Proceedings World Geothermal Congress 2015
Melbourne, Australia, 19-25 April 2015

# Chemistry and Control of Silica at Los Azufres Geothermal Field, Michoacan, Mexico

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**Keywords:** Silica, brine chemistry, modeling, Los Azufres, deposit control

## ABSTRACT

Injection wells at the Los Azufres geothermal field in Michoacan, Mexico are damaged by silica deposits. A mixture of flashed brine and cooling tower blowdown is reinjected. The wells at Los Azufres produce both steam and brine, whereby the ratio of steam to separated brine is greater than would be the case where steam is generated by flashing brine. Therefore, the proportion of cooling tower blowdown in the reinjected mixture is unusually large, typically about 25% by volume.

Silica polymerization in Los Azufres brine was modeled to improve understanding of silica chemistry and propose solutions. Modeling the kinetics of silica polymerization using computer code SILNUC indicated that polymerization of silica and formation of silica deposits can be controlled by decreasing pH of the brine. The most practical way to decrease pH is to saturate the cooling tower blowdown with condenser vent gas (which comprises mostly carbon dioxide) before combining it with the brine. Decreasing pH and introducing oxygen will make the brine mildly corrosive, but corrosion can easily be controlled using a suitable inhibitor. It was determined that silica polymerization involves heterogeneous nucleation induced by particles of aluminosilicate minerals which begin to form immediately after steam is separated from the brine. Therefore, silica polymerization can be further retarded by adding a silicate inhibitor to the brine below the bubble point in the production wells.

A test of silica control utilizing carbon dioxide is underway at Los Azufres with results expected in time to be reported at the Congress.

## 1. INTRODUCTION

Most wells at the Los Azufres Geothermal Field in Michoacan, Mexico have multiple fluid entries, whereby both brine and steam enter the wellbore and a mixture is produced, wherein the ratio of vapor to liquid is much larger than would result from flashing the brine.

Steam is separated from the mixture at about 8 bar-a, and the brine is discharged to a weir box, where in flashes again at ambient atmospheric pressure, which is about 0.73 bar-a due to the high elevation of the field (about 2,700 meters above sea level). The discharged brine flows by gravity to injection wells through pipes made of high density polyethylene (HDPE). Cooling tower blowdown (that is, excess condensate) is added to the brine, and the mixture is reinjected. Because of the high vapor to liquid ratio in the fluid produced, the proportion of cooling tower blowdown to brine is substantial: typically about 1:3.

Heavy deposits of silica are present in weir boxes located at the production wells and injection wells, and progressive damage to injection wells has been noted.

The primary purpose of the study reported here was to elucidate the formation of silica deposits believed to be damaging the injection wells, and to propose corrective measures.

Some recently drilled wells as Los Azufres produce mostly geothermal brine, which begins to flash in the wellbore, rather than a mixture of brine and steam; well Az-02A is one such well. The second purpose of this study was to predict possible problems that might be encountered in such wells, and propose solutions.

Calculations were performed using the analyzed composition of brine from Az-02A and the calculated composition of cooling water (derived from steam condensate) and condenser vent gas from Los Azufres Unit 13 as fairly representative of conditions at the Los Azufres geothermal field.

## 2. RECONSTRUCTION OF THE INITIAL COMPOSITION OF BRINE IN THE GEOTHERMAL RESERVOIR

In order to predict precipitation of solids from the brine, it is necessary to first reconstruct the composition of the brine as it existed in the reservoir. The analyzed composition of a sample of brine from Well Az-02A collected October 15, 2012 served as the starting point. This sample had been flashed to atmospheric pressure. The calculation was performed using the commercially available computer program Geochemist's Workbench, Standard Edition, v. 9.03.

The brine analysis provided is presented in Table 1 together with the reconstructed composition of the brine in the geothermal reservoir. The initial temperature was determined based on total silica concentration and separator pressure. The concentration of other species was adjusted to compensate for steam loss = 30.05%. The concentration of $CO_2$ was then adjusted to make the brine saturated in respect to calcite at that temperature, given the concentration of calcium and bicarbonate reported in the analysis after adjusting for steam loss. The concentration of $H_2S$ was determined based on the solubility of orpiment ($As_2S_3$). The concentrations of Al, Fe and Mg were not reported because they were too small to measure; these concentrations were calculated by assuming equilibrium with corresponding minerals likely present in the reservoir.

**Table 1. Brine from Az-02A as reported and reconstructed in the reservoir**

| Species | Sample Analyzed (mmol/kg-$H_2O$) | Brine in Reservoir (mmol/kg-$H_2O$) | Calculated Value based on Solubility of: |
|---|---|---|---|
| Li | 4.22 | 2.95 | |
| Na | 140.6 | 98.35 | |
| K | 12.0 | 8.39 | |
| Rb | 0.042 | 0.029 | |
| Mg | nil | 0.00771 | Tremolite |
| Ca | 2.66 | 1.86 | |
| Al | – | 0.00721 | Anorthite |
| Fe | nil | 0.00150 | Pyrite |
| As | 0.051 | 0.036 | |
| Cl | 162.31 | 112.36 | Charge Balance |
| $SO_4^{-2}$ | 0.388 | 0.271 | |
| $HCO_3^-$ | 0.72 | 0.518 | |
| $B(OH)_3$ | 34.9 | 24.4 | |
| $SiO_2$ | 10.08 | 7.05 | |
| $CO_2$ | – | 19.85 | Calcite |
| $H_2S$ | – | 1.16 | Orpiment |
| T(℃) | Ambient | 245.8 | Quartz |
| pH | 7.06 | 5.93 | Calcite |

Nominal compositions as modeled by Geochemist's Workbench of the various minerals discussed are presented in Table 2.

**Table 2. Minerals assumed present in reservoir or potentially precipitated**

| Assumed present in reservoir | |
|---|---|
| Anorthite | $CaAl_2Si_2O_4$ |
| Calcite | $CaCO_3$ |
| Orpiment | $As_2S_3$ |
| Quartz | $SiO_2$ |
| Pyrite | $FeS_2$ |
| Tremolite | $Ca_2Mg_5Si_8O_{22}(OH)_2$ |
| Precipitated | |
| Amorphous silica | $SiO_2$ |
| Beidellite-Ca | $Ca_{0.33}Al_4[Si_{7.34}Al_{0.66}O_{20}](OH)_4 \cdot nH_2O$ |
| Beidellite-Na | $Na_{0.66}Al_4[Si_{7.34}Al_{0.66}O_{20}](OH)_4 \cdot nH_2O$ |
| Orpiment | $As_2S_3$ |
| Minnesotaite | $Fe_3Si_4O_{10}(OH)_2$ |
| Phengite | $KAlMg[Si_4O_{10}](OH)_2$ |

The composition of cooling water from Los Azufres Unit 13, unmodified and saturated with condenser vent gas, is shown in Table 3. These compositions were calculated using the computer program CNDSR (Weres, 1984) and a model originally developed to represent Los Humeros Unit 9 (another 25 MW Alstom unit) provided with Los Azufres Unit 13 steam.

## 3. MINERALS POTENTIALLY PRECIPITATED FROM THE FLASHED BRINE

Table 4 lists minerals potentially precipitated at various location calculated using Geochemist's Workbench. The values of T and pH employed, and the amount of steam separated were calculated using proprietary program BRINE (a close derivative of

CNDSR). The amount of each mineral potentially precipitated was calculated assuming that full equilibrium was attained at that stage, but that nothing had precipitated at a previous stage. Because the silicate minerals precipitate more quickly than amorphous silica, their precipitation was calculated assuming that no amorphous silica has precipitated.

**Table 3. Calculated cooling water composition, Los Azufres Unit 13, Concentrations in mg-moles/kg**

| | Cooling Tower Basin | Saturated with Condenser Vent Gas |
|---|---|---|
| $CO_2$ | 4.383 | 27.949 |
| $H_2S$ | 0.0 | 0.516 |
| $NH_3$ | 6.785 | 6.785 |
| $H_2S_2O_3$ | 1.099 | 1.099 |
| pH | 7.95 | 5.62 |

**Table 4. Summary of minerals potentially precipitated**

| | Wellbore at 30 bar-a | First flash at 8.0 bar-a | Weir box at 0.73 bar-a | Cool to 40°C | Add 25% condensate with $CO_2$ |
|---|---|---|---|---|---|
| T(℃) | 232.7 | 170.3 | 91.1 | 40.0 | 36.0 |
| pH | 6.46 | 6.68 | 6.95 | 7.34 | 5.72 |
| Log S (Am-$SiO_2$) | –0.40 | –0.16 | 0.26 | 0.60 | 0.51 |
| Log S (Calcite) | 0.25 | –0.46 | –2.89 | < –3.0 | –1.96 |
| Amount potentially precipitated (mg/kg) assuming no precipitation at any earlier stage | | | | | |
| Amorphous $SiO_2$ | 0.0 | 0.0 | 268.3 | 451.6 | 418.2 |
| Calcite | 9.58 | 0.0 | 0.0 | 0.0 | 0.0 |
| Beidellite-Ca | 0.58 | 0.0 | 0.0 | 0.0 | 0.0 |
| Beidellite-Na | 0.0 | 0.0 | 0.0 | 0.0 | 1.14 |
| Minnesotaite | 0.0 | 0.19 | 0.22 | 0.23 | 0.0 |
| Phengite | 0.0 | 2.85 | 2.86 | 2.86 | 0.0 |
| Tremolite | 1.19 | 0.0 | 0.0 | 0.0 | 0.0 |
| Orpiment | 0.0 | 2.40 | 0.09 | 0.11 | 6.27 |

### 3.1. Calcite

In Az–02A supersaturation in respect to calcite starts at the bubble point, but disappears by the time the brine reaches the wellhead. This unusual behavior is due to the large concentration of boric acid in the brine, which limits the pH increase caused by separating steam from the brine. Maximum supersaturation (log S = 0.25) is calculated at 30 bar pressure inside the wellbore. In the absence of a calcite inhibitor, calcite would deposit in the wellbore of Az–02A in the interval where pressure decreases from 45 to 30 bar-a. These conclusions apply to Az-02A and other wells at Los Azufres which produce brine rather than a mixture of steam and brine. Calcite deposits have not been reported in the more numerous wells which produce a mixture of steam and brine. The native steam contains more $CO_2$ than steam separated from brine, depressing pH and preventing supersaturation in respect to calcite.

### 3.2. Silicates

A small amount of several clay minerals and tremolite are predicted to precipitate after steam is separated from the brine. The precipitation of these silicate minerals is easily controlled by applying a silicate inhibitor. While silicate minerals themselves are at most a minor issue at Az–02A, they have a large effect upon the behavior of silica.

### 3.3. Orpiment

Orpiment is predicted at Az–02A because of the unusually large concentration of As in the brine. The brine becomes supersaturated in respect to orpiment at 14.6 bar in the wellbore, and deposits of orpiment may form in the wellhead, two phase pipeline and steam separator. The degree of supersaturation decreases when more steam is separated in the weir box, stripping $H_2S$ from the brine. The brine again becomes supersaturated in respect to orpiment after cooling water saturated with condenser vent gas has been added to it, returning $H_2S$ to the brine. Precipitation of orpiment represents a safety hazard, as this mineral is a highly toxic arsenic compound.

### 3.4. Silica

Formation of silica deposits commonly involves polymerization of silica dissolved in the brine to form colloidal particles of amorphous silica, which then adhere to solid surfaces through electrostatic forces mediated by divalent cations. The particles are subsequently cemented to form solid deposits by further deposition of silica between them. At high levels of supersaturation (above about S = 2.5) colloidal particles are massively produced by homogeneous nucleation; at lower levels of supersaturation, heterogeneous nucleation predominates, typically induced by nucleii of aluminosilicate minerals or other silicates. Deposition of dissolved silica directly upon solid surfaces is very much slower and rarely produces visible deposits; this process is insignificant at Los Azufres and most other geothermal installations.

The program SILNUC was used to model polymerization of silica in the brine. This program accurately represents the polymerization of silica in solution to form of colloidal particles of amorphous silica over the range of conditions relevant to flashed geothermal brines (Weres *et al.*, 1981).

Table 5 and Figures 1 and 2 illustrate the effect of temperature and the presence of aluminosilicate particles which serve as heteronuclei upon polymerization of dissolved silica to form colloidal particles of amorphous silica.

**Table 5. Effect of temperature and presence of heteronuclei upon silica polymerization**

| | | | | **Best Case** Homogeneous Nucleation Only | | **Worst Case** Heterogeneous Nucleation by Aluminosilicates in addition to Homogeneous Nucleation | | |
|---|---|---|---|---|---|---|---|---|
| Location | T (°C) | pH | Total $SiO_2$ (mg/kg) | $t_{Max}$ (hr) | Max. Polym. Rate (mg/kg/hr) | Initial Colloid (mg/kg) | $t_{Max}$ (hr) | Max. Polym. Rate (mg/kg/hr) |
| Weir box | 91 | 6.95 | 606 | 152 | 0.87 | 6.05 | 0.34 | 184 |
| Cool to 80°C | 80 | 7.02 | 606 | 6.8 | 20.7 | 6.05 | 0.32 | 213 |
| Cool to 70°C | 70 | 7.09 | 606 | 1.33 | 122 | 6.05 | 0.37 | 229 |
| Cool to 60°C | 60 | 7.17 | 606 | 0.51 | 324 | 6.05 | 0.45 | 272 |
| Cool to 50°C | 50 | 7.25 | 606 | 0.30 | 474 | 6.05 | 0.30 | 440 |
| Cool to 40°C | 40 | 7.34 | 606 | 0.22 | 499 | 6.05 | 0.22 | 484 |
| Injection well | 36 | 5.72 | 456 | 2,250 | 0.080 | 4.59 | 33 | 2.73 |

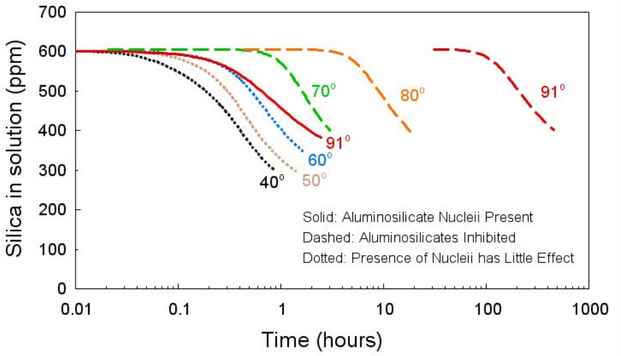

**Fig. 1. The effect of temperature and heteronuclei upon silica polymerization: Silica concentration**

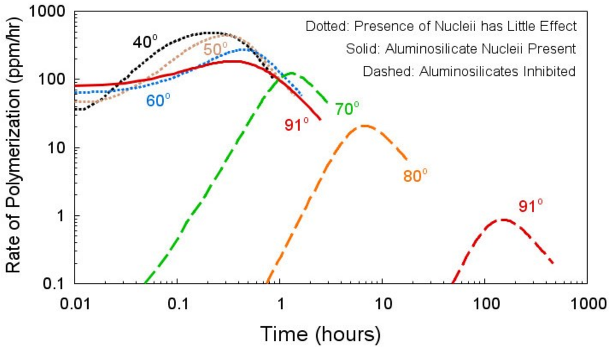

**Fig. 2. The effect of temperature and heteronuclei upon silica polymerization: Rate of polymerization**

In Table 5, "Total $SiO_2$" includes colloidal material as well as silica dissolved in the brine. The "Injection Well" brine is diluted and acidified by addition of 24.8% cooling water saturated with condenser vent gas (Table 3). "Polymerization rate" is the rate of decrease of dissolved silica concentration vs time as monosilicic acid in solution polymerizes to produce colloidal particles of amorphous silica. "Polymerization rate" is not the rate at which silica deposits form, but it allows deposition rates under different conditions to be compared in a semiquantitative fashion.

The calculations assuming Homogeneous Nucleation Only represent a situation wherein no heteronucleii are present in the brine. This condition requires that no aluminosilicate or other mineral particles are available to serve as heteronucleii; this "best case" can be approached by applying an effective silicate inhibitor but can never be fully realized.

The calculations assuming Heterogeneous Nucleation by Aluminosilicates in addition to Homogeneous Nucleation represent a "worst case" wherein no silicate inhibitor is applied and aluminosilicate minerals quickly precipitate from the brine as shown in Table 4. The amount of heteronucleii produced was calculated assuming that silicate minerals precipitate to chemical equilibrium in the Weir Box (Table 4), to form particles with radius equal to a critical nucleus of amorphous silica (R = 1.15 nm) under those conditions. Solid particles carried by the brine (rock dust, etc.) also serve as heteronucleii but their contribution effect usually is small, because they are very much larger and therefore provide little surface area for silica deposition.

While these results exaggerate the difference between the "best case" and "worst case", they illustrate how effective inhibition of silicate minerals would help control silica deposits. Practical experience confirms this to be the case. Most water treatment chemicals sold as "siliCA inhibitors" are actually siliCATE inhibitors and have little effect against silica itself. Nonetheless, these products inhibit silica deposits from geothermal brines under conditions of moderate supersaturation where heterogeneous nucleation predominates. This beneficial effect is indirect; these products actually inhibit the precipitation of silicate minerals which might otherwise serve as heteronucleii promoting the polymerization and deposition of silica.

Homogeneous nucleation is slow above 70°C because supersaturation is small (dashed lines). Below 60°C polymerization is rapid and changes little with further cooling; the presence of heteronucleii has little effect, because the number of silica particles produced by homogeneous nucleation exceeds the number of heteronucleii.

The effect of heteronucleii is pronounced under conditions where homogeneous nucleation is slow; that is, when $T > 70°C$, or when the brine has been diluted and acidified by adding 24.8% cooling water saturated with condenser vent gas (the last line in Table 5).

Heterogenous nucleation is important even though the mass of heteronucleii initially present is only equal to 1% of the silica in solution (6.05 ppm vs. 606 ppm). The reason is that the heteronucleii are very small; radius = 1.51 nm in this calculation. This radius corresponds to specific area A/M = 900 $m^2/g$, whereby 6.05 ppm would provide 5.4 $m^2$/kg-brine of surface area for dissolved silica to deposit upon. The surface area of particles produced by homogeneous nucleation is even larger; for example, at 40°C and t = 0.22 hours, 121 ppm colloidal silica is present in the brine with A/M = 1,470 $m^2/g$ and a total surface area = 178 $m^2$/kg-brine.

## 4. BRINE TREATMENTS COMPARED

Figures 3 and 4 present results calculated assuming a more realistic situation wherein the brine cools as it flows from the weir box to the injection well. The process steps modeled were:

1. Initial composition and T of brine in the reservoir as shown in Table 1.
2. Calcite inhibitor is applied downhole through a capillary tube below the bubble point.
3. Steam is separated from the brine at 8.0 bar-a.
4. The separated brine is discharged into the weir box at 0.73 bar-a and 91.1°C with further loss of steam.
5. If not inhibited, aluminosilicate minerals precipitate in the weir box in the amounts shown in Table 4, producing 6.05 ppm heteronucleii with R = 1.51 nm.
6. Temperature of brine flowing out of the weir box drops to 70° at t = 3 min.
7. Silica control treatment (if any) is applied at t = 3 min and 70°C.
8. Brine reaches the injection well at t = 10 min with T = 36 or 40°C, depending on whether-or-not cooling water has been added.
9. Brine temperature is unchanged at t > 10 minutes; that is, after it has been reinjected.

As before, separate calculations were performed assuming:

(a) Homogeneous nucleation only (fully effective silicate inhibitor applied), and

(b) Heterogeneous nucleation induced by aluminosilicate particles in addition to homogeneous nucleation (no silicate inhibitor applied).

Four additional treatment options to control silica were modeled:

a. No additional treatment.

b. At t = 3 min and 70°C, add 24.8% unmodified cooling water from Unit 13, diluting the brine and decreasing T to 58.5°C.

c. Add sulfuric acid to adjust pH to 5.7 at 70°C without diluting the brine.

d. At t = 3 min and 70°C, add 24.8% cooling water saturated with condenser vent gas, diluting the brine, lowering pH to 5.7 and decreasing T to 58.5°C.

Diluting the brine with unmodified cooling water from Unit 13 (Table 3) would have a limited beneficial effect (dotted red lines in Figures 3 and 4). Because the pH of the unmodified cooling water is higher than the pH of the brine (7.95 vs. 7.34), adding the unmodified cooling water would raise the pH of the brine to 7.86, largely cancelling the benefit from diluting the brine. With-or-without a silicate inhibitor, reinjecting the brine without decreasing pH will damage the injection well and receiving formation (dotted lines in Figures 3 and 4).

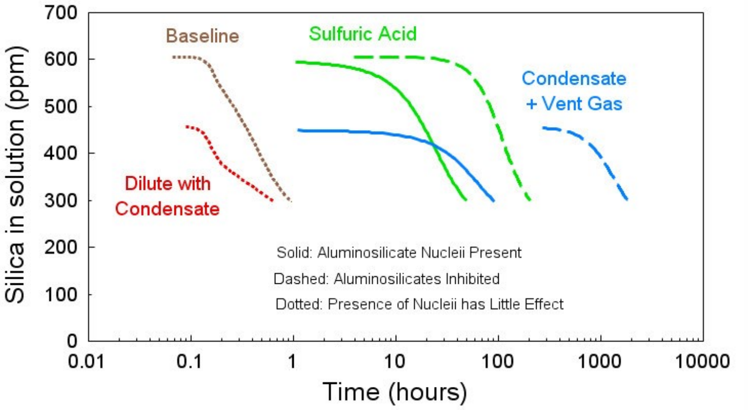

**Fig. 3. Brine treatments compared: Silica concentration**

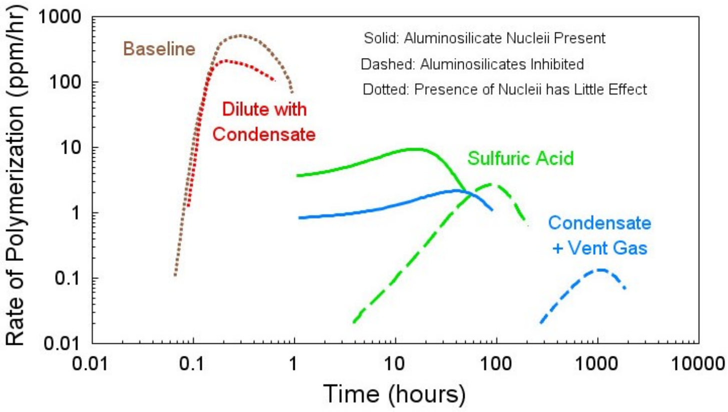

**Fig. 4. Brine treatments compared: Rate of polymerization**

Decreasing brine pH to 5.7 would greatly decrease the rate of silica polymerization at the injection well and in the receiving formation (blue and green lines).

Applying a silicate inhibitor to limit heterogeneous nucleation would amplify the beneficial effect of decreasing brine pH (compare dashed lines to solid lines).

Acidifying the brine by adding 24.8% cooling water saturated with condenser vent gas (blue lines) would dilute the brine in addition to lowering pH, whereby the beneficial effect would be greater than produced by using sulfuric acid (green lines) to attain the same pH. The greatest benefit is obtained by applying a silicate inhibitor, and diluting the flashed brine with cooling water saturated with condenser vent gas (dashed blue lines).

Using $CO_2$ to decrease brine pH is safer than using sulfuric acid in regard to corrosion. Brine pH is controlled and buffered by the ratio of $CO_2$ to bicarbonate in solution. Adding sulfuric acid converts bicarbonate to $CO_2$ destroying this buffer. Adding 37 ppm sulfuric acid to the brine will decrease pH of the flashed brine to 5.7 (Fig. 5). Adding 46 ppm, a 25% excess, will decrease pH to 3.9, with severe corrosion resulting. Adding $CO_2$ decreases pH without eliminating bicarbonate, and the brine remains well-buffered. Adding 135 ppm $CO_2$ to the flashed brine will decrease pH to 5.7; a 25% excess (170 ppm) will further decrease pH to 5.6 (Fig.6). Thus, adjusting pH using $CO_2$ is much easier to control and much safer than using sulfuric acid.

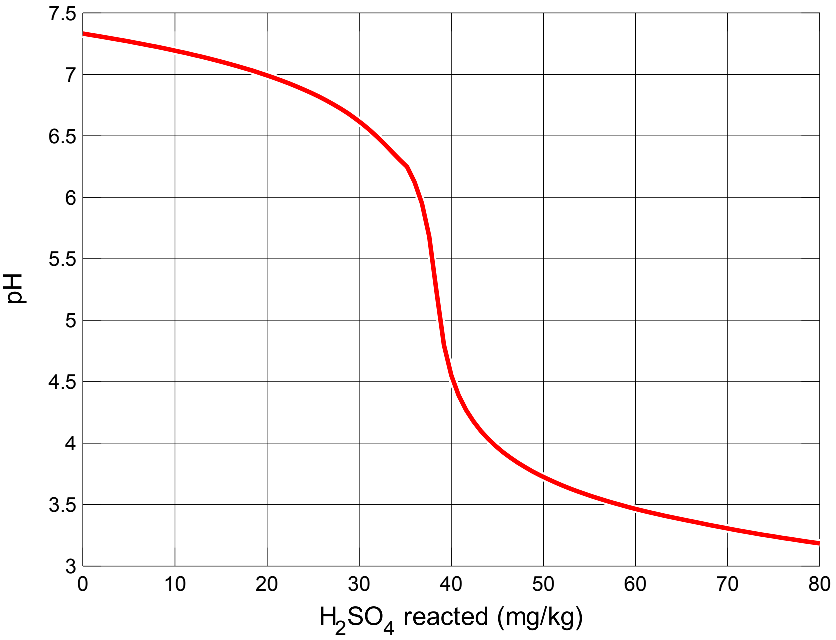

**Fig. 5. Adjusting the pH of flashed, undiluted brine at 40°C using sulfuric acid**

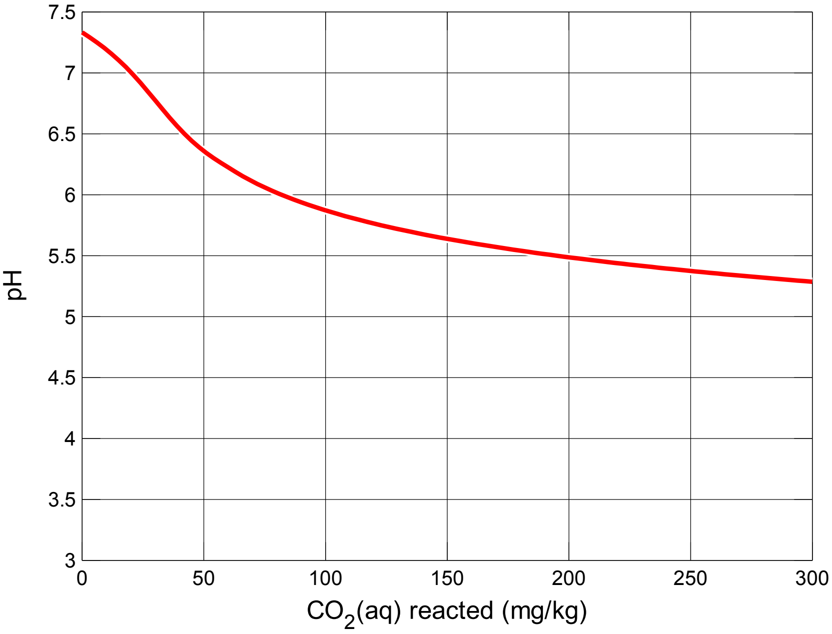

**Fig. 6. Adjusting the pH of flashed, undiluted brine at 40°C using carbon dioxide**

## 5. CONCLUSIONS AND RECOMMENDATIONS

Substantial capabilities for modeling the chemistry and behavior of geothermal fluids exist, but the models calculated necessarily are simplified approximations of reality and the practical conclusions flowing from them often are inferred rather than explicit; so it is with the modeling work summarized here.

The actual rate of silica deposition upon solid surfaces has not been calculated, but the calculated "polymerization rate" gives fair indication of when and where silica deposits are likely to form. If the maximum polymerization rate is reached in a fraction of one hour, silica deposits will be produced in surface equipment and the injection well will be damaged; this is the actual situation at Los Azufres. If by decreasing pH and/or applying inhibitors the peak polymerization rate can be delayed by a few hours, silica deposits will be produced in the receiving formation near to the wellbore. Whether-or-not deposits at that location actually damage the well will depend on the properties of the receiving formation. The permeability of sandstone characterized by primary porosity could be severely degraded, while extensively fractured igneous or metamorphic rock might be little effected.

If, however, the peak polymerization rate can be delayed by many hours, whatever deposition may occur will be far from the wellbore and the brine can safely be reinjected. This is the goal of brine treatment to protect the surface equipment and injection wells.

Based on the results presented above, the following brine treatment program is recommended for the Los Azufres geothermal field under present day operating conditions:

1. In wells that produce mostly brine rather than a mixture of steam and brine, apply a calcite inhibitor below the bubble point through a capillary tube to prevent calcite deposits.

2. Optionally, apply a silicate inhibitor below the bubble point in all production wells to make it easier to control silica deposits further downstream. Blended inhibitors effective against calcite and silicates are available and convenient.

3. Most important, add cooling water saturated with condenser vent gas to the flashed brine at T > 60°C; that is, before rapid polymerization of silica begins. A target pH about 5.7 would be highly effective, but the precise value is not critical.

4. Lowering pH will make the brine more corrosive, however implemented. Therefore, a suitable corrosion inhibitor should be applied, preferably before the brine is acidified.

### 5.1. Possibilities for increasing power output

The recommendations above apply to present day operating conditions at Los Azufres: one stage of steam separation, after which the brine is discharged at atmospheric pressure before being reinjected. The calculated results obtained further suggest possibilities that would allow more power to be generated:

A. Applying a silicate inhibitor in the productions wells would control silica deposits in the weir box. The same prediction applies to a second stage steam separator operating slightly above atmospheric pressure. Thus, additional low pressure steam could be provided to a turbine without problems related to brine chemistry.

B. It may also be possible to add a binary heat exchanger downstream of the second stage flash. The modeling results predict little deposition of silica or silicates down to at least 70°C if a silicate inhibitor is applied.

C. As an alternative, brine treated with a silicate inhibitor and discharged from the high pressure steam separator could be provided directly to a binary heat exchanger without further separation of steam. In this case, silica deposits would be even easier to control, because brine separated from steam at 8 bar and cooled to 70°C would have lower pH (6.83 vs. 7.09) and lower silica concentration (509 ppm vs. 606 ppm) than brine flashed a second time at atmospheric pressure.

## 6. ACKNOWLEDGMENTS

I would like to thank Miguel Angel Ramírez Montes of the CFE Geothermal Office in Morelia, Michoacan for permission to submit this paper, and Abraham Molina Martínez for providing the chemical analyses and other data used.

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