FIELD TESTING OF pH MODIFICATION SILICA INHIBITION WITH CHEMICAL CORROSION INHIBITION

A.I. Remoroza, A.V. Mejorada, A.T.N. Salazar

Energy Development Corporation
Fort Bonifacio
Taguig City, MetroManila, 1630, Philippines
e-mail: remoroza.ai@energy.com.ph

ABSTRACT

A field experiment was conducted at Nasuji Sector, Southern Negros Geothermal Production Field, Philippines to evaluate the use of high temperature corrosion inhibitor in brine treated with sulfuric acid. The brine with approximately 400 ppm excess silica (SiO_2) was acid treated to inhibit silica polymerization.

The brine from the first separator vessel was acid treated to reduced the pH to about 4 - 4.5 and was conductively cooled from ~160 to ~120°C to simulate the temperature drop after a second flash system. The chemical corrosion inhibitor was introduced right after cooling and the corrosion rates were monitored using corrosion probes and metal coupons inserted at different sections along the pipe.

The experiment showed that the chemical corrosion inhibitor, at 10 ppm concentration, could inhibit corrosion of carbon steel pipes and lower the corrosion rate by as much as 70%, at a temperature of ~120°C and at a pH range of~ 4.0 to 4.5.

INTRODUCTION

The Northern Negros Geothermal Production Field (NNGPF) will use a second flash system to generate additional power output, which will drop the brine temperature from 160°C after the first flash to ~120°C after the second flash. The expected silica saturation index at the second flash is 1.96 (or 96% oversaturated). This is roughly equivalent to 400 ppm of excess silica (SiO_2) that has the potential to deposit in the re-injection system.

To prevent deposition in the re-injection system, pH modification will be used to delay silica polymerization until it reaches the well formation. However, pH modification could induce corrosion problems along the line, as reducing pH could increase the corrosion rate and the probability of material failure.

In this study, the use of high temperature corrosion inhibitor in pH-modified brine is investigated.

EXPERIMENTAL DESIGN / METHODOLOGY

The expected silica level of the NNGPF mixed brine after the second flash is ~950 ppm or roughly 400 ppm in excess of saturation. Since the study was conducted before NNGPF commissioning, field testing was done on brine at the Nasuji Sector of the Southern Negros Geothermal Production Field, which approximates the NNGPF brine chemistry.

The pilot test facility for the pH modification and corrosion inhibition studies is basically a compartmentalized pipeline where each section is set to a specific condition (Fig.1).

The first section of the pipeline serves as the blank or reference line condition; it has the same brine temperature as that of main reinjection line (approx. 160°C). Sulfuric acid is introduced at the second section, dropping the pH from ~7.0 to 4.5 while maintaining brine temperature at about 160°C. A series of cooling coils between the second and third sections of the pipe drops the pH-modified brine temperature to ~120°C. Between the fourth and final sections is where corrosion inhibitor is injected.

Corrosometer probes where placed at key locations to determine the corrosion rate at specific intervals. Metal coupons were also placed at each section to determine material loss due to corrosion. These corrosion coupons were polished, cleaned and weighed prior to testing.

Two-inch (2) diameter pipe was used for the test, with each section approximately 10 feet long to
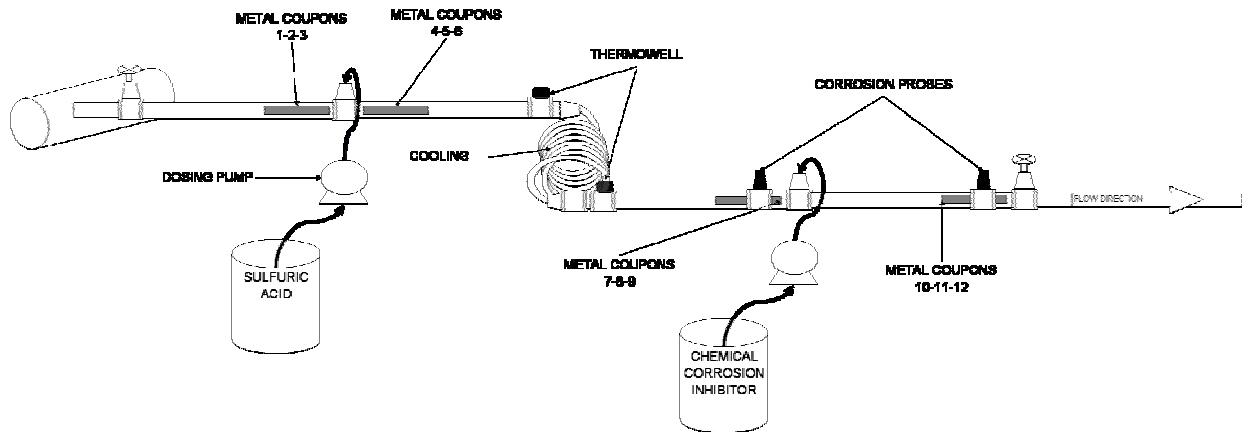
Figure 1. Schematic diagram of pH modification Silica Inhibition with Corrosion Inhibition Experimental Set-up

ensure adequate mixing of the brine with the chemical introduced. Sections of the pipe were insulated using abaca fiber to maintain constant temperature (Fig. 2). A high temperature corrosion inhibitor was used to control corrosion in the experiment and was injected at a concentration of 10 ppm. The chemistry, temperature, pH and flow rates were monitored; the test was run for a month to achieve stable corrosion rates.
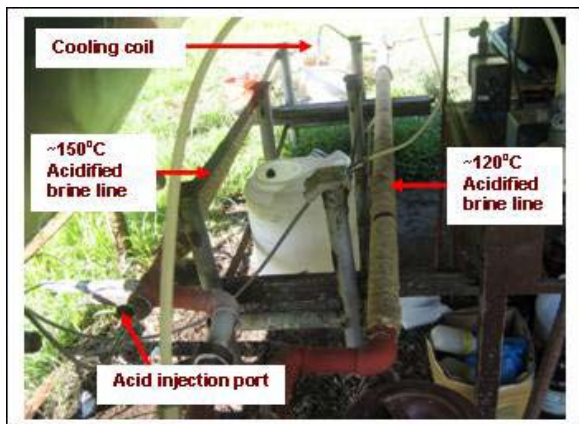

Figure 2. Nasuji Testing Facility showing pre-cooled and cooled section of the brine line.

EXPERIMENTAL RESULTS AND DISCUSSION

Metal Coupons

The metal coupons labeled 4 –12 were intended to measure material loss due to corrosion. These coupons, however, appeared to gain weight at the end of the test. The weight gain is suspected to be due to the considerable deposits formed on the exposed surface of the metal coupons. Therefore, no viable material loss measurement can be established with these results.

Petrological analyses of deposits formed on metal coupons 4 -12, scraped off using plastic spatula, yielded generally soft and easily removable deposits. Coupons 4 - 6 are greenish gray in color, very thin deposits covering almost the entire surface, very similar texture/structure, with small ripple marks, relatively thicker deposition noted at the edges, soft and can easily be wiped and removed. Coupons 7-9 have thick whitish gray deposits showing wider ripple marks, soft and can easily be wiped and removed. Coupons 10-12 have light brownish deposits covering most of the metal surface, exhibits ripple marks, soft and can easily be wiped and removed.

Generally for coupons 4-12, two layers of silica deposits formed on the surface of corrosion coupons: a thin and dense basal layer that is attached to corrosion products (hematized magnetite), and an overlying porous, thicker layer of globular silica dendrites (Delfin & Rosell, 2006).

Deposits from coupons 1-3, on the other hand, were identified as amorphous silica scales, relatively hard and adherent to the metal coupon surfaces. Further, these are white to off white, grayish, exhibiting ripple marks, non-uniform or irregular deposition and thick deposition noted at edges, brittle and easily breaks (Fig. 3– 6).

Figure 3. Metal coupons 1 – 3, blank/reference line condition, ~160°C, un-acidified

Figure 4. Metal coupons 4 – 6, ~150°C, acidified pH ~4.5

Figure 5. Metal coupons 7 – 9, ~120oC, acidified pH ~ 4.5

Figure 6. Metal coupons 10 –12, ~120oC, acidified pH~4.5 and with corrosion inhibitor

Corrosion Rates

Corrosion rates of the acid-treated brine were measured for more than 30 days. The average corrosion rate of the ~120°C, acid-treated brine was computed at 0.165 mm/year, while the ~120°C acid-treated brine with corrosion inhibitor had an average corrosion rate of 0.048 mm/year (Fig. 7). This translates to a ~70% decline of the corrosion rate due to the 10 ppm injection of the inhibitor. Towards the end of the experiment the corrosion rates measured were ~0.1 mm/year and ~0.02 mm/year, respectively and could still go down as the passivating film formed along the pipe walls thicken. For reference,

the allowable corrosion rate of carbon steel pipes is 0.125 mm/year for a 25-year life span.

pH Modification Method Of Silica Inhibition

Diluted sulfuric acid was used to reduce the pH from ~7 to ~4.5, aimed at delaying the polymerization of monomeric silica. The pH target of ~4.5 was constrained by allowable limits of carbon steel, with the hope that this is low enough for the pH modification of brine to be effective in delaying the silica polymerization. In addition, previous polymerization test results from NNGPF well PT-5D indicated that a pH of 4.2 was sufficient to delay polymerization of excess silica. However, based on the results of the experiment, significant deposition was observed in the metal coupons even in acid-treated brine. The characteristic of the silica deposited in the acid treated brine is different from the untreated brine in that the latter deposits are hard, adherent and brittle whereas in the former the silica deposits are soft and can easily be removed.
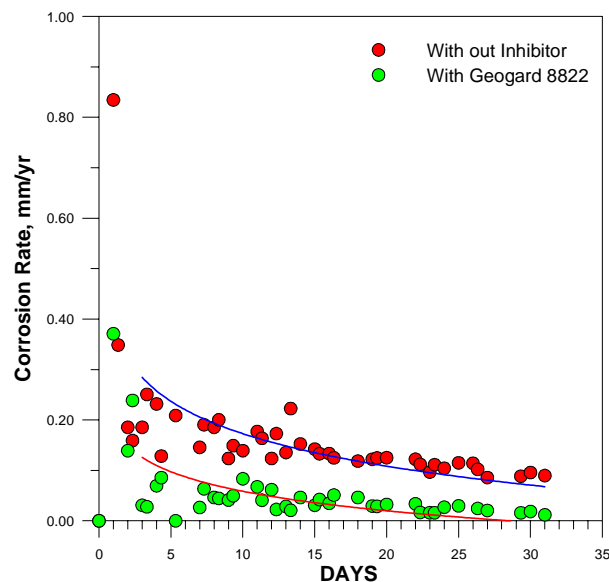

Figure 7. Measured corrosion rates based on corrosometer readings

Several studies have been made on the relationships of pH and silica polymerizations at laboratory conditions (Iler, 1978). Baumann as cited by Iler first observed that at certain conditions of pH (5.8 to 9) and silica concentration, there is an "induction period" during which there is little or no polymerization of monomer. It was also concluded by many investigators that polymerization of monomers involves a reaction between $Si(OH)_4$ and $=Si^-$ ions, whether the latter is in solution as $-SiO_3^-$ or on a polymer as an ionized $=Si^-$ group. This explains the autocatalytic effect as the ionization constants of SiOH group on the polymer increases with molecular

size, until such time that there is offsetting decrease in the concentration of $Si(OH)_4$. One can also consider the induction phenomenon in terms of nucleation of colloidal particles (Marsh, Klein, Vermeulen in Iler, 1978).

The combination of the metal ion with silicic acid maybe regarded as an adsorption of metal hydroxide on the silica. Combination does not occur much below the pH at which the metal hydroxide would be formed. It is possible therefore, especially at low pH, that the combination between silicic acid and metal ion involves the association of polymeric units both of silica and of basic metal cations as there are multiple points of attachments. Polysilicic acid can enter chelate-like bonding with a metal atom (see diagram below).
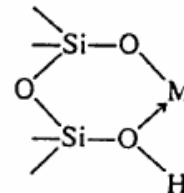
These chelate-like bonding of colloidal silica with metal ions in the brine can explain the observed coloration of precipitated amorphous silica in metal coupons 4 –12. This can also explain why the amorphous silica formed in metal coupons 4 –12 is loosely attached; the bonding sites of the colloidal silica were reduced due to adsorbed metal ions. The different coloration of the metal coupons is due to the preferred metal ions adsorbed at different conditions. The brownish coloration of metal coupons 10 –12 can also be attributed to adsorbed organic polymer from the injected corrosion inhibitor.

CONCLUSIONS

The experiment showed that high temperature corrosion inhibitor at 10 ppm concentration could inhibit corrosion of carbon steel pipes and lower the corrosion rate by as much as 70% at a temperature of ~120°C and at a pH range of~ 4.0 to 4.5.

The Nasuji brine apparently showed a short induction time as metal coupons 1 – 3 exhibited significant silica depositions. The residence time between the separator vessel and metal coupons 1-3 is less than 5 minutes. That explains the silica depositions in metal coupons 4 –12; colloidal silica already exists when acid is introduced to the system and the change in pH resulted in the association of colloidal silica with metal ions to form colored precipitate.

The chelate-like bonding of colloidal silica with metal ions in the brine resulted in the coloration and

loosely attached precipitated amorphous silica in metal coupons 4 –12. The bonding sites of the colloidal silica were reduced due to adsorbed metal ions. The different coloration of the metal coupons was due to the preferred metal ions adsorbed at different conditions. The brownish coloration of metal coupons 10 –12 can also be attributed to adsorbed organic polymer from the injected corrosion inhibitor.

Polymerization tests should be done on the actual NNGPF brine to determine induction time and the optimum pH to hold the colloidal silica in the solution (equivalent to the residence time of the brine from the second flash vessel to the well total depth). If the induction time is greater or equal to the residence time then no acid injection may be needed after the second flash. But if acid injection is unavoidable, corrosion inhibitor (at 10 ppm concentration) may be required to ensure the integrity of the pipe against corrosion. Another possibility is that protective layer of silica deposits will form in the pipeline even with acid injection but not massive enough to cause re-injection capacity problem.

REFERENCES

ILER, R.K. 1978. *The Chemistry of Silica: Solubility, Polymerization, Colloid and Surface Properties, and Biochemistry*. New York, USA: John Wiley and Sons.

ROSELL, J.B and M.C.Z. DELFIN. 2006. *SilicaDeposits in SNGPF Corrosion Coupons (April 2006)*. PNOC-EDC internal report.