

Evaluation of NaOH Injection in the Neutralization of Highly Acidic Cl-SO₄ and SiO₂-Saturated Geothermal Fluids

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ABSTRACT

Some production wells in the Mt. Apo Geothermal Project in the Philippines have highly acidic, SO₄-rich, silica-saturated fluid discharges. Downhole chemistry simulations using SOLVEQ-XPT show that the pH of the fluids is about 5 deep in the reservoir, but drops to 3.5-2.5 at shallow depths and in surface facilities. Monitoring of corrosion in these acid-discharging wells shows that corrosion rates are higher than acceptable for commercial well utilization of more than 25 years.

One of the methods to reduce corrosion is to modify the chemistry of the acidic fluid by neutralization using a base such as NaOH, but this poses a risk of mineral scaling and wellbore blockage. Published studies of field tests conducted in other geothermal projects, however, showed that scaling can be minimized and that it is both a factor of geothermal fluid chemistry and process optimization.

This study presents the results of the series of caustic injection side-stream tests conducted in one of the acidic geothermal wells in Mt. Apo, and discusses the mineral and fluid equilibrium changes with caustic addition using the titration model of CHIM-XPT geochemical software. Initial results showed that increasing the pH of a highly acidic SiO₂-saturated geothermal fluid increases the risk of silica scaling due to the accelerated polymerization of silica and not due to reduced solubility. Further tests of operating parameters are recommended prior to downhole tests of caustic injection.

1. INTRODUCTION

The Mt. Apo Geothermal Project (MAGP) is located at the northwestern flank of Mt. Apo. It is geographically divided into two production sectors, namely, Sandawa and Marbel. The Sandawa sector is characterized by reservoir fluid temperatures greater than 300°C, and forms the upflow region of the geothermal resource. Some wells in the Sandawa sector however have highly acidic fluid discharges that are generally corrosive to surface pipe facilities.

One of the production wells with low pH discharge is well KN2D with brine pH of 2.5 at lab conditions (20°C). Even with highly acidic fluid, there was no corrosion issue recorded in KN2D for over 10 years of production since 1999. This is mainly attributed to its high discharge silica content (~1000 mg/kg) leading to a silica saturation index of 1.4-1.6. At this excess silica level, thin layers of amorphous silica deposits along the pipeline walls that help prevent the propagation of corrosion. At very low pH, the coagulation of the excess silica to polymeric forms is also retarded (Iler, 1978), thereby preventing massive silica scaling in surface facilities. Thus, the low pH and high dissolved silica in KN2D complement each other to make the well usable.

Recently, however, a pinhole-size leak was recorded along the by-pass line of the KN2D branchline and another one in the upper portion of the production tee. Parallel UT measurements also noted significant thinning in some portions of the pipe over the last two years. Recent corrosion rate measurements using carbon steel coupons showed elevated corrosion rates compared to the observed corrosion performance of the well over the last 10 years.

Increasing the pH of acidic fluid discharge to reduce the risks of corrosion has been adopted in some geothermal projects with varied results. However, in most cases, introducing NaOH led to massive mineral deposition that required mechanical work-over to make the well usable again. To evaluate this risk in well KN2D, geochemical modeling of the titration of KN2D brine with NaOH using SOLVEQ-XPT and CHIM-XPT was conducted to determine the optimum operating parameters at which scaling remains tolerable. A side-stream test was also conducted to determine the actual performance of NaOH injection with respect to corrosion mitigation.

2. GEOCHEMICAL MODELING

To better understand the chemistry involved in the addition of caustic soda in KN2D fluid, a geochemical model was derived using SOLVEQ-XPT and CHIM-XPT. This involved determining KN2D multi-phase equilibria at deep conditions, boiling the derived equilibrated fluid back to the surface, and then introducing caustic soda through fluid-fluid mixing (Fig. 1).

2.1 Deep Fluid Equilibria

KN2D multiphase equilibria at deep conditions were computed using SOLVEQ-XPT. The process involves completely redissolving the gas components back into the water in the assumption of a liquid-only reservoir fluid. In addition, FixAl method was introduced to compensate for the lack of Al analysis in the sampled water (Pang and Reed, 1997). In this case, Al is fixed in the mineral kaolinite. The solution was then heated from 20°C to 350°C and the log Q/K graph plotted as shown in Fig. 2.

The prevalence of Fe-bearing minerals in equilibrium at 240°C suggests likely reaction of the acidic reservoir fluid with the steel casing. To eliminate the effect of such secondary reactions within the wellbore on the fluid composition, the derived deep water

was forced equilibrated with pyrite, a mineral found abundant in KN2D core samples. The resulting log Q/K plot showed another convergence point at 310-340°C, which is close to actual measured downhole temperature of the well (315°C), thus we infer that the corrected Fe concentration is much closer to that in the reservoir.

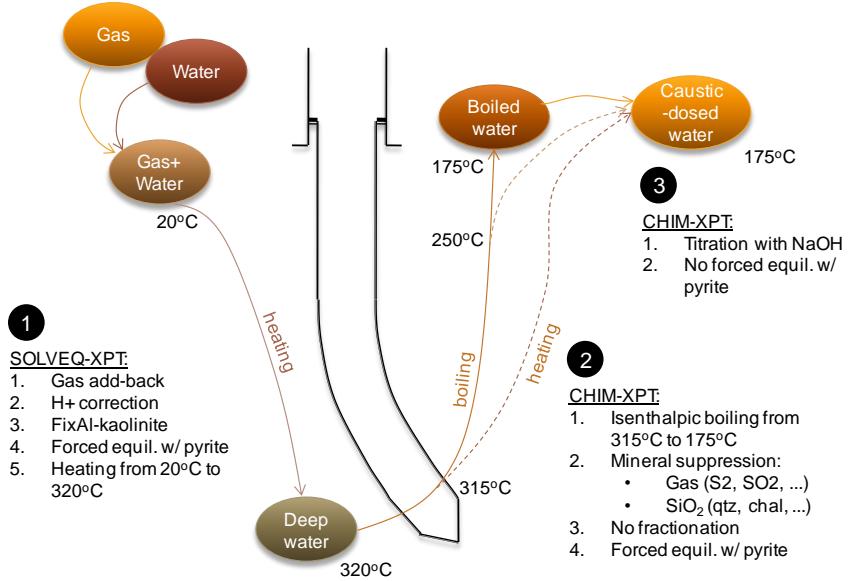


Figure 1: Geochemical modeling process used to determine the KN2D fluid equilibrium changes with addition of caustic.

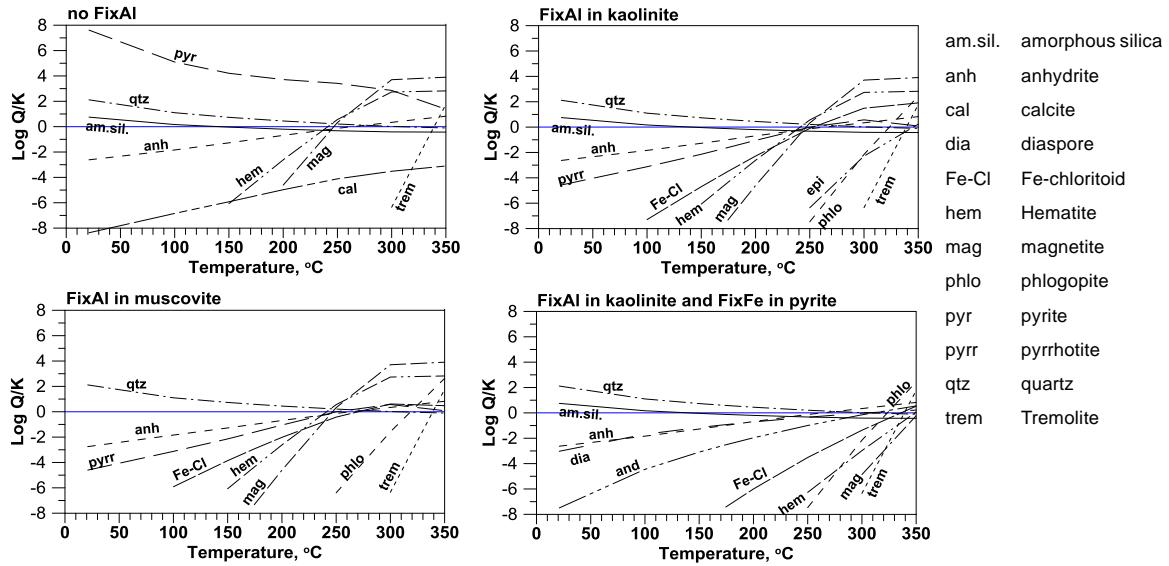


Figure 2: KN2D log Q/K plot showed convergence at 240°C, which is below 315°C, the actual measured downhole temperature of the well. Fixing Al with muscovite and kaolinite showed another convergence point, this time at 310-340°C. Forced equilibration with pyrite shifted the Fe species, i.e. hematite and magnetite, to a single high temperature convergence point.

2.2. Isenthalpic Boiling

The derived KN2D fluid equilibrium at depth was then boiled using CHIM-XPT. Boiling started at 315°C, the temperature at which the fluid is in equilibrium at the reservoir, down to 175°C, the measured fluid temperature along the side-stream test rig. Boiling within the wellbore is considered adiabatic, thus the enthalpy is conserved throughout the boiling process. Fractionation was set to zero to keep the precipitates in contact with the solution. This permits some precipitates to re-dissolve back into the solution when the thermodynamic conditions change.

Results of the boiling model showed a linear drop in fluid pH from 4.85 at 315°C to 3.5 at 175°C. The subtle inflection in the pH trend at 260°C corresponds to initial increases in the concentrations of SO₄, Ca, Mg, and Fe. These trends are accompanied by decreasing amounts of anhydrite, antigorite, and pyrite, which dissolved as the fluid boils. SiO₂ remains relatively stable throughout the hot temperature range (200-315°C), with only a minor inflection above 240°C. This may just be an influence of the re-equilibration of the minerals stated above. From 190°C and below, SiO₂ concentration drops as amorphous silica precipitates.

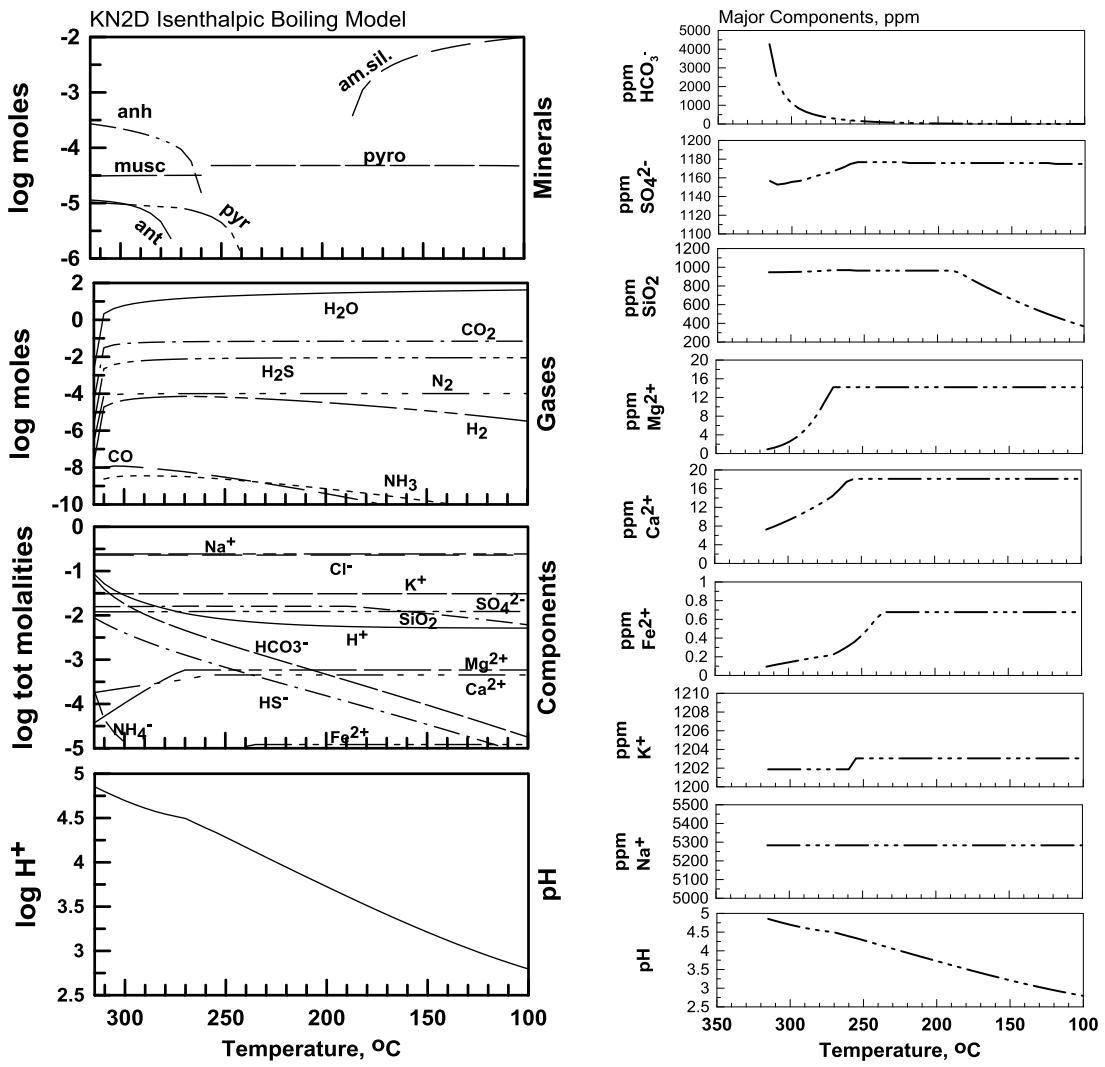


Figure 3: (Left) Isenthalpic boiling model of KN2D fluid from 315°C to 175°C using CHIM-XPT. (Right) A closer look at the individual component boiling trends shows amorphous silica precipitating at < 200°C. Ca, Mg, and Fe, showed slight inflections at 220-270°C. (Minerals: anh – anhydrite, musc – muscovite, pyro – pyrrhotite, pyr – pyrite, ant – antigorite)

2.3. NaOH Titration

The effects of the addition of NaOH to KN2D fluid at 175°C using CHIM-XPT are shown in Fig. 4. The resulting pH curve follows closely with the titration curve derived from actual laboratory test. At the start of the titration, minor additions of NaOH lead to a steep increase in pH from 3.5 to 6. Beyond this point, considerably more caustic is necessary to increase the pH further. The plot of Na concentration with pH shows this effect (Figure 4).

At pH 3.5-6, silica concentrations remained stable at 255 ppm (Fig. 4). However, this value is significantly lower than pre-titration levels of 800 ppm (Fig. 3). This drop in the aqueous silica concentration is due to the equilibration process of CHIM-XPT prior titration, reducing the concentration of fluid components below or at saturation only. In this case, CHIM-XPT equilibrates SiO₂ with quartz which has a lower solubility at lower temperatures than amorphous silica, thus the difference in the SiO₂ concentrations. The solubility of quartz at 175°C is ~200 ppm (Hitchen, 1935), while the solubility of amorphous silica is ~ 800 ppm (Fournier and Rowe, 1966). The geochemical model indicates that the fluid, even before titration, already has a high risk for silica scaling. At higher pH though (pH>6), quartz starts to re-dissolve in the solution as shown by the increasing aqueous concentration trend.

Other aqueous species also exhibit significant changes with increase in pH. For instance, Mg starts to precipitate from the solution at pH 5.5, followed by Ca at pH 6.5 as calcite forms. Fe concentrations also drop with additions of caustic, but increase from pH 6.5 and beyond. Cl, K, B, and SO₄, remained stable across the entire pH range, as expected from inert species.

3. SIDE-STREAM TESTS

3.1. Test Rig Design

A side-stream test rig fabricated from 3/4" SS316 pipe insulated with 1" perlite was used to test the results of the geochemical model in actual field conditions. A side-stream test is better than direct dosing of caustic soda into the well or branchline to avoid possible generation losses which may occur with heavy deposition of silica, given the fluid's high silica saturation indices.

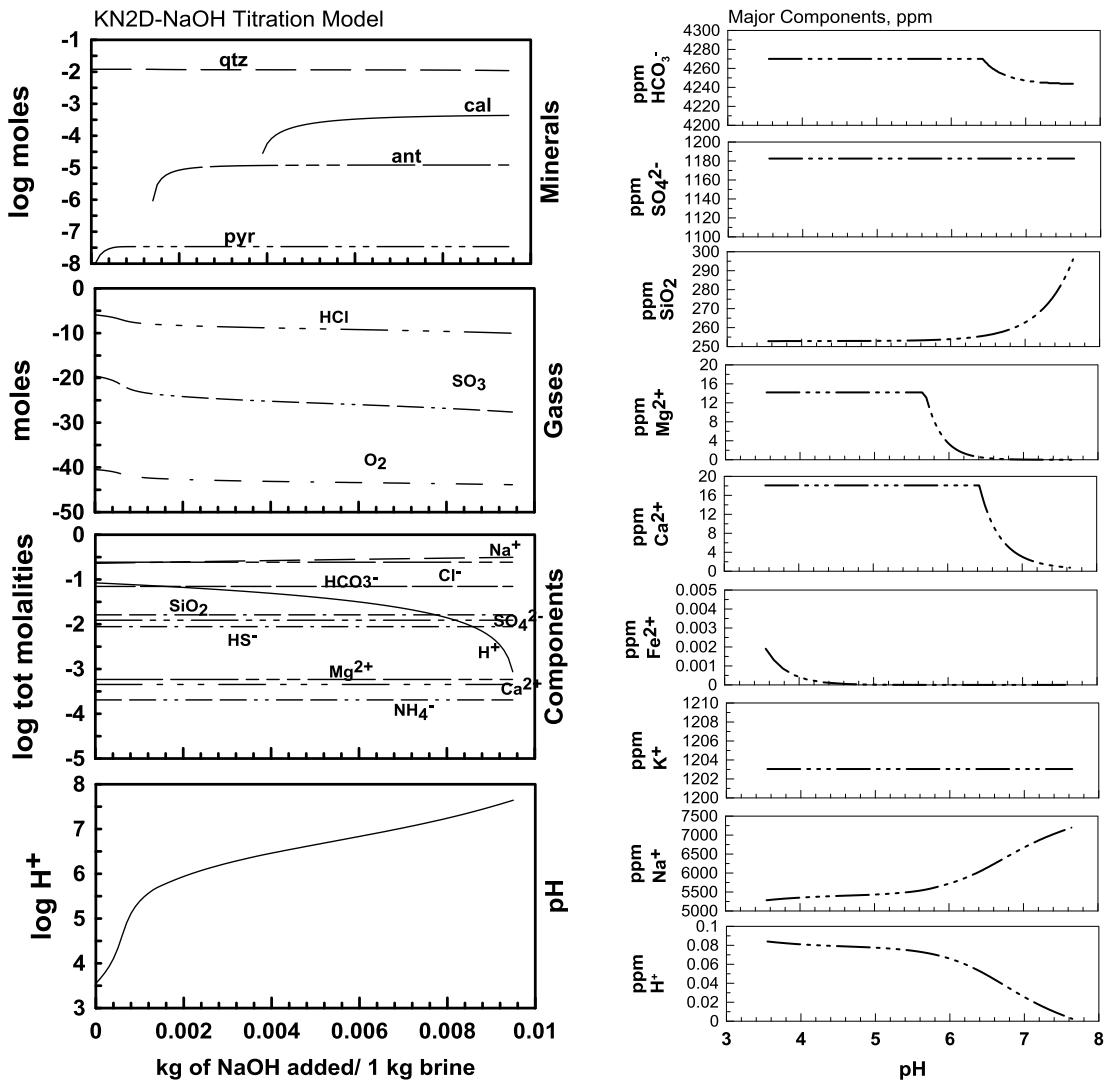


Figure 4: (Left) Geochemical titration modelling of KN2D fluid with NaOH at 175°C. (Right) A closer look at individual component titration trends shows that Ca and Mg precipitate above pH 6. SiO₂ precipitates even at pH 3 and redissolves back into solution at higher pH (>6). (Minerals: qtz – quartz, cal – calcite, ant – antigorite, pyr – pyrite)

The side-stream test set-up is shown in Figure 5. The test rig was designed to allow the geothermal fluid tapped from the two-phase line to flow continuously at a controlled rate. This is provided by an outlet valve which is also used to keep the pressure drop from the two-phase line to the pipe outlet at a minimum through throttling. The fluid is allowed to flow through a 1/2" cooling coil dipped in continuously flowing fresh water to cool down the fluid and eliminate flashing upon sampling.

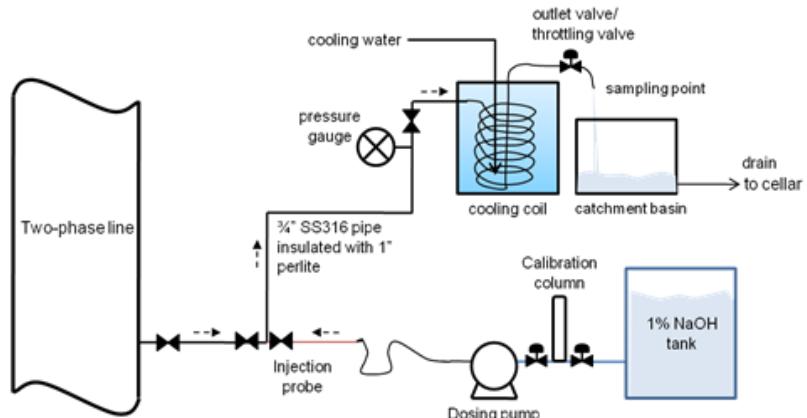


Figure 5: Schematic diagram of the side-stream test set-up

The two-phase line has a pipe surface temperature of 180°C and line pressure of 110 psig. The side-stream test rig, on the other hand, has a pipe surface temperature of 175°C and line pressure of 105 psig. These were determined from an initial test for 1800 ml/min of flowing geothermal fluid dosed with 32 ml/min of water (20°C) for one week. During the entire duration of the test, no silica deposition was recorded as indicated by constant aqueous silica concentration at the outlet.

3.2. Caustic Dosing

To raise the fluid pH from 2.5 to 4.5, 32 ml/min of 1% NaOH was injected into 1800 ml/min of flowing fluid through a side-stream test rig. These values were determined from a titration simulation using SOLVEQ/CHIM-XPT geochemical software and confirmed during the field tests. A laboratory fluid pH of 4.5 is the designed standard minimum fluid pH to eliminate corrosion in carbon steel pipes.

The fluid flow rate and pH with time during the injection of caustic soda are shown in Figure 6. The fluid pH was maintained at 4.5 based from the on-field pH paper reading of the outlet flow. The measured pH of fluid samples at laboratory conditions is generally lower than those in the field but still higher than the natural state fluid pH of 2.5

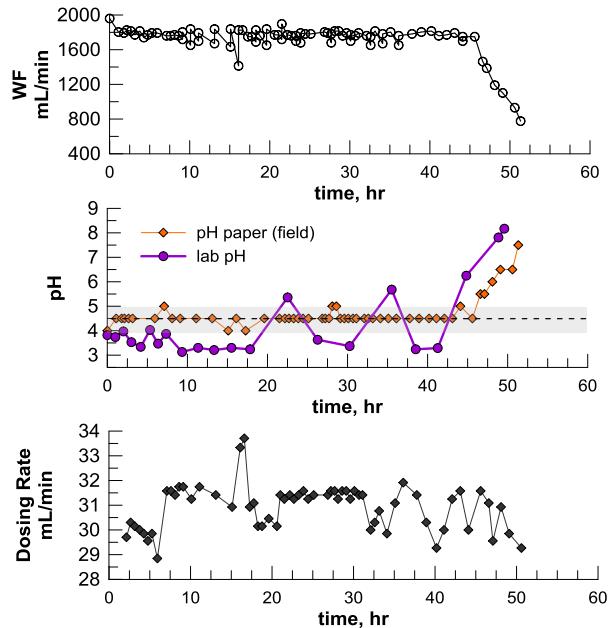


Figure 6: Water flow rate, pH, and caustic dosing rate with time.

A reduction in fluid flow was observed from time to time during the entire duration of the activity. As a result, several adjustments of the throttling valve were made to keep the fluid flow constant at ~1800 ml/min. This was to avoid overdosing of caustic soda which may result to a spike in the pH of the fluid. The persistent reduction in fluid flow with time is strongly suggestive that there is gradual development of constriction inside the pipe. True enough, barely 48 hours of continued dosing, when the outlet valve had already been fully opened, the fluid pH began to rise rapidly as the same amount of caustic soda is continually dosed with decreasing rate of fluid discharge.

3.3. Pipe Inspection

Inspection of the pipe segments after the dosing activity showed moderate to heavy silica deposition from the dosing point towards the pipe outlet. No deposition was noted prior the dosing point, indicating that the deposits were a result of caustic injection. The amount of silica deposits per pipe length ranged from 0.20 g/cm in the dosing point segment to 0.99 g/cm near the pipe outlet. The increasing mass of deposits from the dosing point to the outlet indicates that deposition is not instantaneous and occurs throughout the entire pipe length.



Figure 7: KN2D pH modification side-stream test pipe inspection. Inspection of the pipe segments after the dosing activity showed heavy silica deposition from the dosing point towards the pipe outlet. Heavy silica deposits were noted upon inspection of the injection probe (a), pipe segment after dosing point (b), and pressure gauge tee (c).

The apparent layering noted in the deposits (Fig. 7b) suggests that deposition happened at different times, or continuously over a period of time. A moderately dry gray to black layer of deposit appeared to be cemented near the pipe wall. This contrasts with the wet brown gel-like deposit near the center, which is directly exposed to the flowing fluid. On inspection, the deposits were found to have reduced the effective diameter of the pipe by 60-70%.

3.4. Petrology

XRD analyses on the sampled deposits showed peaks of amorphous silica, halite, quartz, and pyrite (Fig. 8). FTIR analyses showed that amorphous silica comprised 98% of the deposits consisting of dark brown, loosely consolidated, or lumped masses associated with impurities. The remaining 2% consisted of subrounded, very fine fragments of rocks and opaques with sizes <0.02 mm. The results of the XRD analysis match well with the results of the titration model using CHIM-XPT.

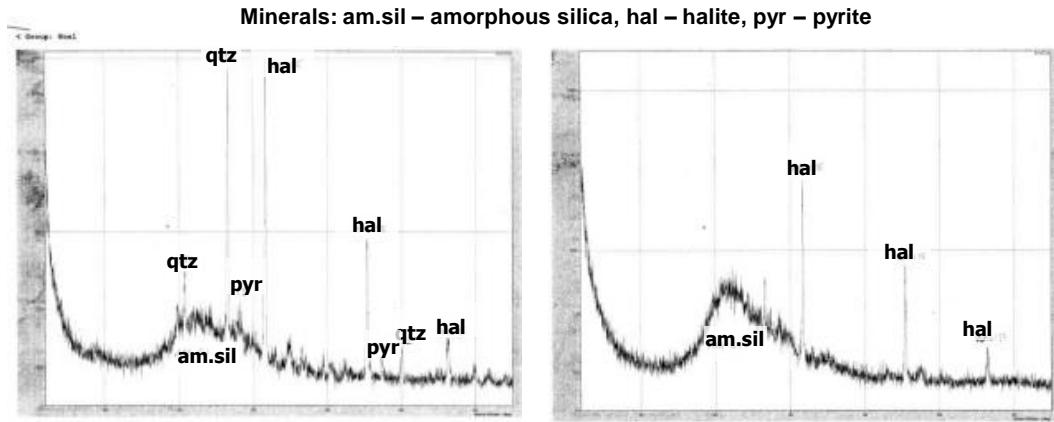


Figure 8: XRD analysis of deposit samples. (Left) Deposits collected in the injection probe, where the deposition started, show mostly peaks of amorphous silica with some pyrite, halite, and quartz. (Right) Deposits collected in the throttling valve segment, near the side-stream outlet, show mostly peaks of amorphous silica and halite.

3.5. Geochemistry

Samples of caustic-dosed fluids were collected and analyzed to identify changes in the fluid chemistry through time. The results of the analysis were compared to a calculated trend accounting for simple mixing only. Deviation from this trend indicates chemical changes in the fluid with respect to the given species.

Na concentrations ranged from 5300-6100 mg/kg for the duration of the activity, mostly occurring at \sim 1800 ml/min of water flow (Fig. 9). The higher concentration of Na after 18 hours of testing indicates sporadic overdosing of NaOH while the fluid flow fluctuates from time to time (Fig. 6). Na plots closely with the simple mixing line at lower flow rates, suggesting dominance of mixing process.

The SiO_2 concentration trend with time, unlike Na, remained stable at 1000 mg/kg at 1800 ml/min of flow rate. At this temperature (175°C) and pH (4.5), the solubility of amorphous silica is only 800 mg/kg, indicating a supersaturation of 200 mg/kg (Fig. 3 and 4). While highly supersaturated, silica concentration started to drop dramatically only after 48 hours into the experiment. At this point, the analyzed SiO_2 starts to deviate heavily from the simple mixing trend. This is due to the removal of SiO_2 from the solution in the form of amorphous silica deposits, which was confirmed during pipe inspection (Fig. 7).

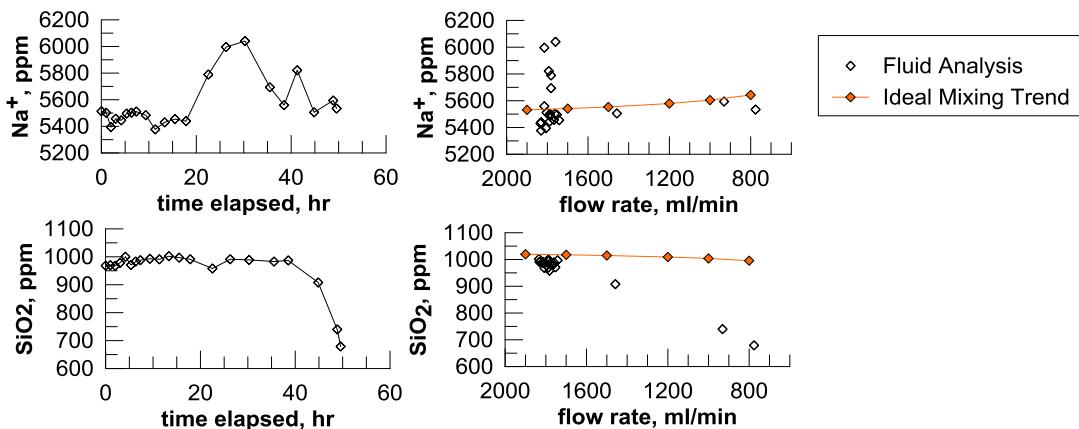


Figure 9: Na and SiO_2 concentration trends (in mg/kg) with time and at varying fluid flow rates (ml/min). Orange line corresponds to calculated values for simple mixing of KN2D fluid and NaOH.

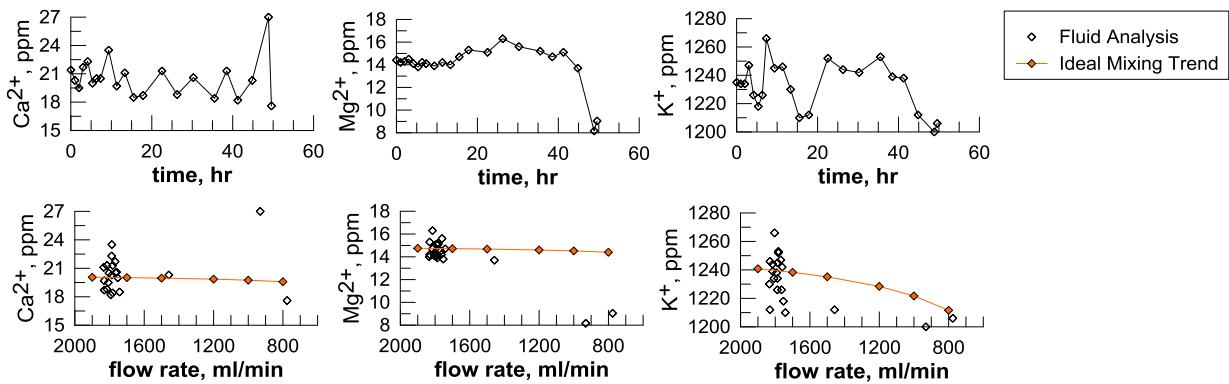


Figure 10: Ca, Mg, and K trends (in mg/kg) with time and at varying fluid flow rates (ml/min). Orange line corresponds to calculated values for simple mixing of KN2D fluid and NaOH.

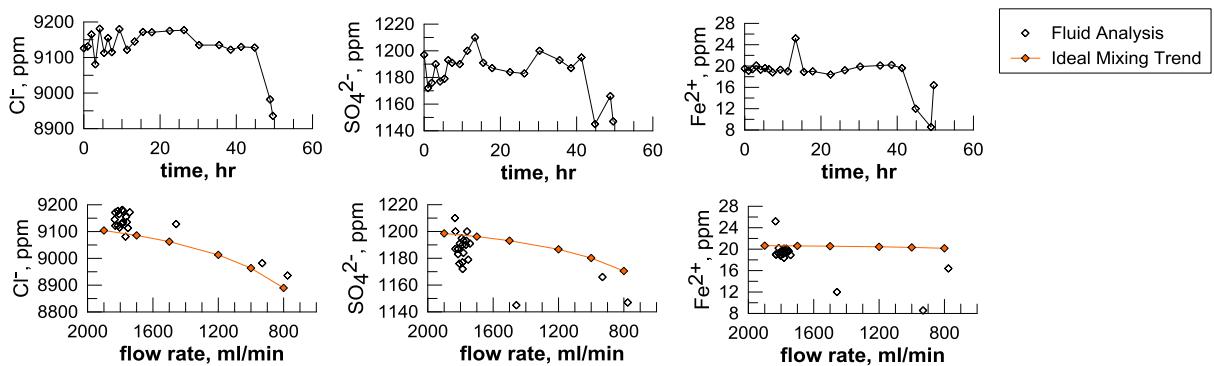


Figure 11: Cl, SO₄, and Fe concentration trends (in mg/kg) with time and at varying fluid flow rates (ml/min). Orange line corresponds to calculated values for simple mixing of KN2D fluid and NaOH.

The behavior of silica deposition observed in the side stream tests is highly similar to the observation of White (1956) while studying the polymerization of silica in hot spring waters. He noted an “induction time” of silica polymerization, wherein dissolved silica concentration does not change for some period of time at the start of the experiment, but drops fairly thereafter. Further studies on silica polymerization by others identified this phenomenon to be due to the formation of silica polymers and colloidal particles, which is usually slow and rate-limiting in the overall silica polymerization process (Weres, 1981). This is then followed by the more rapid coagulation of the colloidal particles and their subsequent adherence and deposition to metal surfaces.

The results of the side-stream test indicate that the precipitation of silica from solution is highly governed by the kinetics of silica polymerization. While increasing the fluid pH from 2.5 to 4.5 does not lead to a reduction in the solubility of silica based on thermodynamic equilibrium data (Fig. 4), the polymerization rate of silica increased with an increase in the pH (Baumann, 1959), resulting in accelerated silica scaling.

These results are not entirely surprising. Under low pH of 2.5, colloidal silica formation is effectively retarded and silica deposition is minimized (Iler, 1978) as has been observed in the field despite the presence SiO₂-supersaturated fluids.

Concentration trends of the other species in the geothermal brine during the side-stream test are shown in Fig. 10 and 11. Ca, K, and SO₄ generally varied more in concentration range at ~1800 ml/min, than did Mg, Cl, and Fe, which remained relatively stable. Cl closely followed the mixing trend throughout the duration of the caustic injection, as is expected from an inert species. Mg, K, SO₄, and Fe, however, started to deviate from the mixing trend at lower flow rates and higher fluid pH, similar to the SiO₂ concentration trend (Fig. 9). Mg and Ca are expected to precipitate at higher pH, but K and SO₄ are not (Fig. 4). The latter species might have been carried over by polymeric SiO₂ through intermolecular interactions and removed from the solution as amorphous silica deposits.

4. SUMMARY AND CONCLUSIONS

SOLVEQ-XPT and CHIM-XPT geochemical software can be used to evaluate the acidity of a geothermal fluid and its scaling tendencies at different temperatures and with the addition of a base such as NaOH based on multiphase thermodynamic equilibria.

The low pH of 2.5 of a Cl-SO₄ and silica-saturated fluid effectively retards the polymerization of silica into colloidal particles despite supersaturation, thereby minimizing silica scaling along the two phase lines. Increasing this pH to 4.5 by the addition of NaOH does not decrease the solubility of silica at the same temperature, but accelerates the polymerization process and promotes massive deposition over time.

Corrosion mitigation of an acidic geothermal fluid by pH modification using a base such as NaOH is therefore challenging but can still be utilized with improved operating conditions. This includes lowering the target pH to a value that achieves acceptable silica polymerization rate or modifying the dosing schedule to halt after polymeric silica formation but before silica deposition.

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