement of this value with those of quartz suspensions (-35 to -40 mV) and mixed iron–silica flocs from our previous study (-38 mV) indicates that the SiO_2 component of the flocs must overwhelmingly govern the zeta potential of the colloids (*4, 7*). It must be added that a direct comparison is risky at best and may not be valid, as conditions vary considerably among the three systems. Measurements of electrophoretic mobility of particles generated in the presence of Fe^{3+} (as $Fe_2(SO_4)_3$) yielded the zeta potential values given in Table 3. An increase in the amount of iron present appears to alter the charge characteristics of the colloids in a direction approaching that from our previous work (*4*) and shows the increased influence of Fe^{3+} hydrolysis products on the zeta potential. Also shown in Table 3 is a zeta potential of -9 ± 3 mV observed when only NaOH was used to enhance silica flocculation. The low zeta potential value is representative of the high degree of settling that the particles exhibited under these conditions, is in line with the poor stability of colloids bearing low negative surface charges, and contrasts well with the highly stable nature of the cooled, untreated brine (zp = -45 mV).

TABLE 3

Zeta Potential of Flocs Generated from Treatments of HGP-A Flashed Brine[a]

Flocculant	None	Fe^{3+}	Fe^{3+}	Fe^{3+}	NaOH	$Fe^{3+\,b}$
ζ-Potential (mV)	-45 ± 3	-39 ± 2	-36 ± 2	-27	-9 ± 3	-38
$[Fe^{3+}]$ (*M*)	0	5.3×10^{-5}	1.3×10^{-4}	2.6×10^{-4}	0	2×10^{-3}
pH	7.7	8.0	8.0	8.0	>9	8.0

[a] Ambient temperature, 67–100 mV applied potential, 30–40 $m\mho$/cm conductivity, 1.8×10^{-2} *M* SiO_2.

[b] From De Carlo and Thomas (*4*), 6.5×10^{-3} to 8.2×10^{-3} *M* SiO_2.

A further discussion of the zeta potential of the flocs generated in this study is not warranted, as the effect of cooling the brine fluids on surface charge characteristics and flocculation behavior may be reflected in our measurements which may deviate considerably from those at high temperature.

It may be of interest to note that in many instances during extended periods of applied potential to the UVA II cell, a significant amount of cohesive gelatinous silica formed at the cathode. Further investigation of this effect may be warranted, because in an electrical power plant situation such as HGP-A this process may prove to be a means of enhancing the deposition of silica. No additional observations on this behavior were attempted in this study.

CONCLUSIONS

Silica can be effectively removed from hot (60–90°C) spent geothermal fluids (flashed brine) by means of adsorptive bubble flotation on a bench-scale batch process basis. Flotation behavior as well as removal efficiency appear to be optimum when employing a concentration of 2.6×10^{-4} *M* Fe^{3+} as its sulfate salt and lauryl ammonium chloride as the collector at pH 8. Careful control of physical parameters such as cell vertical alignment and gas flow rate contribute greatly to the effectiveness of the system. High gas flow rates lead to the irreversible redistribution of the floc in the mother liquor, although this problem may be alleviated by the use of higher molecular weight cationic alkyl surfactants which would present a longer hydrophobic tail and enhance their concentration (stability) at the air/water interface.

Although flocculation by aluminum salts is also effective, the particles generated do not have surface charge characteristics compatible with the surfactants used at slightly alkaline pH. Collection is possible at higher pH but leads to increased causticity of the fluids. It is suggested that further studies evaluate the behavior of branched alkyl surfactants. Additionally, more stringent control of the fluid temperature would enable us to maintain a higher fluid heat content that could then be used in heat exchangers once a continuous flow system is developed. We recommend further investigations into the surface charge characteristics of the flocs in order to gain a better insight into the surface activity of the SiO_2 and to allow better predictions of its scaling behavior.

Acknowledgments

We thank Donald M. Thomas, geothermal research group leader, Hawaii Institute of Geophysics, for use of unpublished data and for enlightening discussions. Technical assistance was provided by Amy Murakami and Michael Tanaka. We gratefully acknowledge the Hawaii Electric Light Company, operator of HGP-A Geothermal Generator Facility, for their cooperation.

This research was sponsored in part by the Hawaii Natural Energy Institute through Department of Energy Contract DE FG03-84 and DE FG03-85 F15799. The Zeta Meter used in these studies was provided by Ed Laws through Solar Energy Research Institute Subcontract XE-09013-01. This is Hawaii Institute of Geophysics Contribution No. 1857.

REFERENCES

1. D. M. Thomas, *Proc. Pac. Geotherm. Conf. 1982,* 273–278.

2. A. Waibel, *Trans.-Geotherm. Resour. Counc., 7,* 205–209 (1983).

3. C. Stone and P. F. Fan, *Geology, 6,* 401–404 (1978).

4. E. H. De Carlo and D. M. Thomas, *Environ. Sci. Technol., 19,* 538–544 (1985).

5. R. O. Fournier and J. J. Rowe, *Am. J. Sci., 264,* 685–697 (1966).

6. R. K. Iler, *The Chemistry of Silica,* Wiley, New York, 1979.

7. M. C. Fuerstenau (ed.), *Flotation: A. M. Gaudin Memorial, Volume I,* American Institute of Mining, Metallurgical, and Petroleum Engineers, New York, 1976.

8. R. Lemlich, *Adsorptive Bubble Separation Techniques,* Academic, New York, 1972.

9. P. Somasundaran, *AIChE Symp. Ser., 71*(150) (1975).

10. D. J. Wilson and E. L. Thackston, EPA Report 600/2-80-138, Environmental Protection Agency, Cincinnati, Ohio, 1980.

11. W. T. Shannon, W. R. Owers, and H. P. Rothbaum, *Geothermics, 11,* 43–58 (1982).

12. D. H. Buisson, H. P. Rothbaum, and W. T. Shannon, *Ibid., 8,* 97–110 (1979).

13. F. Sebba, *Ion Flotation,* Elsevier, Amsterdam, 1962.

14. A. N. Clarke and D. J. Wilson, *Foam Flotation: Theory and Applications,* Dekker, New York, 1983.

15. M. Hiraide and A. Mizuike, *Rev. Anal. Chem., 6,* 151–168 (1982).

16. R. B. Grieves, in *Treatise on Analytical Chemistry,* Part 1, Vol. 5 (P. J. Elving, ed.), Wiley, New York, 1982, pp. 371–448.

17. E. H. De Carlo, H. Zeitlin, and Q. Fernando, *Anal. Chem., 53,* 1104–1107 (1981).

18. E. H. De Carlo, H. Zeitlin, and Q. Fernando, *Ibid., 54,* 898–902 (1982).

19. E. H. De Carlo, B. Bleasdell, H. Zeitlin, and Q. Fernando, *Sep. Sci. Technol., 17,* 1205–1218 (1982).

20. E. H. De Carlo, B. Bleasdell, H. Zeitlin, and Q. Fernando, *Ibid., 18,* 1023–1044 (1983).

21. G. A. Parks, *Adv. Chem. Ser., 67,* 121–160 (1967).

22. G. A. Parks, *Chem. Rev., 65,* 177–198 (1965).

23. F. Hazel, R. V. Schock, and M. Gordon, *J. Am. Chem. Soc., 71,* 2256–2257 (1949).

24. B. L. Currin, R. Moffat-Kennedy, A. N. Clark, and D. J. Wilson, *Sep. Sci. Technol., 13,* 573–586 (1978).

25. D. M. Thomas, University of Hawaii, Personal Communication, 1985.

26. A. L. G. Rees, *J. Phys. Chem.*, *55*, 1340–1345 (1951).
27. I. L. Thomas and K. H. McCorkle, *J. Colloid Interface Sci.*, *36*, 110–118 (1971).
28. C. R. O'Melia and W. J. Stumm, *Ibid.*, *23*, 437 (1967).

Received by editor May 9, 1986