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Mitigation of Silica Deposition in Wellbore Formation in Malitbog Sector, Tongonan Leyte, Philippines

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ABSTRACT

Brine being injected in Malitbog is oversaturated with respect to silica. While maintenance of pipelines in 1999 – 2003 showed minimal silica scaling (3.0-8.0 mm total), the injection wells have recurring injection capacity declines. Well 5R1D, after being mechanically cleared, barely gained capacity from 98 to 123 kg/s, but showed increased capacity from 44 to 137 kg/s after acidizing. Well 5R4, after acidizing, regained full capacity from 76 to 201 kg/s. Injection capacity decline indicates silica deposition is occurring in the wellbore formation.

Tests were conducted to determine the effectiveness of Geogard SX (GSX) and pH Modification in controlling silica scaling at low excess silica in the brine (~ 50 – 120 ppm silica; SSI = 1.10 – 1.18). A pilot set-up mimicking the pipelines and wellbore formation incorporated retention and formation vessels. Induction time (IT) in a polymerization vessel of the untreated brine (pH = 6.8) is 45 – 55 minutes, while in the acid treated brine (pH = 5.3 – 5.6), monomeric and total silica were maintained for at least 75 minutes, which was the end of the induction test based on the available sampled brine in the polymerization vessel. The residence time (RT) of the brine to the wellbore loss zone is 23 minutes, confirming that silica will deposit in the formation and not upstream.

In the untreated brine test, silica deposition occurred in the inspection pipe (31.3-50.7 mm/yr) and formation materials, while in the pH Modification test, no silica deposition occurred anywhere in the line. These were confirmed by inspection, flowrate, formation weight, petrologic analysis and brine chemistry monitoring. However, in the acid treated test, corrosion rate was relatively high and attributed to overdosing resulting to brine pH sometimes way below the target pH. In the GSX test at 0.5 ppm dosing, silica deposition still occurred in the inspection pipe and formation materials but at very low thickness and deposition rates (2.4-11.9 mm/yr). These were also confirmed by inspection, flowrate, formation weight, petrologic analysis and brine chemistry monitoring.

Of the two methods tested, pH Modification is the most cost effective mitigating solution to silica deposition in Malitbog. However, GSX inhibition (up to 2.0 ppm) is still cheaper than work-over and acidizing.

1. INTRODUCTION

The Malitbog Fluid Collection and Recycling System (FCRS) in Tongonan Geothermal Field has been experiencing problems in disposing the separated brine (275 kg/s) from the Malitbog sector due to recurring brine injection capacity shortfall. The brine reinjected in the Malitbog injection wells (5R1D, 5R4 and 5R7D) is oversaturated with respect to silica at Silica Saturation Index (SSI) of 1.10-1.20 and excess silica of 50-120 ppm at 160^{o}C injection temperature (Table 1). Though, maintenance of injection pipelines and surface facilities in 1999 – 2003 showed minimal silica scaling (3.0-8.0 mm thickness), the injection wells in Pad 5R1 have recurring injection capacity declines. Well 5R1D, after being mechanically cleared in August 2000, barely gained capacity from 98 to 123 kg/s, but showed increased capacity from 44 to 137 kg/s after acidizing in May 2002. With the poor results of mechanical clearing in well 5R1D in year 2000, well 5R4 was acidized in April 2001 and it regained full capacity from 76 to 201 kg/s. The injection capacity declines indicate that silica deposition is occurring in the wellbore formation and not in the FCRS piping and surface facilities.

Table 1. Malitbog baseline brine chemistry.

Parameter	August 11, 2003	October 27, 2003
pH	7.04	6.71
SiO_2 (ppm)	776	788
Cl (ppm)	10,660	10,802
SSI	1.18 (160^{o}C) Line Temp	1.20 (160^{o}C) Line Temp
H_2S (ppm)	4.91	2.18
CO_2 (ppm)	13.2	12.5
SO_4 (ppm)	22.8	20.2
HCO_3 (ppm)	6.7	4.62
NH_3 (ppm)	1.32	2.77
Fe (ppm)	0.35	0.54
B (ppm)	206	219
Na (ppm)	5949	5772
K (ppm)	1428	1338
Ca (ppm)	259	228
Mg (ppm)	0.31	0.19

Tests were therefore designed and conducted between November 2002 to November 2003, to evaluate the effectiveness of two methods in controlling silica scaling in the wellbore formation. One method involves the use of Geogard SX (a chemical inhibitor) dosed into the brine at 0.5 ppm (Baltasar, 1998). The other involves modifying the brine pH by dosing sulfuric acid (H_2SO_4) into the brine to reduce its pH and prolong start of silica polymerization at location farther away from the wellbore formation (Candelaria, 1996). The methods are described in this study as GSX and pH MOD Tests, respectively. The main objectives of the tests are: (1) to find a solution to the silica deposition problem in Malitbog; (2) to reduce the maintenance cost of re-injection wells; and (3) to provide Malitbog sector sufficient brine injection capacity that is sustainable for a longer period of time.

2. FIELD ARRANGEMENT AND SET-UP

2.1 Induction Time Determination

The induction time of silica in the brine, or the time it takes for the excess silica to start polymerizing (Iler, 1979), was determined using a polymerization vessel (Fig. 1). This sample collection vessel is heated by the brine flowing in the outer chamber to maintain the temperature of the sample in the inner chamber close to the line temperature. The brine sample collected is aged inside the inner chamber through time and spot collection at fixed time intervals (2-5 minutes) of 2 mL aged sample is then analyzed for monomeric and total silica. This is also conducted for the pH MOD run, by injecting small quantities of sulfuric acid to modify and reduce the pH of the aged sample. The time it takes for the monomeric silica concentration to start dropping is the determined induction time.

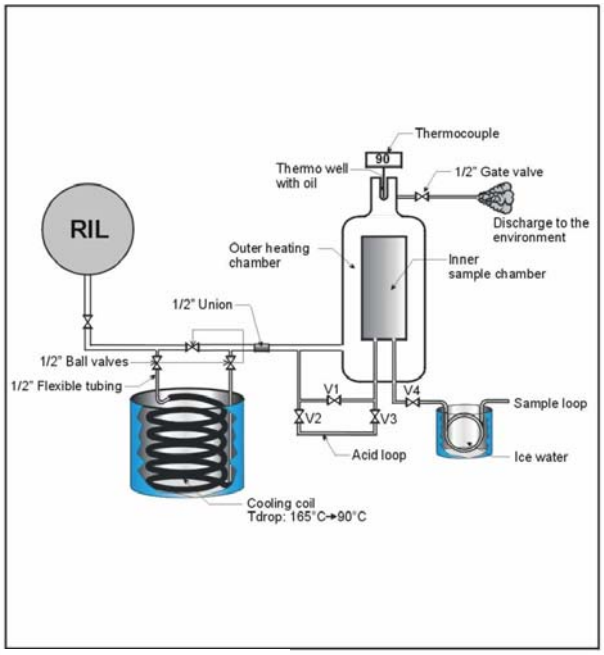


Figure 1: Silica polymerization set-up.

2.2 Silica Inhibition Set-Up

A pilot test set-up was designed (Fig. 2) and installed (Fig. 3) to mimic the residence time (23 minutes) of the brine from the separator vessel to the shallowest wellbore loss zone in well 5R1D. The residence time is approximated by the flow of the sampled brine from the main reinjection line through the retention vessels. The wellbore formation is duplicated by placing identical formation materials (Mamban Formation) in a 6" diameter by 12" length mid-pipe of the formation vessel. Core samples during drilling of Malitbog wells were just broken into formation pieces and placed in the mid-pipe of the formation vessel. The actual surface area for deposition was not determined, but the formation pieces were arranged in such a way that allows brine sample to freely flow. Cooling coils are installed before the retention vessel, before the formation vessel, and after the formation vessel to characterize the chemistry of the brine sample as it travels through the set-up. Pressure gauges were installed in each retention vessel. A by-pass line after the retention vessel is provided to check any observed decline in sample flowrate through the formation vessel. The flowrate through time is monitored in the installed mini-silencer at the end (outlet) of the set-up. For the pH MOD Test, an acid dosing tank and dosing pump were installed before the retention vessel.

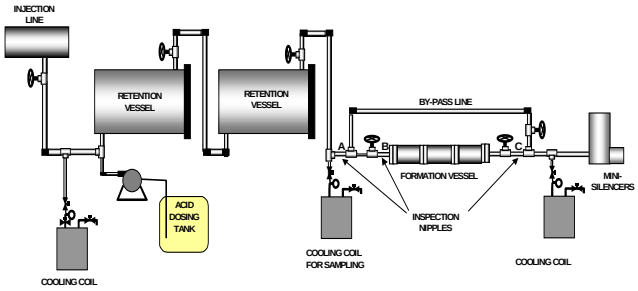


Figure 2: Malitbog silica inhibition schematic diagram.



Figure 3: Malitbog silica inhibition pilot test set-up.

3. RESULTS AND DISCUSSIONS

3.1 Induction Time Tests

Three induction time tests were conducted using the polymerization vessel, two for the untreated brine to determine the time for the excess silica to start polymerizing in the baseline condition, and one with the brine pH modified to 5.3 – 5.6. The target pH of 5.3 – 5.6 in the pH MOD induction time test was determined earlier in a similar induction time test using a mini-silencer, with brine sample allowed to flash to ambient condition. This case is the worst condition because the brine temperature is allowed to reduce to 93.5^{o}C and silica over-saturation increases to SSI=2.57. Since silica polymerization time was extended for at least 60 minutes in the worst condition (with brine pH modified to 5.3 – 5.6), this was the target pH range used in the pH MOD test. Results of the induction time tests (Fig. 4) showed that in the untreated brine (pH = 6.8), induction time is between 45 – 55 minutes and this was repeatable in two trials. About 80-100 ppm monomeric silica polymerizes, which is within the calculated excess silica in the brine. In the acid treated brine (pH = 5.3 – 5.6), monomeric and total silica concentrations were maintained for at least 75 minutes, which was the end of the induction test based on the available sampled brine in the polymerization vessel. The actual induction time could be longer and can be determined by increasing the time between sampling interval in the induction test. Since the residence time (RT) of the brine in the Malitbog FCRS from the separator to the shallowest wellbore loss zone in well 5R1D is calculated to be 23 minutes, the induction time test results confirm that silica will deposit in the wellbore formation and not upstream in the FCRS surface facilities.

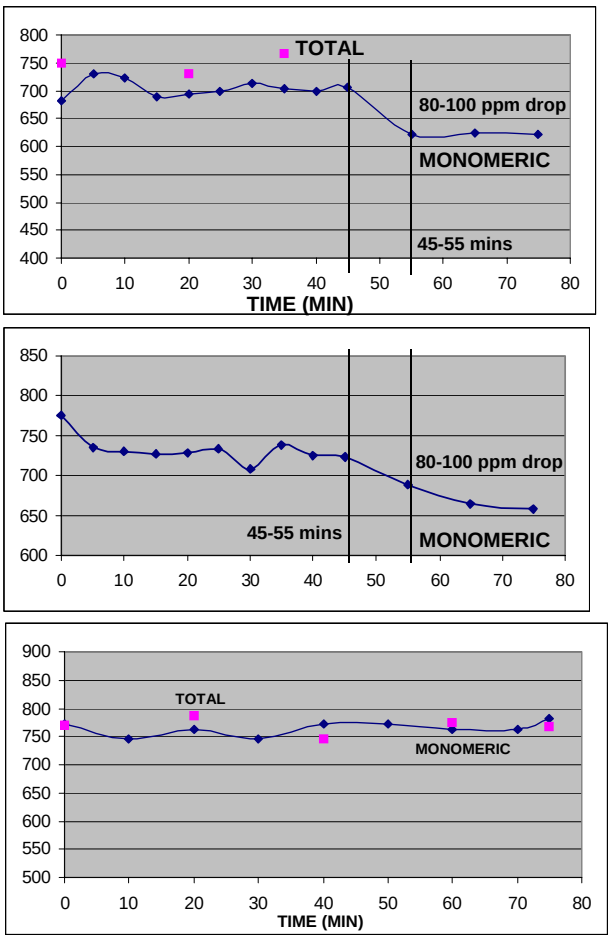


Figure 4: Results of Malitbog brine induction time determination.

3.2 Flowrate, Inspection and Formation Weights

Physical measurements and documentation were conducted during the entire duration of the tests. Sample flowrate was monitored by conducting daily measurements using a 2000mL graduated cylinder at the mini-silencer outlet. Inspection, internal diameter measurements and photo-documentation of the three inspection nipples (2 pcs. carbon steel and 1 pc. stainless steel) installed in series in the set-up was conducted before installation and after harvest at the end of the tests. The formation materials were also inspected, photo-documented and the weight measured before being placed in the formation vessel and after harvest at the end of the tests, to determine silica deposition after exposure to the flowing brine sample. The exposure time for each test runs between 33-36 days.

The results of the sample flowrate monitoring (Fig. 5) shows that in the untreated test, the sample flowrate declined from as high as 0.21 kg/s to a low of 0.15 kg/s. The decline was significant after the 20th day of the test. In the pH MOD test, the sample flowrate was maintained between a range of 0.19-0.21 kg/s, with average of 0.2041 kg/s throughout the test. In the GSX test, the sample flowrate slightly declined gradually from 0.22 to 0.21 kg/s. Also, a more stable sample flowrate was attained in the GSX test than in the untreated and pH MOD tests because of more stable brine flow in the Malitbog main reinjection line. During the untreated and pH MOD tests, the brine flow in the main reinjection line was varying due to some field activities conducted (e.g. well opening changes), to contain a current field operation problem. The flowrate monitoring indicates that silica deposition in the formation vessel occurred in the untreated test, effectively blocking and reducing the sample flow. In the pH MOD and GSX tests, silica deposition either did not occur, or was at very low thickness and deposition rate, that it was not able to block and reduce the sample flow. However, changes in sample flowrate were not correlated to pressure data because only the retention vessel pressure was monitored (with no pressure changes observed). The inspection and photo-documentation of the formation materials after being harvested proved the initial indications.

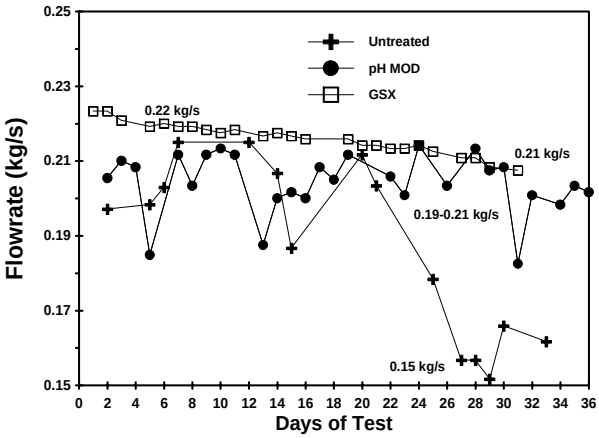


Figure 5: Results of brine flowrate measurements during the untreated, pH MOD and GSX tests.

Shown in Figures 6, 7 and 8 are the photo-documentation of the inspection nipples, formation vessel and formation materials in the untreated, pH MOD and GSX tests, respectively. In the untreated test (Fig. 6), massive and thick (0.6-4.7 mm) silica deposits were found in the inspection nipples, formation vessel and formation materials. It also coated and cemented the surface of the formation materials and was uniformly deposited in the entire length of the formation vessel. The silica deposits were very adherent and hard to remove. In the pH MOD test (Fig. 7), no silica deposition was observed in the inspection nipples, formation vessel and formation materials. While in the GSX test (Fig. 8), silica deposition was still noted in the inspection nipples, formation vessel and formation materials, but these were significantly of lower thickness (0.04-1.0 mm) and deposition rate than the untreated test.

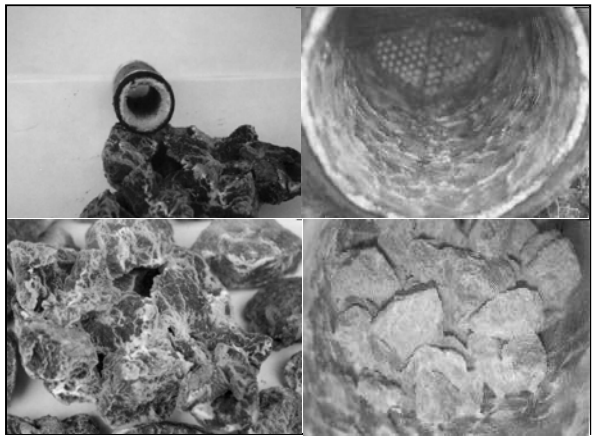


Figure 6: Photo-documentation of inspection nipple, formation vessel and formation materials exposed to untreated Malitbog brine.



Figure 7: Photo-documentation of inspection nipple, formation vessel and formation materials exposed to pH Modified Malitbog brine.



Figure 8: Photo-documentation of inspection nipple, formation vessel and formation materials exposed to GSX treated Malitbog brine.

Table 2 presents the measured silica scale thickness in the inspection nipples and the difference in the weights of the formation materials after exposure to the flowing brine sample. In the untreated test, the silica scale thickness ranges between 2.9 – 4.7 mm (31.3-50.7 mm/yr), with thickest at the first inspection nipple (Nipple A). There was also a corresponding weight gained by the formation materials of around 0.30 kg in 33 days exposure. In the pH MOD test, only in inspection Nipple B (stainless steel) where a positive change in the internal diameter was observed at 0.02 mm thickness (0.2 mm/yr). In inspection Nipples A and C (carbon steel), negative changes in internal diameter were observed, indicating that the internal diameters became bigger and loss of material or corrosion occurred. Occurrence of corrosion was validated later by UT measurements in the inspection nipples. There was also a corresponding weight lost by the formation materials of around 0.25 kg in 36 days exposure. In the GSX test, the silica scale thickness in the inspection nipples ranges between 0.2-1.0 mm (2.4-11.9 mm/yr), much lower than in the untreated test. There was also a corresponding weight gained by the formation materials of around 0.15 kg in 30 days exposure, lower by half than in the untreated test. These results are still consistent with the results of the flowrate monitoring and photo-documentation wherein silica deposition were only significant in the untreated test, at lower rates in the GSX test, and negligible in the pH MOD test.

Table 2. Scale thickness in inspection nipples and formation weight difference after harvest.

Test	Days of Test	Nipple A (mm)	Nipple B (mm)	Nipple C (mm)	Formation Weight Diff (kg)
Baseline untreated	33	4.722	2.900	3.349	0.30
pH MOD	36	-0.020	0.020	-0.002	-0.25
GSX (0.5 ppm)	30	0.200	1.000	0.800	0.15

3.3 Geochemical Evaluation

3.3.1 Brine Chemistry Monitoring

Water samples were collected daily (except on Sundays) at the three sampling locations using the installed cooling coils (Fig. 2). These were analyzed for pH, total silica, chloride and dissolved iron. Chloride was used as a parameter to determine the quality of sample (i.e. to indicate dilution or flashing), although this is no longer discussed in this paper, as most of the plotted results for total silica and dissolved iron came from good quality samples indicated by stable chloride levels. Also, no sample collection was conducted during erratic main brine line flow due to problems in injection capacity.

In the untreated test total silica monitoring (Fig. 9), total silica concentrations after the formation vessel were 20-100 ppm lower than concentrations before the brine sample enters the formation vessel, indicating that about 20-100 ppm silica are deposited in the formation materials. These levels are within the calculated excess silica in the brine. Except for three outliers, the total silica concentrations are generally maintained before the retention vessel and before the formation vessel, supporting the results of the induction time test wherein it was determined that silica will only significantly deposit after about 45-55 minutes or just before it enters the formation vessel.

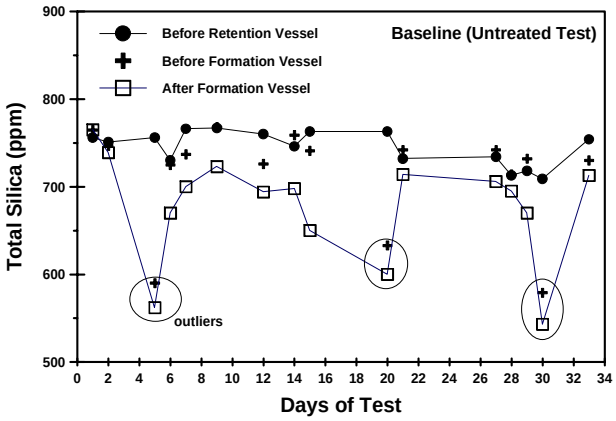


Figure 9: Total silica monitoring in three sampling locations during untreated test.

In the pH MOD test, brine pH monitoring (Fig. 10) showed baseline (untreated) pH at around 6.8-7.0, while the sulfuric acid dosed section mostly at pH range of 4.5 – 5.7. The brine pH before and after the formation vessel was also maintained, indicating no neutralization as the acid-dosed brine comes in contact with the formation materials. The lower pH range was attained by dosing a prepared sulfuric acid solution (0.02N) at an average dosing rate of 2.53 LPH. There were instances of overdosing (pH of 3.3 – 4.5) and underdosing (pH of 5.8 – 6.0) due to the manual control of the dosing pump and the in-exactness of the concentration of the prepared acid solution. The intermittent overdosing is the main cause of the corrosion observed in the pH MOD test. In the total silica monitoring of the pH MOD test (Fig. 11), total silica concentrations were generally maintained before and after the formation vessel, indicating no significant deposition in the formation materials. This result is consistent with the acid-treated induction time test, and documentation of the inspection nipples and formation materials in the pH Mod test. However, it was observed that total silica before the formation vessel was slightly higher than before the retention vessel, indicating some flashing occurring in the retention vessels.

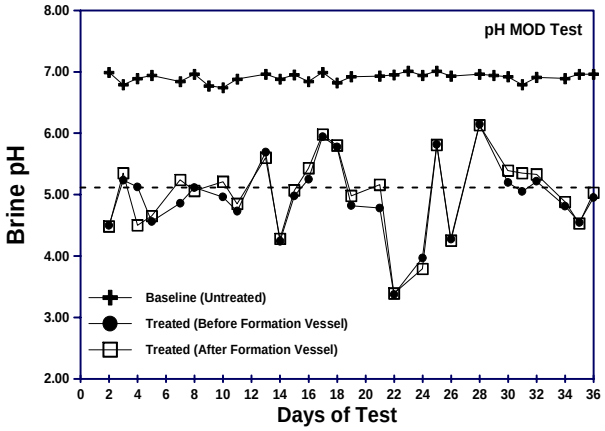


Figure 10: pH monitoring in three sampling locations during pH Modification test.

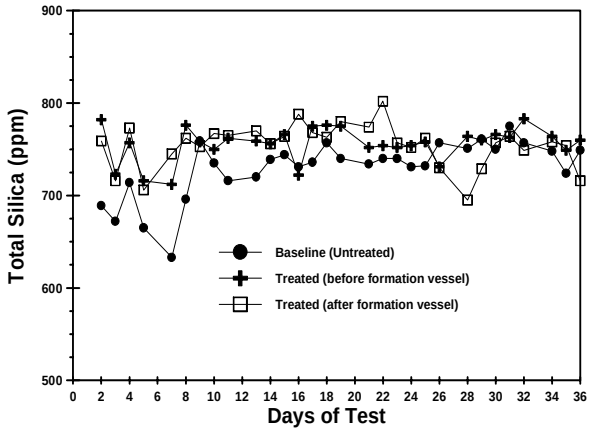


Figure 11: Total silica monitoring in three sampling locations during pH Modification test.

In the GSX test total silica monitoring (Fig. 12), a slight decline in total silica concentrations (5-25 ppm) were observed before and after the formation vessel, indicating slight deposition occurring in the formation materials. This was consistent in the documentation of the inspection nipples and formation materials in the GSX test. However, around 10-25 ppm silica is also observed to be lost between the retention vessels, indicating that minute amount of silica has also deposited in the retention vessels. This remains to be documented as the retention vessels composed of flanged 36" diameter pipes still has to be opened. This will be opened once no further tests are considered and total dismantling of the set-up is decided.

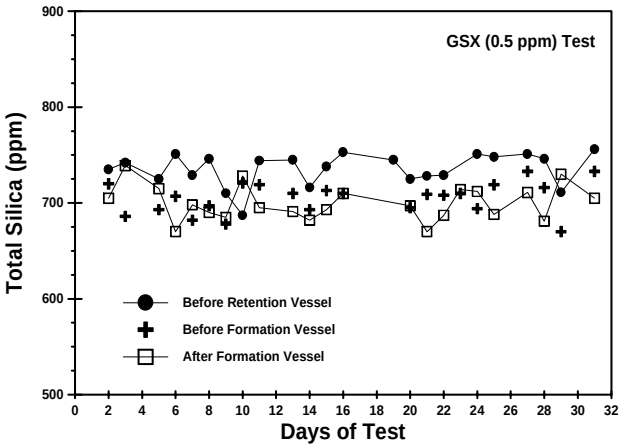


Figure 12: Total silica monitoring in three sampling locations during GSX test.

3.3.2 Petrologic Evaluation

The formation materials were harvested at the end of each test and samples were sent for petrologic analysis. Results shown in Table 3 indicate that the samples collected from the untreated and GSX test, have amorphous silica formed around the rock fragment as glassy, colorless to whitish deposits. The deposits in the untreated test were relatively hard and brittle, while in the GSX test they can easily be removed by a knife. The silica layer was also thickest in the untreated test (0.6 – 3.0 mm) as compared to the GSX test (0.04 – 1.0 mm). The sizes of the silica globules formed were generally the same for both untreated and GSX tests (0.02 – 0.08 mm). Also, of the four rock samples collected in the GSX test and sent for petrologic analysis, two showed silica deposits in the surface while the two other samples have nil silica deposits. This also confirms that the silica deposition in the GSX test was of significantly less magnitude than the untreated test. In the pH MOD test, the two rock samples sent for petrologic analysis all showed no silica deposition. The petrologic analysis describes the composition of the formation material (i.e. volcanic breccia intensely altered to Quartz + drusy Anhydrite + Opaques + Smectite + Vermiculite + Illite + Calcite + Chalcopyrite).

3.3.3 Corrosion and UT Measurements

Ultrasonic Thickness (UT) gauging was conducted in the three inspection nipples installed during the pH MOD test. Results shown in Table 4 indicate relatively high thinning rates (1.05-2.19 mm/yr) in the carbon steel inspection nipples (Nipples A and C) and negligible thinning rates (0-0.08 mm/yr) in the stainless steel inspection nipple (Nipple

B). This supported the results of the inspection nipple internal diameter measurements in the pH MOD test indicating material loss. The material loss or corrosion observed is attributed to the episodes of uncorrected overdosing (pH=3.3-4.5) during the pH MOD test. However, dissolved iron monitoring during pH MOD and GSX tests (Fig. 13), indicated no significant difference in dissolved iron concentrations monitored in the pH MOD and GSX test brine, indicating that corrosion was not that significant to elevate the dissolved iron concentrations in the pH MOD test. Thus, automated dosing rate control and monitoring of the resulting brine pH will be a significant factor in the design of future industrial scale pH MOD applications. If in future monitoring of industrial scale installation, the corrosion rates measured are still high, then it would be more prudent to shift the solution to be dosed from sulfuric acid to GSX, but at dosing rates higher than 0.5 ppm.

Table 3. Petrologic analysis of formation materials exposed to the brine

Test	Petrologic Analysis
Baseline (Untreated)	Megascopic description: Amorphous silica formed around the rock fragment as glassy, colorless to whitish deposits which are relatively hard and brittle. Microscopic analysis: Two distinct layers of amorphous silica (isotropic to slightly anisotropic) are observed: Basal layer (nearest to rock) is a flat structureless band of massive amorphous silica with an almost uniform thickness of ~0.1 mm. Outer layer is porous forming dendritic structures with globular silica aggregates (sizes of silica globules = 0.02 to 0.05 mm); layer thickness ranges from 0.6 to 3.0 mm.
pH MOD	*Sample 1* is composed of one fragment (size~28 x 8 mm) of volcanic breccia intensely altered to Quartz + drusy Anhydrite + Opaques + Smectite + Vermiculite + Illite + Calcite + Chalcopyrite. *Sample 2* consists of one fragment (size ~ 32 x 15 mm) of volcanic breccia same as Sample1 but crosscut by drusy Anhydrite veins and opaques + quartz veinlets.
GSX (0.5 ppm)	*Megascopic description:* Amorphous silica formed around the surface of rock fragments as gray, glassy deposits in dendritic patterns. The silica deposits can easily be removed by a knife. Out of four rock samples, two develop silica deposits on the surface while the other two samples have nil silica. *Microscopic analysis:* Amorphous silica deposited on surface of rock samples as a single layer with thickness ranging from 0.04-1.0 mm. Silica layer is generally flat and structureless, but becomes porous in some portions. It is isotropic to slightly anisotropic forming globular aggregates (sizes of silica globules range from 0.04 - 0.08 mm).

Table 4. Thinning rate (UT Gauging) in inspection nipples during pH MOD test.

Side	Nipple A (Carbon Steel) (mm/yr)	Nipple B (Stainless Steel) (mm/yr)	Nipple C (Carbon Steel) (mm/yr)
1 – 1200	1.29575	0	1.78485
2 – 0300	1.13515	0.0803	2.19000
3 – 0600	1.37970	0	1.05485
4 – 0900	1.05485	0	1.94545

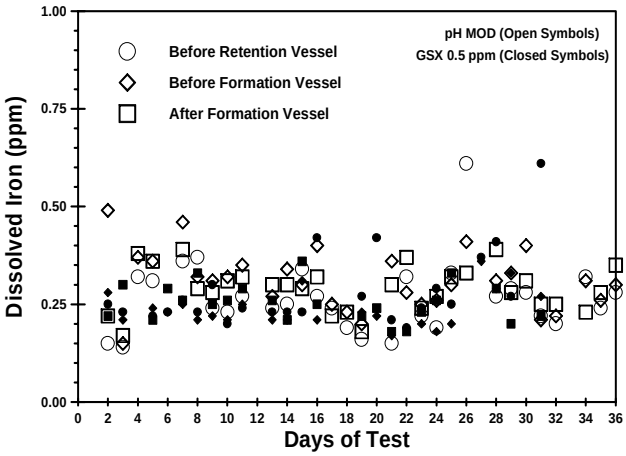


Figure 13: Dissolved iron monitoring during pH Modification and GSX tests.

4. COST EVALUATION

Table 5 shows the cost evaluation for the two methods tested as compared to the current silica deposition clearing employed by PNOC-EDC which is mechanically working-over and acidizing the well. These are calculated with the assumption of one (1) work-over and acidizing operation (P16 million per acidizing job) is conducted every two years for injection wells 5R1D and 5R4. The chemical cost is calculated at brine flow rate of 275 kg/s, the typical total brine load in Malitbog FCRS. Industrial grade sulfuric acid was canvassed to be P4.00 per kg (PASAR sourced), while GSX is priced at US$ 18.00 (P990.00) per kg (latest price quotation from supplier). The capital cost for the dosing pumps, solution tank, electrical, mechanical and piping requirements for the industrial scale installation was patterned after the capital cost of the caustic soda dosing in the Upper Mahiao Zero Effluent Disposal System. GSX dosing was also varied from 0.5 ppm to 3.0 ppm dosing in view of the slight ineffectivity of 0.5 ppm GSX dosing. The cost evaluation and comparison shows that pH Modification is the most cost effective mitigating solution to the silica deposition problem in Malitbog wellbore formation. However, GSX inhibition (up to 2.0 ppm dosing) is still cheaper than work-over and acidizing.

Table 5. Cost evaluation of the different methods in silica mitigation in Malitbog.

Method	Well Work-Over / Acidizing	pH MOD	GSX
Capital Cost	-	MP 1929.10	MP 1672.60
Operating Cost	MP 32,000.00	P4.00 /kg MP 1,625.94	P990.00 /kg
0.5 ppm			MP 6,227.02
2.0 ppm			MP 24,908.08
3.0 ppm			MP 37,362.12
Total	MP 32,000.00	MP 3,555.04	MP 7,899.62

Note : Using Malitbog brine, with SSI of 1.10-1.18
1 work-over / acidizing every 728 days (2 yrs.) in 2 RI wells
brine flow rate of 275 kg/s
MP – thousand pesos (P55.00 = $1.00)

5. SUMMARY

Injection capacity declines in wells 5R1D and 5R4 indicate silica deposition occurring in wellbore formation. Tests in March to November 2003 determined the effectiveness of Geogard SX (a chemical inhibitor) and brine pH Modification in controlling silica scaling. The time it takes silica to start polymerizing was determined to be 45-55 minutes in the untreated brine (pH=6.8), while in the acid treated brine (pH=5.3-5.6), silica concentration was maintained for at least 75 minutes, which was the end of the induction test based on the available sampled brine in the polymerization vessel. The travel time of the brine to the wellbore loss zone takes 23 minutes, confirming that silica deposits in the wellbore formation. In the untreated brine test, thick silica deposited in the inspection pipe (31.3-50.7 mm/yr) and formation materials, while in the pH Modification test, no silica was deposited anywhere in the line and formation materials. In the GSX test, silica deposited in the inspection pipe and formation materials but at very low thickness and deposition rates (2.4-11.9 mm/yr). These were confirmed by inspection, flowrate, formation weight, petrologic analysis and brine chemistry monitoring. Of the methods tested, pH Modification is the most cost effective mitigating solution to silica deposition in wellbore formation in Malitbog. However, GSX inhibition (up to 2.0 ppm dosing) is still cheaper than work-over and acidizing. With pH MOD extending the induction time of the brine much longer than the baseline, it is hoped that the silica-rich brine will travel farther away from the wellbore and re-equilibrate with reservoir fluids at hotter formation temperatures.

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