



UNITED NATIONS
UNIVERSITY

GEOTHERMAL TRAINING PROGRAMME



pH MODIFICATIONS FOR SILICA CONTROL IN GEOTHERMAL FLUIDS

Carlos E. Guerra and Patricia E. Jacobo

LaGeo S.A. de C.V.

15 Avenida Sur, Colonia Utila

Santa Tecla, La Libertad

EL SALVADOR

eguerra@lageo.com.sv, pjacobo@lageo.com.sv

ABSTRACT

Silica scaling has historically caused operational problems that can lead to limitations in power production. Once formed, silica scale can restrict fluid flow, reduce heat transfer efficiency and is costly to remove from equipment. There are many methods for controlling the precipitation of silica from geothermal water depending on the fluid temperature. Brine pH modification has been shown to be effective and the most inexpensive compared to others inhibitors. However, because the dosage of a strong acid (HCl or H₂SO₄) has high sensitivity to change pH in the range of 5.0-6.0, it requires a constant control of inhibition operation system. In order to avoid silica polymerization in brine from Ahuachapan Geothermal field, the dosing of hydrochloric acid (HCl) to pH of 5.5 produced the best results. In that way for the injection water cooling to 90°C, the monomeric silica level stayed stable during the 120 min of study. For cooling to 80°C, the polymerization degree was minimal in the first 75 min, but increased soon after until reaching 9.8% of silica polymerization at 120 min. Excellent control of silica deposition was obtained at all brine temperatures for pH 5.0 with HCl or H₂SO₄ dosing trials in Berlin and Ahuachapan Geothermal field. However, this pH lead to corrosion issues and for that reason pH range of 5.5 to 6.0 is appropriated to the brine. Nevertheless, the measured scaling rate at pH 5.5 is somewhat better than at pH 6.0.

1. INTRODUCTION

Amorphous silica is one of the major and most common scaling problems as its solubility decreases with decreasing temperatures. Depending on the conditions, amorphous silica scales may form anywhere from the production wells, surface facilities to downstream of injection wells (Erlindo C, 2006).

In order to prevent the deposition of amorphous silica in geothermal installations, it is common to keep its temperature above that corresponding with saturation for amorphous silica. This limits the amount of heat that can be extracted from the fluid discharged from production wells (Erlindo C, 2006).

As the brine is processed through flash vessels the concentration of silica increases and the brine temperature is further decreased. Under these conditions, silica is over saturated and will precipitate

as amorphous silica or it will react with available cations (e.g. Fe, Mg, Ca, Zn, etc.) and form co-precipitated silicate deposits. These deposits cause serious reduction in fluid flow from production wells, flash vessels, binary units and the injection system. In addition to causing flow reduction, silica scaling seriously affects heat transfer in binary unit equipment (Burton, et al, 2003).

When geothermal waters become over saturated with respect to amorphous silica two kinds of processes have the tendency to take place. One is deposition of monomeric silica directly onto available surface and the other is polymerization of monomeric silica to form silica polymers. Which process takes place in spent high temperature geothermal waters depends to some extent on the waters environment (Gunnarsson et al., 2010). If the waters are in turbulent flow where there is surface available for monomeric deposition onto the surface silica scaling is likely to take place, but if the waters are placed in quiet environment silica polymerization is the favorable process.

Brine in the reservoir is in equilibrium with quartz but brine becomes supersaturated with respect to amorphous silica due to boiling as the fluid flows up the well, monomeric silica begins to polymerize after a time known as the “induction period”. Studies about the silica induction period and polymerization rate, helped develop other approaches to controlling silica precipitation from geothermal brines, aside from avoiding over saturation (Erlindo C., 2006). These include: (1) lowering the pH by acidification, (2) brine aging to convert monomeric silica to colloidal silica, (3) use of inhibitors which claim to prevent or reduce silica scaling, (4) precipitation of the silica with lime or by bubbling CO₂ through the solution, (5) mixing the brine with steam condensate, (6) removal of colloidal silica by coagulation and (7) settling and controlling separator pressure to maintain the temperature of the brine above the silica super saturation temperature.

2. CASE HISTORIES ABOUT BRINE pH EFFECT ON SILICA DEPOSITION

2.1 Broadlands Geothermal Field, New Zealand

In New Zealand, silica scaling tests were performed at the Broadlands field (BROWN et al. 1983) using “doubly flashed” 100°C separated brine with an initial monomeric silica content of about 810 ppm. Here too, the polymerization rate was measured using monomeric silica decrease titration. “Oversaturation” was determined to range from 2.2 to 2.5. Rapid polymerization was observed at pH = 6 while at pH = 5 nearly no polymerization occurred for up to 200 minutes. Nevertheless since acidification “only delays silica deposition”, the authors do not recommend reinjection of such treated brine because of the risk that “some silica must precipitate in the well” (Grassiani M., 2000).

2.2 Mak-Ban Philippines

By the end of 1989, a field silica scaling test on hot (180°C) spent reinjection brine (860 ppm SiO₂) was attempted at the Mak-Ban Philippines geothermal power plant, in preparation for the future installation of an ORC heat recovery repowering system using that brine. On cooling the brine throughout the plant heat exchangers from a slightly silica oversaturated condition at 173-180°C to 137-140°C, the saturation index rises to about 1.7. As a result of the earlier conclusions drawn from the pH modification study, an acid injection system was installed by the brine supplier at the brine inlet of the power plant, where in-situ continuous pH control (to 5.5 ± 0.5) is performed. The Mak-Ban geopower bottoming cycle using air cooled ORMAT® Energy Converters (OECs) was the first in the world to introduce acid treatment in order to prevent (eventually by reduction of the silica polarization rate) silica scaling by reducing the pH from 6.3 to about 5.5 (Grassiani M., 2000).

2.3 Berlin Geothermal Field, El Salvador

During 2003-2011, LaGeo S.A. de C.V. formulated and undertook a series of pilot sized silica scaling trials at the Berlin geothermal field, test the effectiveness of acid dosing and inhibitors at various brine

temperatures. The objective for those works was to optimize the size of a brine binary power plant with respect to silica scaling issues, in the size range of about 5 to 10MWe. This paper briefly describes the methodology used and the results obtained from the trials.

For the accomplishment of the test, the equipment designed by Sinclair Knight Merz (SKM) was used, which it is constituted by a heat exchanger, residence tank, deposition tubing, metering pumps of chemical agents and mixture tanks. Figure 1 show the schematic flow process for test rigs (Guerra et al., 2005).

The polymerization trials took place with flow zero through the residence tank and taking water samples every 15 min during two hours from SV2 valve (Figure 1). In order to determine the behavior of silica polymerization to the conditions previously established for the fluid, pH, monomeric silica, and chlorides was analyzed to each sample in field laboratory, while total silica concentration was determined in the LaGeo main laboratory. The target of silica polymerization trials, is to determine the induction time available, before the silica deposition is starting to the temperature of the brine in study.

At the start of each rig trial, new lengths of 1/4 inch and 3/8 inch stainless steel deposition tubes were installed in each rig. Brine flow, untreated or treated as required, was then established through the tubes and maintained for typically seven days. The tubes were accurately weighed both before and after each test with an electronic balance reading to +/- 1 gm. The weight gain in the tubes with time was used to determine silica deposition rates.

Separated brine from wells TR-4/5 and TR-2/9

Five silica tests rigs were built by LaGeo and installed in October 2003 on the TR-9 well pad site at

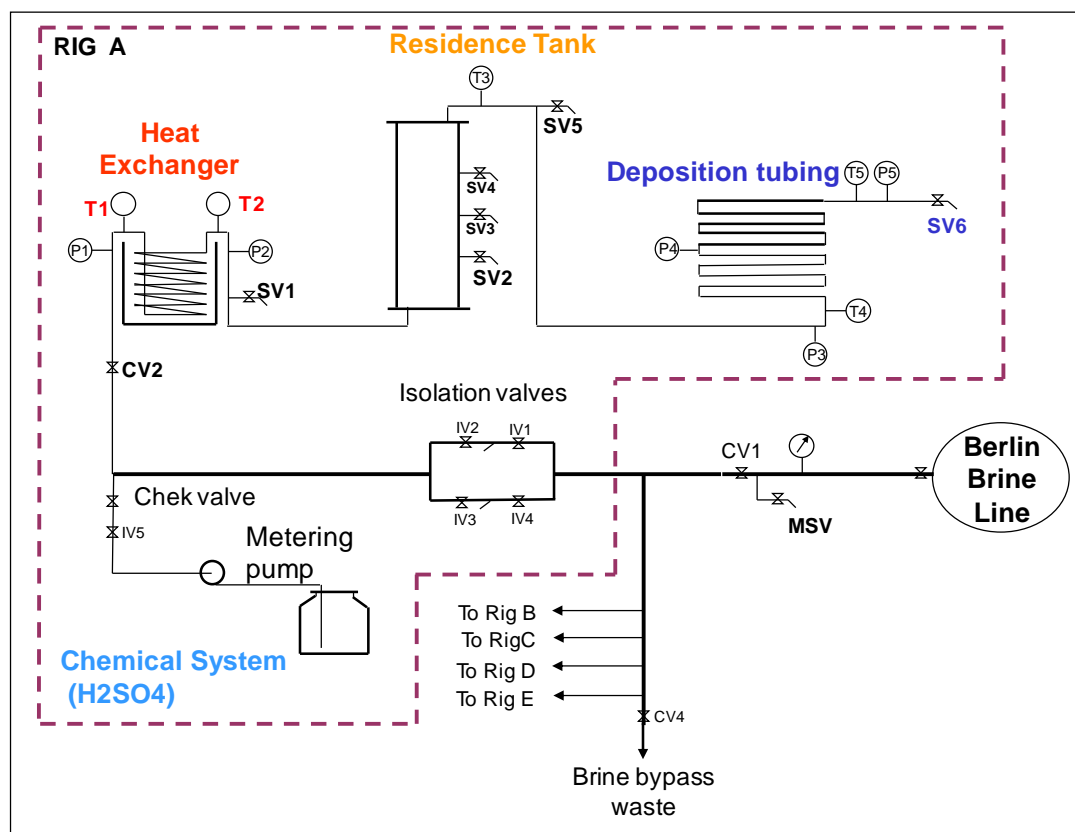


FIGURE 1: Schematic flow process for SKM test rigs

the Berlin geothermal field. Two sources of hot brine (184°C) were piped up to the rigs, one from the TR-4/5 production well pads and the other from production wells TR-2 and TR-9. The trials started in November 2003 and were concluded in February 2004. In summary the trials undertaken included: (1) Untreated brine cooled, (2) Brine dosed with HCl to pH of 5.0, 5.5, 6.0 and (3) Trials with some inhibitors, from a brine line supply temperature of 184°C to 160, 140, 120, 100, 70°C.

According to the depositions trials, it was evident from the untreated and the pH 6.0 acid treated brine, that even a limited degree of brine cooling from 185 to 170°C resulted in significant deposition (e.g. 200 tonnes of silica per year for a 350 kg/s binary power plant) if the brine could not be injected within 60 to 70 minutes from the time of the cooling. This result was in contrast to the polymerization results in Figure 2, which indicate that deposition would not be a problem over a time frame of at least 120 minutes for brine cooled down to 155 to 165°C (Molina et al., 2004).

Treatment with HCl	Brine cooling temp. at which onset of polymerization occurs	
	After 60 min	After 120 min
Untreated	130 to 140°C	155 to 165°C
pH = 6.0	120°C	135°C
pH = 5.5	100°C	120°C
pH = 5.0	80°C	100°C

FIGURE 2: Temperature at which onset of polymerization occurs

Excellent control on silica deposition was obtained at all brine temperatures for the pH 5.0 HCl dosing trials. However, this pH lead to corrosion issues and for that reason pH range of 5.5 to 6.0 is appropriated to the brine in study. The measured scaling rate at pH 5.5 is somewhat better than at pH 6.0. At the upper limit of pH 6.0, the brine can be cooled and held at 130°C for 120 minutes before silica polymerization and silica scaling becomes an issue (Barnett, 2004).

Separated brine from wells TR-17/18

The water separated from the producing wells TR-17 and TR-18 achieves a throughput of 232 kg/s at temperature of 175°C. At the mixing point of both fluids the water temperature decreases to 172 °C. Whereas the brine at this point has an average content of 703 ppm of total silica (Figure 3), the saturation index was calculated at different temperatures (Figure 4). It was observed that at 170°C the fluid is at the limit of oversaturation with respect to the amorphous silica (ISS = 1.0), so hopefully minimal scaling in the transport pipe when the fluid is cooled to that temperature.

For trials temperatures of 100°C and 115°C without chemical treatment to the TR-17/18 brine, the induction time was practically zero, which means that once cooled fluid at such temperatures, the potential silica scaling is high and therefore deposition process is imminent. To 120°C silica has an induction time of 1.25 hours, whereas for 130°C and 140°C is 1.5 hours (Figure 5).

The tests of silica polymerization with separated water from TR-17/18 wells, were performed to a temperature range of 100°C to 160°C, both without chemical treatment such as sulfuric acid dosing (Figure 6). The results are described below:

- Without chemical treatment at 100°C there was a 17.8% of silica polymerization and decreased to 1.8% at 160°C. It was observed that for both 130°C and 140°C the polymerization rate was about 4%;
- The use of sulfuric acid to a pH of 5.5, showed an effective silica polymerization control to temperatures of 100°C, 120°C and 130°C with values of 1.8%, 2.6% and 1.2% respectively.

To the cooled fluid to 130°C a scaling rate of 0.06 g/ton was obtained without chemical treatment, which decreased to 0.01 g/ton with application of sulfuric acid to a pH of 5.5. The fluid cooled to

120°C and without chemical treatment, showed a scaling rate of 0.15 g/ton, which improved with acid dosage to a pH of 5.5 yielding a result of 0.04 g/ton embedding.

Sample point	Na	K	Ca	Mg	Cl	SO4	HCO3	SiO2	Si mon	B	Li	Ph	Fluid Temp
	(ppm)												(°C)
TR-4/5	3775	745	103	0.057	6920	18	4.4	809	759	134	15	6.55	184
TR-2/9	4066	799	127	0.065	7536	16	4.1	827	769	144	17	6.59	184
TR-17/18	3850	638	166	0.109	6819	26	10.1	703	689	138	15	6.89	172

FIGURE 3: Chemical content of Berlin brine

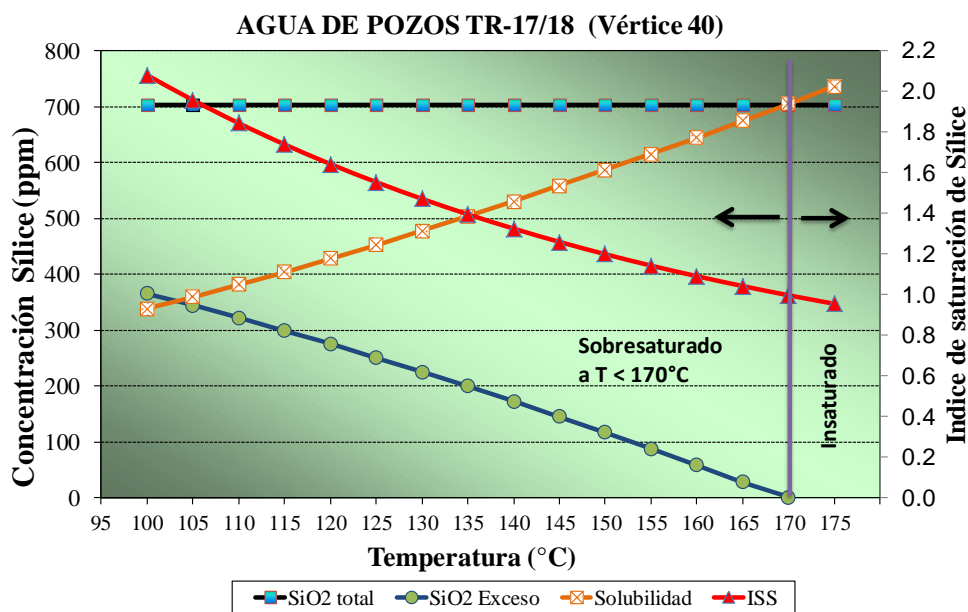


FIGURE 4: SSI of water from TR-17/18

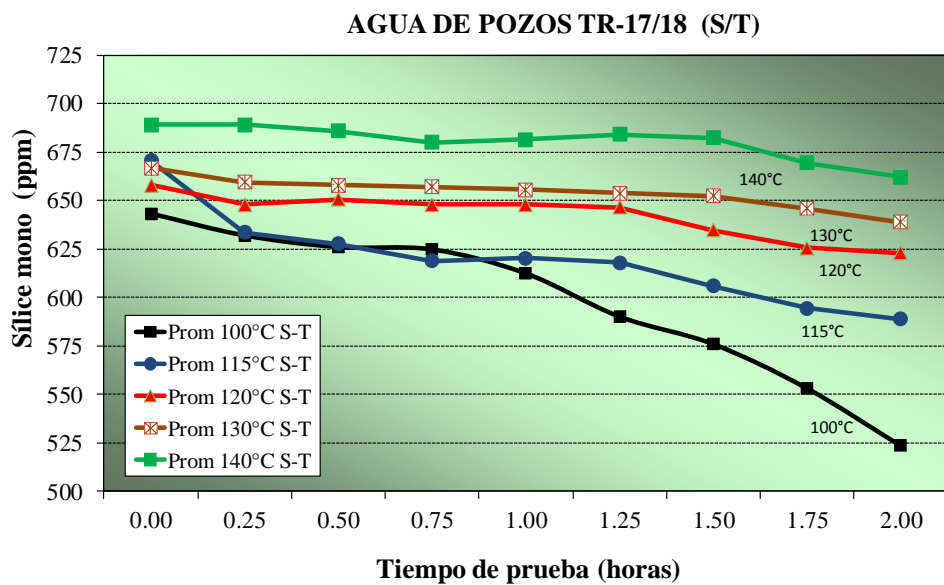


FIGURE 5: Monomeric silica of brine from TR-17/18, without treatment to different temperatures

2.4 Ahuachapan Geothermal Field, El Salvador

The fluid injected to Chipilapa wells, is a mixture of the residual water from different producing wells, after a second vaporization to generate lower pressure steam. After this second vaporization the brine temperature is about 115°C, thus it is considered like cold injection.

In October 2004, five test rigs were settled near the flashers in Ahuachapán Geothermal Power Plant. In this area the feed brine for testing was facilitated, at the initial conditions that the fluid is sending to Chipilapa wells. The study included the following:

- Fluid Cooling from 112°C to 105, 90, 80 and 60°C, without chemical treatment;
- Fluid Cooling from 112°C to 90 and 80°C, applying HCl for pH of 5.5 and 6.0.

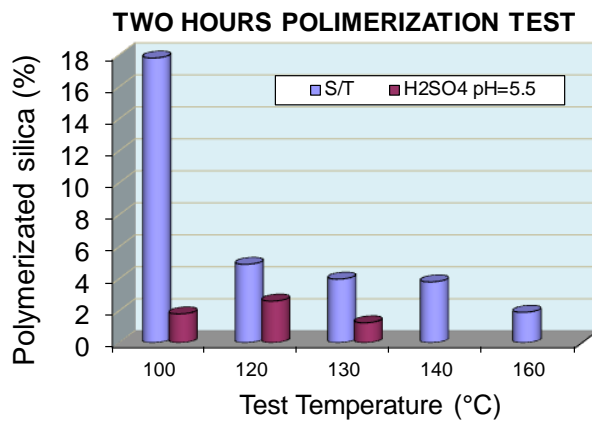


FIGURE 6: Polymerization test with brine from TR-17/18

Figure 7 shows the results of the silica polymerization process to the brine without chemical treatment. For the range of temperatures in study 105, 90, 80 and 60°C, the induction time was practically zero, which means that still to 105°C silica scaling is in process. Nevertheless, it can be appraised a different polymerization speed according to the fluid temperature. For instance, in the first 45 min of test for the fluid temperature of 105°C, it has polymerized an average of 3.1% of the monomeric silica, whereas for 60°C the polymerization reached in the same time was 18.2%.

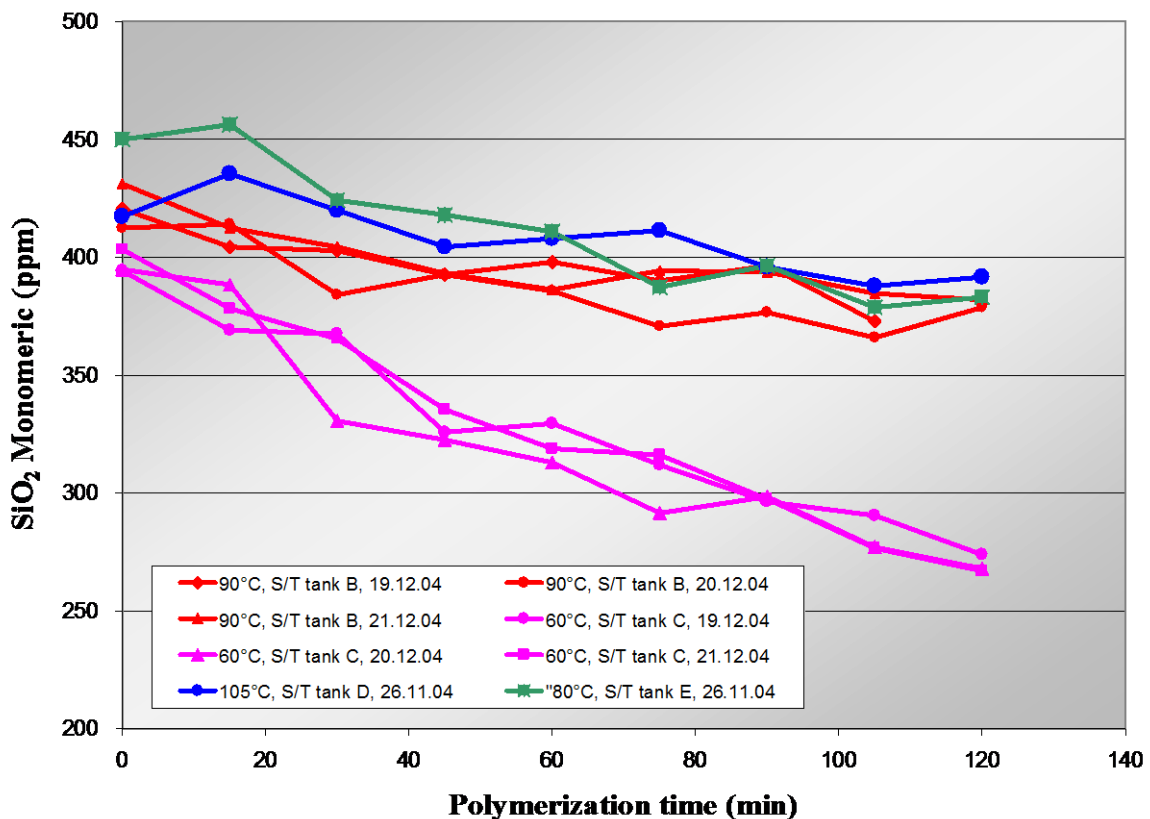


FIGURE 7: Silica polymerization without treatment. Ahuachapan 2004

In the first 45 min of test with HCl to pH of 6.0 for the fluid to 90°C, it has polymerized an average of 4.4% of the monomeric silica, whereas for 80°C the polymerization reached in the same time was 9.4%.

Acid dosing to obtain pH of 5.5 in the fluid cooled to 90°C, accomplished stopping the silica polymerization during the first 75 min of test and after 120 min a low polymerization (3%) is observed. For the test to 80°C after 45 min, the polymerization rate is only 2.8%, and after 120 min it has reached 9.8% (Figure 8). These results indicate that lowering the pH to 5.5 in the injection brine to Chipilapa, is effective to control the silica polymerization for the fluid cooled to 90°C.

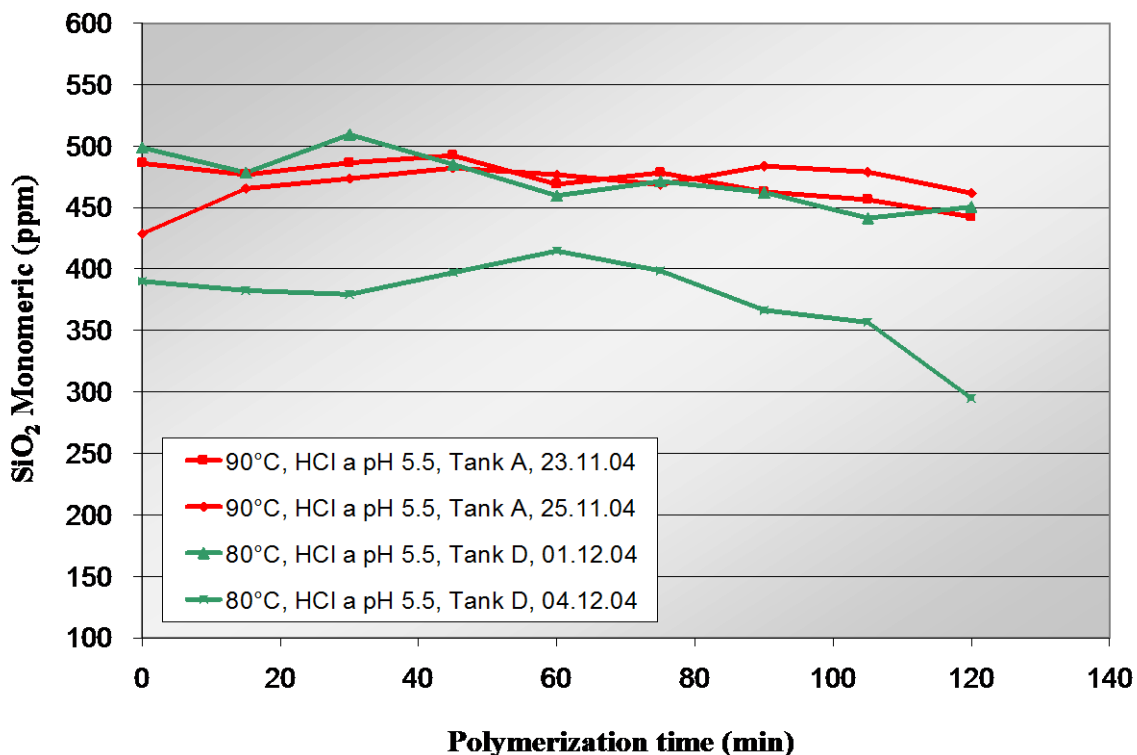


FIGURE 8: Silica polymerization with treatment to pH of 5.5 Ahuachapan 2004

2.5 Berlin Binary Power Plant

Post commissioning period, the Binary Cycle Power Plant (BCPP) resumed operations in June 5, 2008, and since has been operating with a few interruptions generating an average of 7.2 MWe/hr. Geothermal water that circulates through the plant, lose an average of 45°C in the heat exchange with the working fluid, lowering its temperature to 140° C.

During the first year of operation of the BCPP (2008-2009), the brine was treated to dose HCl in order to reduce the water pH to a value of 5.5. However, due to serious corrosion problems in the acid dosing system (pumps, capillary tube, etc.), it was not possible to obtain continuity in the chemical treatment. As a result, it had silica scaling of 1.0 to 2.8 mm thick in the tubes of heat exchangers. In September 2009, the heat exchangers were subjected to chemical cleaning with a mixture of hydrofluoric acid and phosphoric acid, which was stirred about 90% of the inlay.

After seven months of operation of the BCPP (after the first chemical cleaning), the exchanger tubes presented embedding 0.5-1.8 mm thick, so they were subjected to a second chemical cleaning in May 2010. Since this date sulfuric acid was used for brine treatment to pH 5.5-5.6, which helped to decrease the corrosion problems dosing system (Figure 9). The use of H₂SO₄ allowed more effective

chemical treatment than HCl, so that after 15 months of operation the inlay in the exchanger tubes did not exceed 0.4 mm thick and many of them were completely cleaned.

Prices comparison of different silica inhibitors, shows that pH modification using sulfuric acid is the least expensive option for silica control. Treatment of 295 kg/s of brine that passes through the BCPP, requires an intake of 7500 kg per month of concentrated sulfuric acid to decrease fluid pH values in the range of 5.5-5.6, which represents about \$3,000.00 of monthly cost.

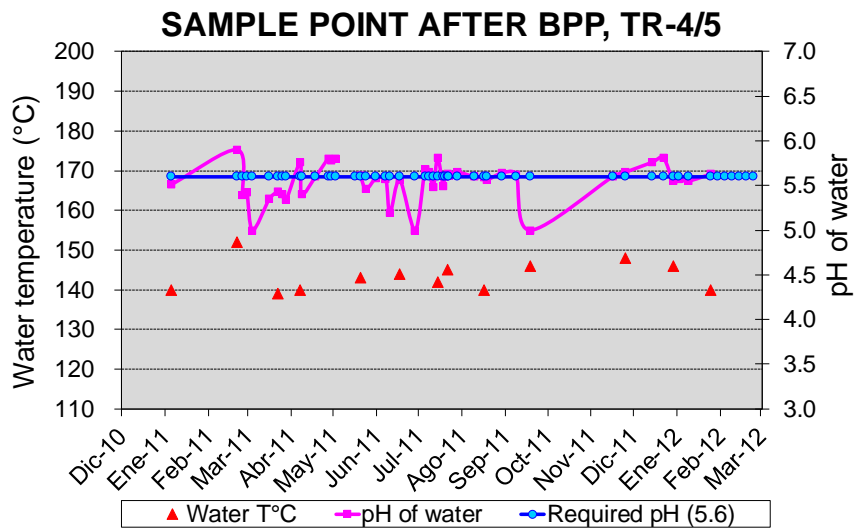


FIGURE 9: Brine pH control at Berlin binary power plant, 2011

3. CONCLUSIONS AND RECOMMENDATIONS

Excellent control on silica deposition was obtained at all brine temperatures for the pH 5.0 with HCl or H₂SO₄ dosing trials. However, this pH lead to corrosion issues and for that reason pH range of 5.5 to 6.0 is appropriated to the brine. Nevertheless, the measured scaling rate at pH 5.5 is somewhat better than at pH 6.0.

There are many methods for controlling the precipitation of silica from the geothermal water depending on the fluid temperature. Brine pH modification has been shown to be effective and the most inexpensive compared to others inhibitors. However, because the dosage of a strong acid (HCl or H₂SO₄) has high sensitivity to change pH in the range of 5.0-6.0 (Figure 10), it requires a constant control of inhibition operation system.

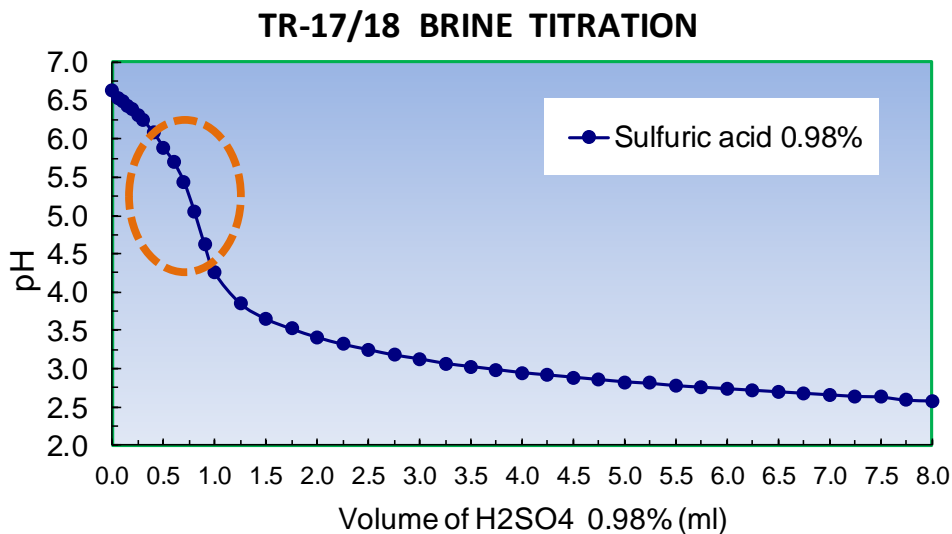


FIGURE 10: Potentiometric titration of TR-17/18 Berlin brine, 2011

ACKNOWLEDGEMENTS

I wish to express my sincere thanks to the LaGeo Company, for their budgetary contribution in order to make possible this silica scaling trials. My sincere gratitude to the special people from Ahuachapan and Berlin Geothermal Power Plant, for their effective help in different activities. I also thank to people from Engineering and Studies Management for the guidance and knowledge shared during the trials and the report write-up.

REFERENCES

- Burton, A., Bourcier, A., Bruton, C., and Leif, R., 2003: Silica scale management: Lowering operating costs through improved scale control, and adding value by extracting marketable by-products. *Geothermal Resources Council Transactions*, 27, 519-522.
- Erlindo C., 2006: An experiment on monomeric and polymeric silica precipitation rates from supersaturated solutions. Report 5 in: *Geothermal Training in Iceland 2006*. UNU-GTP, Iceland, 21-50.
- Guerra C., Jacobo P., Tenorio J., 2005: Silica scaling: polymerization and inhibition trials at ahuachapán geothermal field, El Salvador. *Internal Geothermal Congress, LaGeo S.A. de C.V.*
- Guerra C., 2011: Resultados de pruebas de polimerización e inhibición de incrustación de sílice, con agua separada de pozos TR-17/18. *LaGeo S.A. de C.V., internal report*.
- Gunnarsson I., Ívarsson G., Sigfússon B., Thrastarson E. and Gíslason G., 2010: Reducing silica deposition potential in waste waters from Nesjavellir and Hellisheiði power plants, Iceland. *Proceedings World Geothermal Congress 2010, Bali, Indonesia*, 5 pp.
- Grassiani, M., 2000: Siliceous scaling aspects of geothermal power generation using binary cycle heat recovery. *Proceedings World Geothermal Congress, Kyushu - Tohoku, Japan*, 3167-3171.
- Molina S., Barnett P., Castro M., Guerra C., Henríquez J., 2005: Silica polymerization and deposition trials at the Berlin Geothermal Field, El Salvador. *Proceedings World Geothermal Congress, Antalya, Turkey*, 4 pp.
- Matlick S., Stapleton M., 2004: Successful development of new silica inhibitor technology at Ormesa. *Geothermal Resources Council Transactions*, 28, 425-428.