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EFFECT OF NATURAL ACIDITY TO SEPARATED BRINE WITH VERY HIGH SILICA SUPERSATURATION

James B. Nogara

PNOC Energy Development Corporation, Merritt Road, Fort Bonifacio, Taguig City, Philippines

ABSTRACT

Mindanao-2 power plant is the second power station in Mindanao Geothermal Production Field operated by PNOC-EDC. Steam for the plant is provided by nine production wells. Two production wells KN2D and KN3B produce acid NaCl + $SO_4^=$ *fluids with pH at 25°C ranging from 2.7 to 5.3 and 3.6 to 5.9 respectively. Steam from these two wells contributes about 35% of total high-pressure steam production. Separated brine from the separators used by Mindanao-2 is also acidic with an average pH of 4.3 at 170°C.*

The separated brine from pad C separators is highly over saturated with silica. The silica concentration of the brine average at 1084 mg/kg, which is about 45% over-saturated at the injection temperature. The excess silica is between 300 mg/kg to 400 mg/kg at 170°C. After injection for more than three years at this brine condition, the average thickness of silica scale recovered from the surface equipment and pipeline are on the average about 3 millimeters. This puts the scale rate of the brine at an average of about 1 mm/yr.

The scale recovered from the inspected equipment consists mostly of amorphous silica, corrosion products and rock fragments. The rock fragments were observed to be ubiquitous in all the equipment inspected with an estimated volume of at least 4 cubic meters. These rock fragments are responsible for the decline in the injection capacity of KN1RD and not silica scale deposition.

1.0 INTRODUCTION

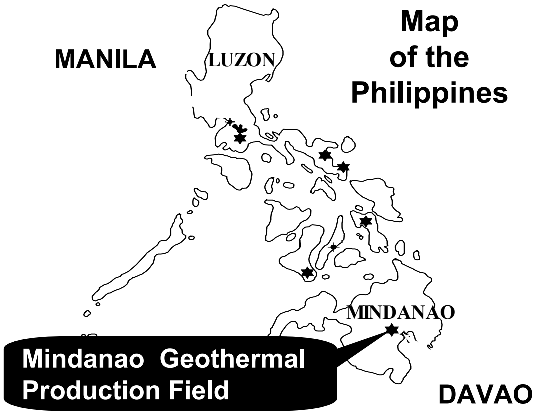

Figure 1. Location of Mindanao geothermal production field (MGPF).

Mindanao-2 power plant is the second geothermal power station in Mindanao Geothermal Production Field operated by PNOC-EDC in the island of Mindanao in the Philippines (Figure 1). Mindanao-2 was commissioned in June 1999 with a base load capacity of 52 MWe. The plant is a dual (high pressure-low pressure) flash type. High-pressure steam that flows at a rate of 390 TPH is supplied by eight production wells. The turbine inlet pressure of the high-pressure steam is 7.0 bar abs. Low-pressure steam comes from second flash of the separated water from adjacent Mindanao-1 high-pressure separators. Turbine inlet pressure of low-pressure steam is 3.6 bar abs. and flows at a rate of 35 TPH.

Mindanao geothermal field is a typical island-arc andesite volcano hosted hydrothermal system. The upflow center of this system is believed to extend from central to the northwest section of a 4.5 x 3-km wide oval shaped depression called Sandawa collapse (Figure 2). Seven out of the nine production wells used in Mindanao-2 were drilled in this sector. Deep temperatures of fluids produced from these wells range from 290-320°C. A shallow two-phase zone formed atop this upflow sector. Three wells: KN5D, TM3D and TM4D tapped this shallow two-phase zone and discharges dry steam at the wellhead. The rest of the production wells tapped the deep liquid reservoir with variable contributions from the two-phase zone. Two wells KN2D and

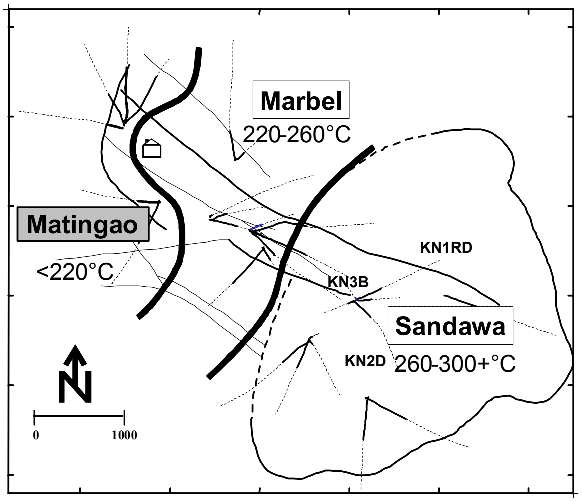

Figure 2. Structural and well location map of Mindanao Geothermal Production Field divided into three sectors: Matingao, Marbel and Sandawa. The subject acid wells are all sited in Sandawa sector. The small envelope in the northwest shows the approximate location of the two power stations in relation to the field.

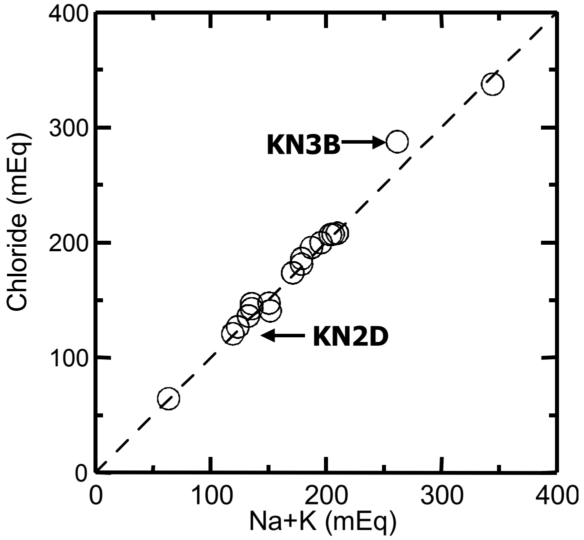

Figure 3. Plot of Cl concentration (milliequivalents) versus the sum of Na and K concentrations.

KN3B, which tapped the deep liquid reservoir, discharged highly acidic fluids. The pH of the fluid from KN2D and KN3B ranged from 2.7 to 5.3 and 3.6 to 5.9 respectively as measured at ambient condition. Four other wells namely KN1D, PS1D, TO1D and TO2D drilled in Sandawa produce or are expected to produce acid fluids. Well KN1D was converted into a re-injection well. PS1D was cement-plugged while TO1D and TO2D remain unused until now. Steam from wells KN2D and KN3B contributes about 35% of the total high-pressure steam for Mindanao-2.

2.0 SOURCE OF ACIDITY

Initial assessment of acidity in the well discharges of some wells in MGPF focused on balance of major ions of the fluid. In the case of KN2D and KN3B fluid, Na+K molar concentration is equal to the molar concentration of chloride (Figure 3). This fluid quality eliminates the likelihood of HCl-type acidity, which manifests as ‘excess’ in chloride concentration (Parilla et al., 1997).

Further studies on fluid-mineral equilibrium of fluids in Sandawa sector showed the latter to be NaCl (+SO_4) type acidity (Salonga, 1995). This fluid contains large amounts of $SO_4^{=}$ and its major dissolved salt is NaCl. At reservoir condition, this fluid exhibits neutral pH and is in equilibrium with K-mica. Acidity of the fluid becomes evident when this fluid undergoes boiling; such as when ascending through the well bore from the reservoir. This increase in acidity is caused by the complete dissociation of H_2SO_4 to H^+ and $SO_4^{=}$. Computer modeling of well bore chemistry by Lichti et al. (1998) clearly demonstrated the relationship of changing sulfur chemistry and pH in this type of fluid.

The primary source of H_2SO_4 at deep reservoir conditions is not identified but is at present postulated as caused by oxidation of SO_2 (from magmatic volatiles) into H_2SO_4 and H_2S in the presence of water. Well KN3B has intersected at depth intrusive complexes (Gonzalez et al., 1994), which could be the source of SO_2 produced during the juvenile stage of the geothermal system.

3.0 OPERATING CONDITIONS

Mindanao-2 power plant utilizes a total of nine production wells. Four of the wells are in Pad F namely TM1D, TM2D, TM3D and TM4D. Three production wells are in Pad C namely KN2D, KN3B and KN5D (Figure 4). The remaining two wells are drilled in Pad B. These are APO2D and MD1D. Wells in pad C and F are connected to two-phase fluid pipe headers and transported to two sets of 20-MW cyclone separators constructed in pad C. The separated brine is re-injected to well KN1RD also in pad C. The

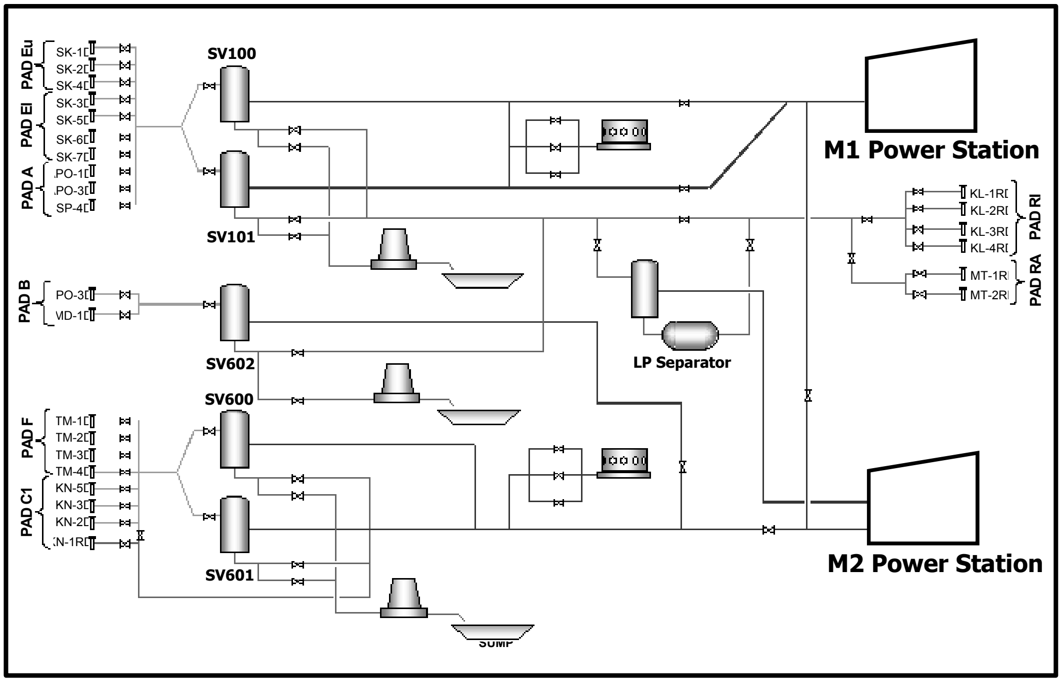

Figure 4. Process flow diagram showing fluid paths to Mindanao-1 and Mindanao-2 power stations. Red lines represent separated water while red lines show steam pathway.

steam is transported through more than 5 kilometers of 42-inch steam pipeline to Mindanao-2 power plant. Production wells in pad B have an independent 10-MW separator. Steam from pad B is transported through 18-inch steam pipeline that merges with the steam line from pad C. In addition to high-pressure steam additional steam is generated from secondary flashing of Mindanao-1 separator brine. About 250 kg/s of brine at a temperature of 170°C is flashed to 149°C to generate about 45 TPH of low-pressure steam that enters the sixth stage blades of the turbine.

The total brine flow from pad C separators varies as a result of changes in well utilization. Well utilization is a function of the power output of the power plant. The re-injection strategy employed in Mindanao-2 involves minimizing the use of the 'watery' production wells given the limited injection capacity of KN1RD but at the same time maximizing the use of 'acid-wells' to prevent silica scaling. Normally injection flow into KN1RD is less than 60 kg/s.

Occasionally, a small percentage of brine from the separator has to be diverted to holding sumps when its flow rate exceeds the capacity of injection well. The dumped brine is allowed to cool to 30-40°C in the sumps and mixed with cold power plant effluents before being injected to a cold injection well KL2RD. This operational set-up was continued for more than three years with only minor modifications.

The injection capacity of KN1RD did not stabilize during two years of operation. The capacity ranged from 25 kg/s to 60 kg/s and appears to fluctuate during use. However, despite the fluctuation there is a noticeable drop in injection capacity with time that eventually led to zero brine acceptance after two years of utilization. The well was worked-over mechanically using drill rig and subsequently 'acidized' with hydrofluoric acid to regain its brine acceptance. The procedure was successful in regaining the injection capacity of the well and in fact improved on the baseline level of brine acceptance.

4.0 PRODUCTION WELL DISCHARGE CHEMISTRY AND BRINE CHEMISTRY MONITORING

The discharge chemistry of KN2D and KN3B has been monitored since the start of their production for Mindanao-2 power station. The monitoring consists of sampling the water and steam fractions of the fluid at the two-phase pipeline using webre mini-separators on a monthly basis. The samples are analyzed for water chemistry consisting of fluid pH, Cl, Fe, $SO_4^{=}$, CO_2, H_2S, SiO_2, B, Na, K, Ca and Mg. The steam fraction are analyzed for the following gases: CO_2, H_2S, CH_4, N, H, Ar and He.

Aside from its regular use as a geochemical tool for geothermal reservoir monitoring, these chemical parameters are used to calculate high temperature pH of the fluid and modeling the fluid-mineral saturation of the fluid at pipeline and well bore conditions. Trends in Fe concentration and pH with time are also valuable indicators of the progress of pipeline corrosion, which is a major concern for these acid wells.

The brine from pad C separators was also sampled monthly using coiled tubing condensers. The brine is analyzed for the following chemical parameters: pH, Na, K, Ca, SiO_2, Cl, CO_2, H_2S and Fe.

Brine chemistry is used mainly to re-calculate the high temperature pH of the brine corresponding to the temperature condition of the re-injection pipeline and well. The level of silica saturation (silica saturation index or SSI) of the brine is also computed from the analyzed silica.

The calculation of high temperature pH is carried-out using WATCH (Arnorsson and Sigurdsson, 1982) chemical specieation software. Silica saturation index (SSI) is computed using the equation:

$$SSI = [SiO_2]/C_e$$

Where: $[SiO_2]$ is the silica concentration of the injected brine in mg/kg and Ce – is the temperature dependent amorphous silica saturation (Henley, 1984) based on the equation:

$$C_e = 10^{[4.52-(731/(t°C + 273.15))]}$$

Where t°C is the measured temperature of the brine.

5.0 INSPECTION OF PAD C SEPARATOR AND BRINE LINE DURING MINDANAO-2 POWER PLANT SHUTDOWNS

Power plant shutdowns present opportunities for inspecting the fluid collection and re-injection systems. Since the start of operation of Mindanao-2 power plant in 1999, there were two occasions coinciding with shutdown periods when pad C separator vessels and brine line going to KN1RD were opened and inspected. The inspection was mainly to document extent of corrosion and silica scale build-up and some maintenance repairs.

In April 2001, pad C separator vessels 600 and 601 were opened including KN1RD brine line. Scales samples were measured for thickness then collected from the pipeline equipment and sent to PNOC-EDC Petrology laboratory for visual analysis of polished and thin sections.

A similar inspection was undertaken in November 2002. The same equipment were opened and inspected. Scale samples as well as solids collected from the equipment were taken and similarly analyzed for mineralogy.

6.0 pH TREND IN KN2D AND KN3B DISCHARGE FLUIDS AND RE-INJECTED BRINE SSI WITH TIME

Figure 5 shows the pH trend of KN2D and KN3B fluids with time. The fluid pH was measured at 25°C. The pH of KN2D fluid ranges from 2.7 to 5.3 while KN3B fluid pH range from 3.6 to 5.9. The average pH for the two wells in the three-year period of utilization is 3.6 and 4.5 respectively.

Shown in Figure 5 is the trend of pH measured at 25°C of brine injected into KN1RD. The pH minimum is 3.3 while the maximum is at 7.0. The average pH of the fluid is 4.3.

In terms of fluid that goes into pad C separator KN2D and KN3B contributes from 48% to 66% of the total flow. The rest of the water flow comes from ‘neutral fluids’ from TM1D and TM2D (TM3D, TM4D and KN5D are ‘dry-steam’ wells), which have pH between 6 to 7 (Figure 6). Despite the substantial neutral-pH fluids mixing with the acid discharges from KN2D and KN3B there is enough free H^+ ions to depress the produced brine to acidic level. Except for very brief periods both KN2D and KN3B have been utilized continuously since 1999. During periods when KN2D was not used, the pH of the brine from pad C separator rose to 5.8. No pH data are available to show the pH level of the brine when KN3B was not used.

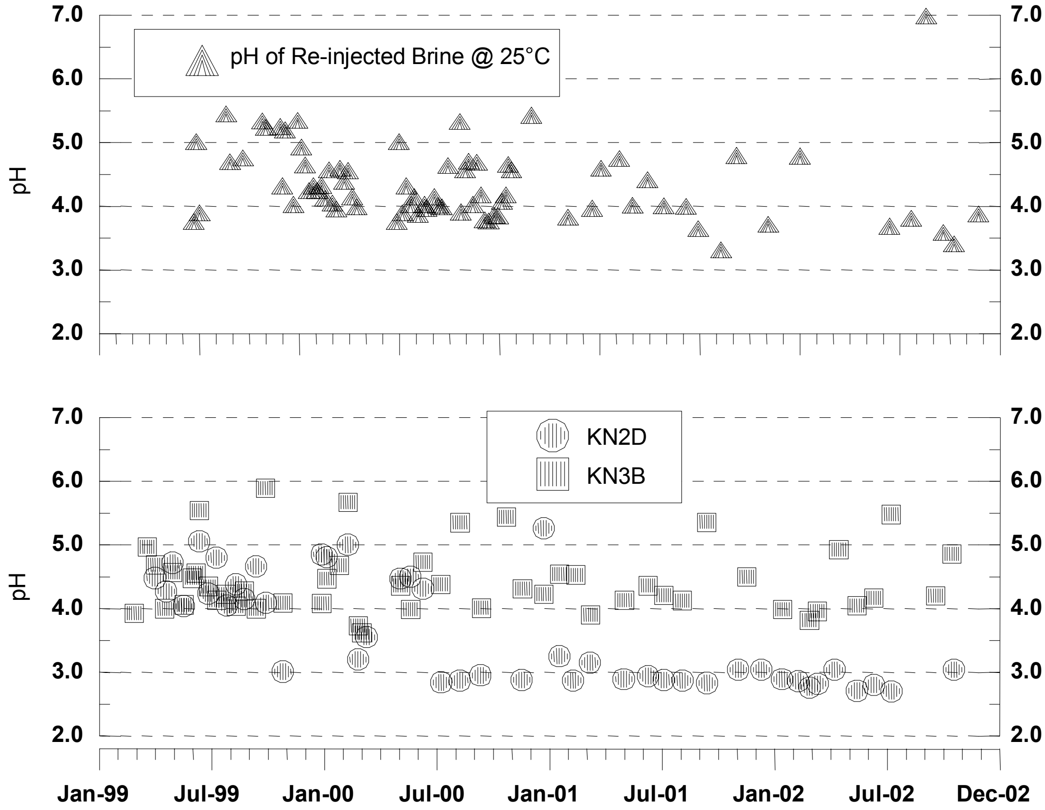

Figure 5. Plot of fluid pH from KN2D and KN3B (below) with time and plot of measured pH at 25°C of injected brine (above).

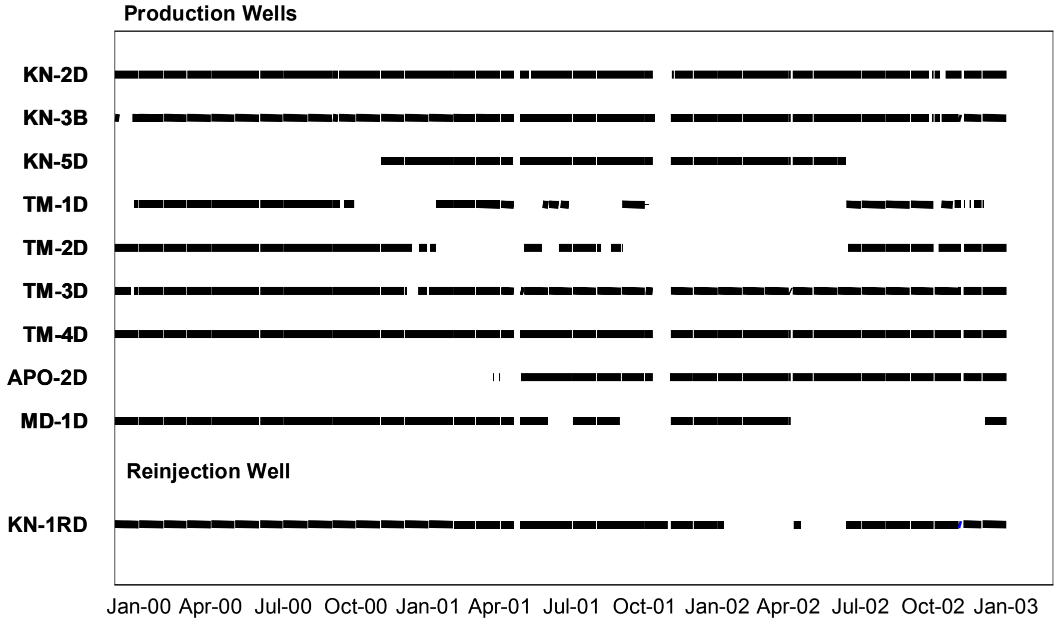

Figure 6. Above plot shows the production and re-injection well utilization history of Mindanao-2 power station since January 2000. Wells KN2D and KN3B were used continuously to acidify the brine into pad C separator and provide about 35% of the total high-pressure steam flow into M2 power station. TM1D and TM2D produce ‘neutral-type’ discharge and have high water fractions.

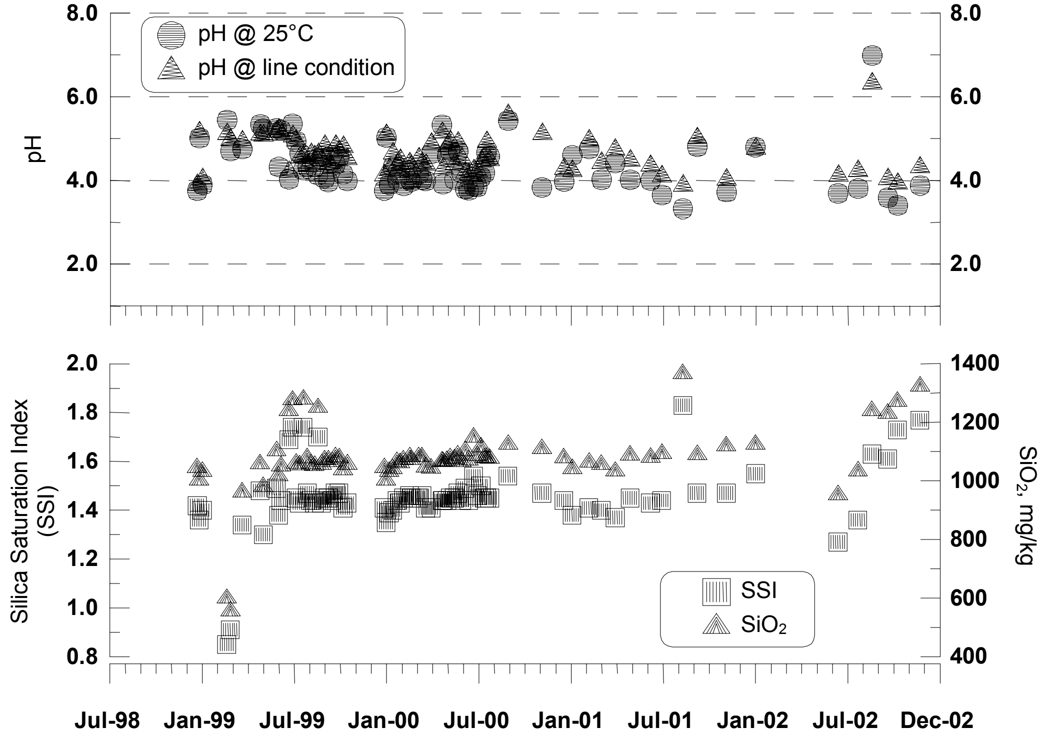

Figure 7. Plot above shows trend of silica concentration and corresponding SSI of brine from pad C separator vessel with time. Above plot shows measured and calculated (at 170°C) pH of the brine.

In Figure 7, the silica concentration and the corresponding silica saturation index (SSI) of injected brine is plotted with time. On the average, the silica concentration of the brine is 1084 mg/kg at a temperature of 170°C. This level corresponds to an average SSI of 1.45 or 45% over saturation. The average excess silica in the brine is about 340 mg/kg.

7.0 DISCUSSION

Scale samples taken from brine pipeline and separator vessels consist mainly of amorphous silica (55% to 90%), corrosion products and some rock fragments. Amorphous silica occurs as hard and very adherent scales (Figure 8). The silica also appears as irregularly layered and has clear to dark brown coloration. Although the scales are hard, the scale itself is porous and dendritic. Some corrosion products such as magnetite and some copper-iron sulfides (chalcopyrite and bornite) are also present in the scale and appear to be cemented together by amorphous silica. The thickness of amorphous silica varies in the different equipment inspected. Around the brine pipeline going into the re-injection well, the thickness of the scale is about 3 mm. In some section of the equipment especially the through conduit valve (TCV) and dump valve of the separator, the amorphous silica scales are up to 30 mm in thickness. These thick scales are not pervasive and form only at sections where fluid are mechanically impeded but do not cover the whole pipe inner surface.

The rock fragments (Figure 9) were found to be ubiquitous in all the inspected equipment and pipelines. Large accumulations were noted in the re-injection line solids trap and the dump line silencer of the pad C separator vessels. The estimated volume of rock fragments is at least 4 cubic meters. Debris recovered from KN1RD when the well was mechanically worked-over showed these rock fragments were also unloaded into the re-injection well along with the brine and caused the well to be blocked. Petro-analysis of the rock fragments shows these to be composed mostly of diorite, andesites and hornfels. The rocks may have come from the production wells and transported into the pipeline and separator vessels during normal production.

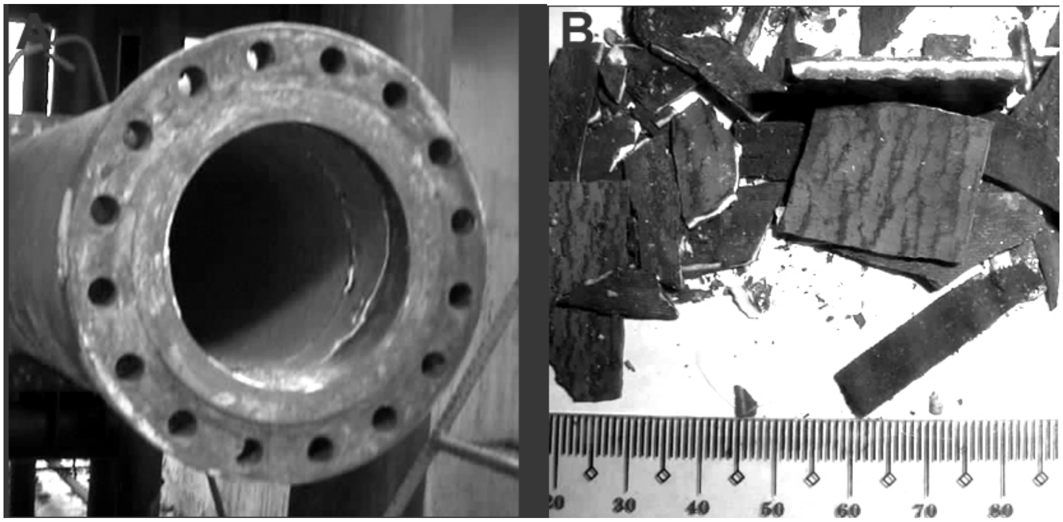

Figure 8. Left photo (A) shows a view of amorphous silica scales adhering to the inner wall of pipeline going into re-injection well KN1RD. Photograph B is a close up view of silica scales taken from pipeline and submitted for petro-analysis. Average thickness of the scale is about 3 millimeter and covers completely the inner surface of the pipe.

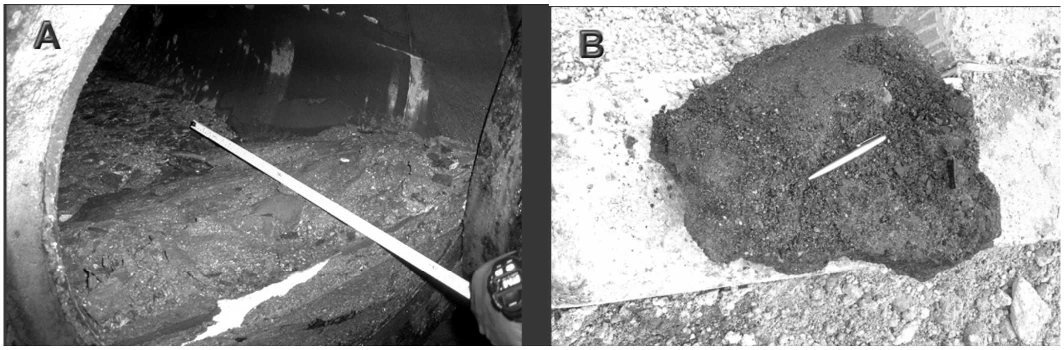

Figure 9. Top photograph (A) shows the accumulated rock fragments inside the solids-trap of brine pipeline going into KN1RD. Cementation by a thin coating of amorphous silica allows these rock fragments to form large but brittle conglomerates an example of which is shown above (B). Work-over of KN1RD proved that a large volume of these rock fragments entered into the well and caused its injection capacity to decline and eventually choke.

The thin silica scales found in the pipeline and surface equipment that transported the acid brine is evidence that massive high molecular weight silica polymers were prevented from developing in the pipeline. The acidic nature of the fluid has lengthened the ‘induction time’ of polymerization of silica (Candelaria, et al., 1999). Considering that the elapsed time, the average silica deposition in the brine pipeline and separator vessels is about 3 mm in 3 years or ~1 mm/yr. This is in sharp contrast to Botong sector of Bacon-Manito Geothermal Field, which has roughly the same silica level in the brine (1000-1300 mg/kg) that produces large silica scales in the separator and re-injection pipeline (Baltazar, et al., 1998). The experience in controlling silica scale by natural acidity of brine observed in M2 validates the experimental results conducted by Brown, et al. (1983) which showed absence of silica scale for 5 to 24 hours for brine acidified with sulfuric acid to pH = 5.

8.0 CONCLUSIONS

The separated brine from pad C separators is highly over saturated with silica. The silica concentration of the brine average at 1084 mg/kg, which is about 45% over-saturated at the injection temperature of 170°C. The pH of the brine range from a minimum is 3.3 to a maximum of 7.0. The average pH of the fluid is 4.3 at line temperature of 170°C. The acidity of the brine is caused by mixing with separated water from two wells KN2D and KN3B that discharges acid fluids. KN2D has an average pH of 3.6 while average pH of KN3B fluid is 4.5 (measured at 25°C).

After injection for more than three years at this brine condition, the average thickness of silica scale recovered from the surface equipment and pipeline are on the average about 3 millimeter. This puts the scale rate of the brine at an average of about 1 mm/yr.

The scale recovered from the inspected equipment consists mostly of amorphous silica, corrosion products and rock fragments. The rock fragments were observed to be ubiquitous in all the equipment inspected with an estimated volume of at least 4 cubic meters. These rock fragments are found to be responsible for the decline in the injection capacity of KN1RD and not silica scale deposition.

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