

Silica Deposition in Near-Wellbore Formation: Study on Mechanism and Management Options Based on Autoclave Experiments

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ABSTRACT

Managing silica scaling in plant surface facilities, injection wells and near-wellbore formation can be a major challenge in geothermal field operations. Determining which management option is appropriate depends on the overall understanding of the mechanism of silica deposition both at the surface and within the reservoir formation. Factors driving silica deposition in plant facilities and injection wellbores seem to be well understood hence effective control of scaling have been implemented by several geothermal plant operators, such as the use of pH-modification technology. The mechanism of silica deposition in near-wellbore formation of an injection well however is not as well understood.

A series of autoclave experiments were conducted to study near-wellbore formation silica scaling. These experiments were mostly designed to investigate water-rock interaction of acid-dosed brine in greywacke formation and its influence on silica deposition. These tests have been used to understand things such as the effects of adding chemical inhibitor and filtrate injection from silica extraction plant. This paper will discuss the autoclave testing methodology and how the results of the study provide better understanding of the mechanism of silica deposition in the reservoir formation, including how the autoclave testing can be used to assist with pre/post-development risk mitigation.

1. INTRODUCTION

Silica scaling is a major issue encountered by many geothermal field operators, particularly across their plant facilities and injection wells. For a flash-plant system, the concentration of silica in the separated brine is increased depending on the plant separation design (i.e. single flash, double flash, etc.). As the pressure is lowered, the temperature of the separated brine will also decrease resulting to a lower silica solubility (Brown, 2013). At this condition, silica scaling can happen due to oversaturation of the separated brine with respect to amorphous silica, exacerbated by elevated aluminum or iron concentrations in the brine.

Figure 1 illustrate the changes in the silica concentration and saturation index as geothermal fluid is extracted from the reservoir and across the flash-plant operation process. Flashing of reservoir fluid to lower temperature can lead to oversaturation of the brine with respect to amorphous silica (above the solid red curve). This condition will increase the potential for silica scaling as the brine silica saturation index (SSI) increases to above 1.0 (Addison et al., 2015). Moreover, the presence of substantial aluminum in the brine can also facilitate the formation of aluminum-rich amorphous silica which has a lower silica solubility curve (dotted red line) compared to pure amorphous silica (Gallup, 1997).

Factors driving silica deposition in plant facilities and injection wellbores seem to be well understood. Several field experiments have shown that the addition of acid slows down silica polymerization in the separated brine (Lawson et al., 2016), and use of pH-modification as a common practice to control silica scaling in plant facilities and injection wells has been well documented (Gallup, 2011; Addison et al., 2015). The mechanism of silica deposition in near-wellbore formation of an injection well however is not as well understood. The relative influence of the fluid oversaturation and the reservoir rock characteristic, including changes in fluid chemistry due to water-rock interaction, on the rate and severity of silica deposition in the near-wellbore formation still need to be assessed.

To better understand the mechanism of near-wellbore formation scaling in an injection well, a series of laboratory experiments that simulate flash-plant process and injection conditions were conducted. These experiments were designed to investigate water-rock interaction of acid-dosed brine with the greywacke reservoir rocks and whether silica deposition is driven solely by the change in fluid chemistry or is influenced by the reservoir rocks and their characteristics. The experiments have been further extended to understand also the effect of adding chemical inhibitors and filtrate injection from a silica extraction plant.

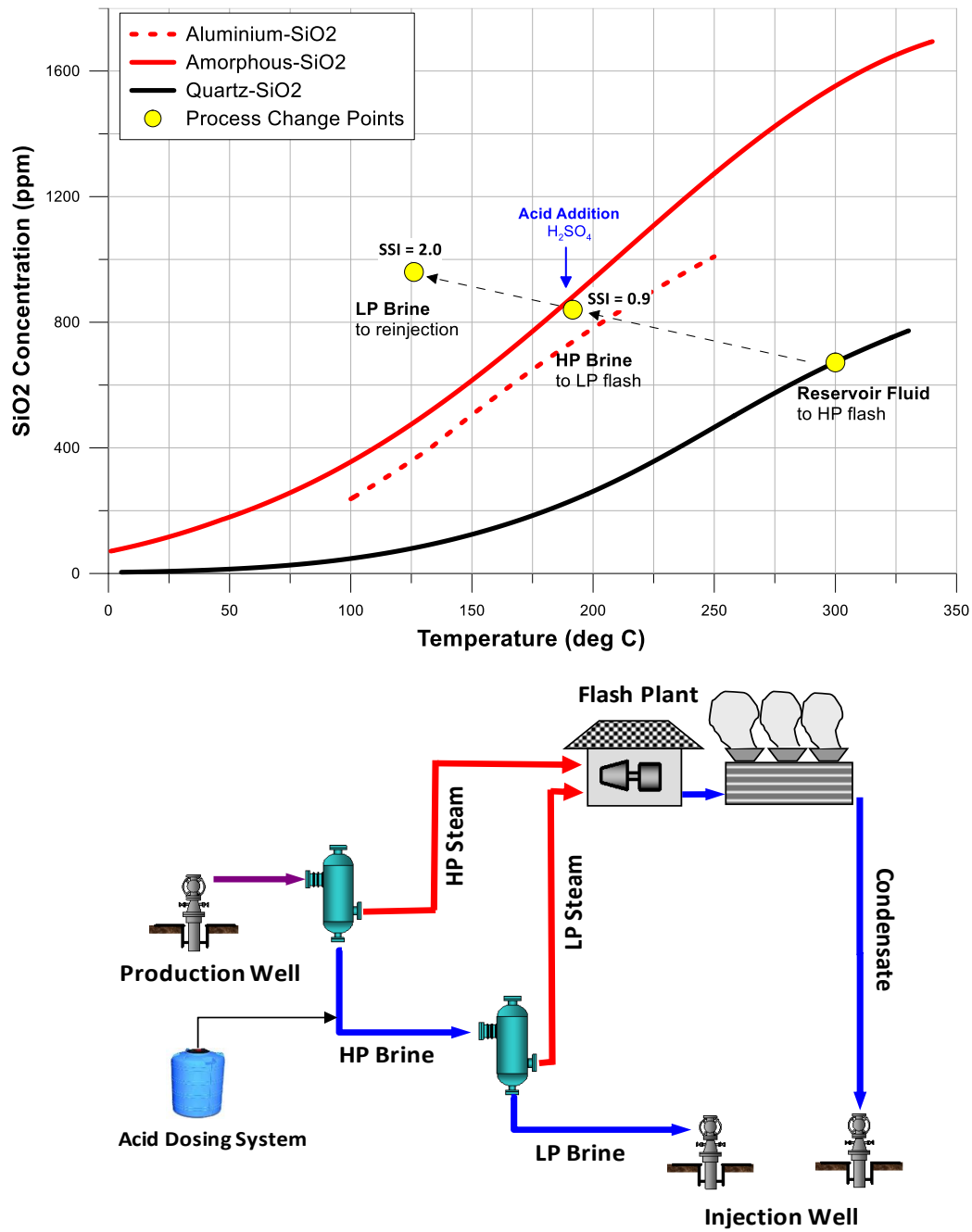


Figure 1: The change in brine silica concentration with temperature across the flash-plant operation process.

2. EXPERIMENTAL STUDY

2.1 Laboratory Set-up

A schematic diagram of the one-pass, continuous-flow apparatus used to simulate fluid-rock interaction at high temperature and pressure condition is shown in Figure 2. The apparatus consists of a separator with a movable piston used to introduce the experimental fluid into the two separate pressure vessels, each contained within an oven. The required continuous flow across the set-up is made possible by a computer-controlled double piston pump that pumps distilled water to displace the piston in the separator and forces the experimental fluid through the pressure vessels. The pore fluid pressure and target temperature across the ovens are maintained by a computer-controlled back pressure regulator and thermocouples, respectively. The process physical parameters such as pressure, temperature and pumped volume are continuously recorded during the entire running operation of the apparatus.

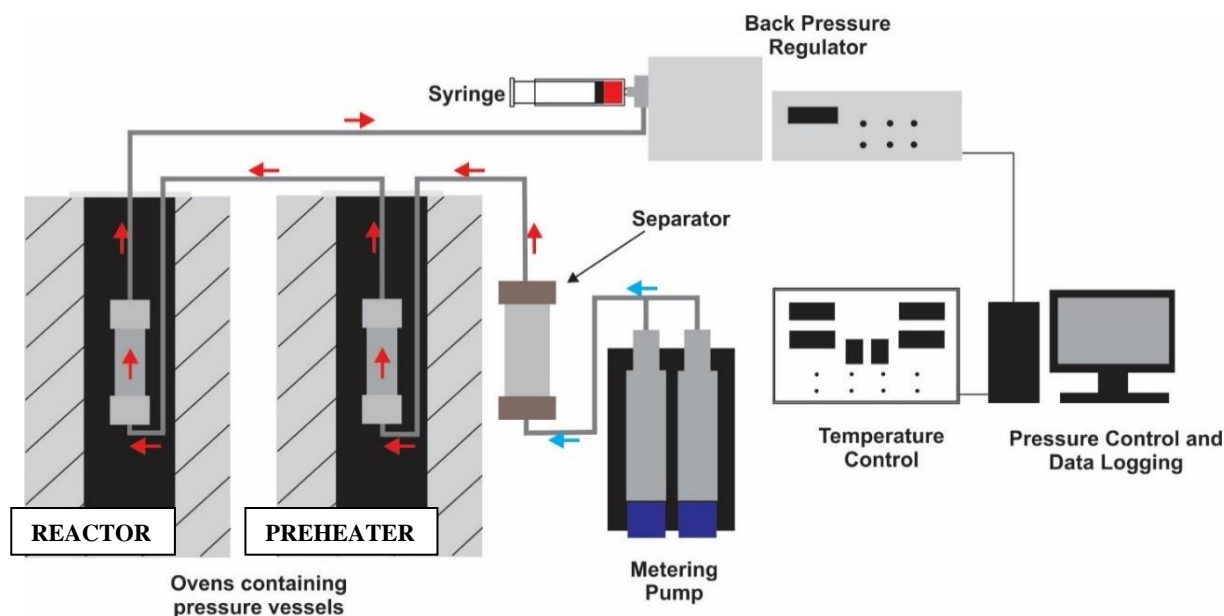


Figure 2: The one-pass, continuous-flow fluid-rock interaction apparatus (modified from Sonney and Mountain, 2013).

Monitoring of the changes in chemistry of the experimental fluid after passing through the apparatus is carried out by regular fluid sampling from the syringe, with the sample analyzed for selected chemical parameters. If the experimental fluid is passed through a rock formation in one of the pressure vessels depending on the experiment design, SEM analysis for any scale deposition or changes in the rock formation material is also carried out at the end of the experiment.

2.2 Experiment Design

2.2.1 Acid-dosed Brine Injection into Greywacke Formation

This experiment simulates the injection of pH-modified brine into a greywacke reservoir rock following the process conditions shown in Figure 1, with the main objective of understanding the scaling mechanism of silica in the formation. The brine is dosed with sulfuric acid to lower its pH to ~ 4.6 (@ 25°C) and has a chemical composition of: 900 ppm Cl, 850 ppm SiO_2 , 3 ppm Ca, 1.5 ppm Al, 0.1 ppm Fe, and up to 400 ppm SO_4 . The rock used in the experiment is from a section of drill core retrieved from ~ 2500 m which has extensive chlorite-rich shears and quartz-calcite veins surrounding a less altered greywacke (Figure 3). Samples of the drill core are coarsely crushed and sieved to obtain the 0.5 - 1.0 mm size fraction, cleaned with distilled water ultrasonically, and packed into the second pressure vessel (REACTOR) as shown in Figure 2. The resulting porosity of the packed greywacke in the pressure vessel is $\sim 50\%$.



Figure 3: Core sample retrieved from ~ 2500 m in the greywacke, the main injection formation.

During the experiment, the first pressure vessel (PREHEATER) is empty and is heated to between $250 - 300^\circ\text{C}$. The acid-dosed brine passes through this vessel which depolymerizes any amorphous SiO_2 colloids present in the brine. The REACTOR vessel containing the greywacke is heated to 150°C . This closely approximates the typical reservoir temperature of the injection area. The pressure in both pressure vessels is maintained up to 200 bars depending on the temperature of the PREHEATER to prevent any boiling. The flow rate of the acid-dosed brine is kept constant between $1 - 10 \text{ ml hr}^{-1}$ depending on the duration of the experiment.

2.2.2 Formation and Brine Matrix Experiment

The experiment in Section 2.2.1 was modified for a formation-brine matrix study: 1) same acid-dosed brine (Brine 1) passed through the greywacke (Greywacke 2) from a different geothermal field; and 2) an acid-dosed brine (Brine 2) with a higher silica oversaturation was passed through the original greywacke (Greywacke 1). This is to evaluate further the relative influence between fluid oversaturation with respect to silica and the characteristics of the greywacke from different geothermal fields. The temperature/pressure conditions of the apparatus were similar to the first experiment to eliminate any other factors that could influence the results.

2.2.3 Chemical Inhibitor Investigation

This experiment was designed to investigate use of chemicals to control silica/metal silicate scaling in the formation. The experiment is subdivided into two stages: Stage 1 is similar to the experiment in Section 2.2.1 and represents the control; and Stage 2 is run with chemical inhibitor added to the acid-dosed brine at the supplier's recommended dosage rates (5 – 20 ppm). There were two chemical inhibitors tested, both used for silica/metal silicate control through ion charge disruption/dispersion process. The chemicals were selected based on known successful application in geothermal fields outside of New Zealand, and for their thermal stability considering the high reservoir temperature of the injection area.

2.2.4 Silica Depleted Filtrate Injection

This experiment was designed to investigate the injection of silica-depleted brine into the greywacke formation to determine if scaling would still be a problem. The brine chemistry in this case has been modified such as the silica saturation index (SSI) is < 1.0 (@ 110°C) or a silica concentration of ~ 250 ppm. The brine has a neutral pH between 7 to 8, with the following chemical composition: 900 ppm Cl, 2 ppm Ca, 0 ppm Al, and 0 ppm Fe.

The experiment is run in two stages: Stage 1 involves running a neutral pH brine (7-8) with a high SiO_2 concentration of 850 ppm and 1.5 ppm Al through the apparatus at same conditions describe in Section 2.2.1. This is the control and was run to create a greywacke substrate already affected by silica scaling; Stage 2 is run with the SiO_2 -depleted brine with a REACTOR vessel temperature set at a target injection temperature of 110°C . This simulates the passage of a silica-depleted brine through a formation already damage by silica scaling. There is no pre-heating of the PREHEATER vessel for this brine prior to passing through the REACTOR vessel. In both stages of the experiment, the REACTOR vessel is filled with the same greywacke as in the two previous experiments above.

3. RESULTS AND DISCUSSION

The results of the first experiment showed that acid-dosed brine is quickly neutralized upon contact with the greywacke. It confirmed the highly reactive nature of the formation which contains a large amount of calcite (3-25%) and other secondary minerals such as chlorite and illite. Figure 4 shows the trends of major chemical parameters monitored during the experiment. The brine pH, after passage through the autoclave formation, increased from 4.6 to 8.0. This is attributed to dissolution of calcite. Moreover, increases in both the calcium and total CO_2 concentrations are observed, consistent with the dissolution of calcite. As the brine pH increases, this increases the deposition rate of aluminous amorphous silica. This is evident in the complete loss of aluminum from the brine and decreases in silica concentration by about 200 mg kg^{-1} , as the pH increased to 8.0.

At about half-way into the experiment, the pH started to drop back to the original pH of 4.6, coinciding with the decrease in both the calcium and total CO_2 concentration. This shows that the calcite ceased to react with the brine as seen by the lack of further changes in the pH. The SEM examination of sectioned greywacke grains from the REACTOR however, showed abundant calcite remaining in the rock. This is explained by silica scale depositing on the rock in the REACTOR covering and blocking access to the remaining calcite, i.e., armoring. This prevents any further neutralization to occur. Correspondingly, an increase in the silica concentration of the brine exiting the autoclave is observed.

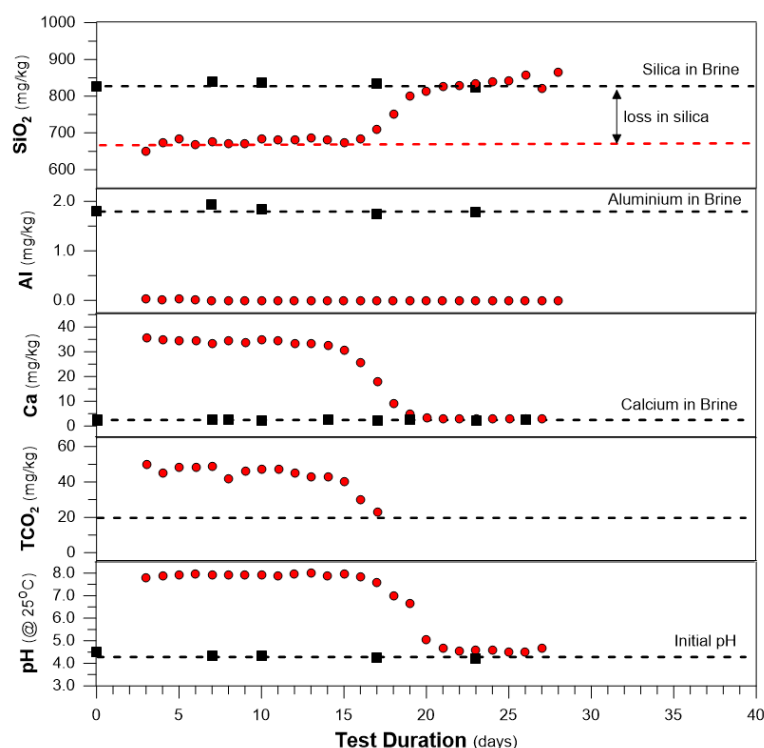


Figure 4: Plot of monitored chemical parameters during the experiment.

A model of silica deposition in near-wellbore formation is illustrated in Figure 5. As the pH of the acid-dosed brine exiting the wellbore increases due to neutralization process, monomeric silica is deposited close to the wellbore. With time, as pH remains elevated, and the surrounding formation cools down, silica colloids are formed in the brine due to silica polymerization at the higher pH and lower temperature. The silica scaling process is further catalyzed by the presence of aluminum ions in the brine. The scale formed in the REACTOR is composed entirely of aluminous amorphous silica. Majority of scale is found near the entry point of the autoclave REACTOR. The deposition of aluminous amorphous silica is believed to be the likely cause of a “skin” developing in near-wellbore formation, subsequently reducing or creating damage to the permeability, and affecting the performance of injection wells.

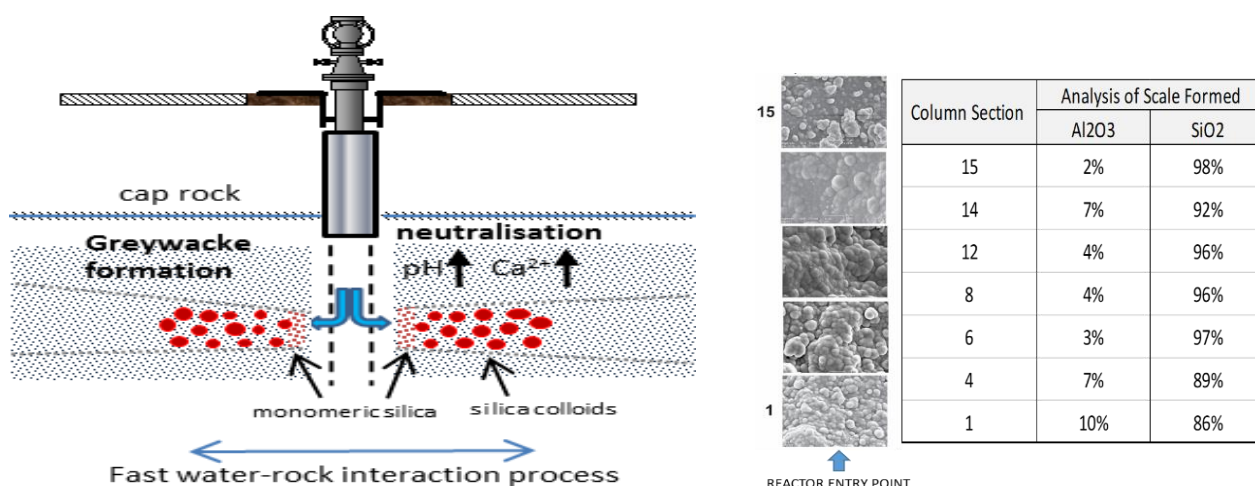


Figure 5: A model of silica deposition in near-wellbore formation (right) and profile of scale deposition in the formation column inside the autoclave based on SEM-EDS analysis.

In the formation and brine matrix experiment, different scaling rates were observed from the results (Table 1). The deposition rate of amorphous silica is calculated from the change in dissolved silica concentration during the experiment. The results are specific to the surface area of the greywacke grains in the REACTOR vessel but this surface area is expected to be similar in all experiments.

Table 1: Comparison of scaling rates for the formation-brine matrix experiments.

	Brine 1 in Greywacke 1	Brine 1 in Greywacke 2	Brine 2 in Greywacke 1
Average Scaling Rate (mg day ⁻¹)	18.4	4.5	66.5
Loss in Silica (mg kg ⁻¹)	~200	~50	~550
Starting Silica Conc. (mg kg ⁻¹)	850	850	1250

The data show that fluid-rock interaction involving Brine 2, with a higher saturation index of 2.1 (@150°C), and the same greywacke (Greywacke 1) rich in reactive minerals such as calcite, results in a higher scaling rate in the formation than with Brine 1. The increase in scaling rate is ~3 times higher with Brine 2 than with Brine 1 which has a saturation index of 1.4 (@150°C). The decrease in silica concentration of the Brine 2 exiting the REACTOR is also larger at ~550 mg kg⁻¹ as compared to ~200 mg kg⁻¹ for Brine 1 (Figure 6, right).

When Brine 1 was reacted with a different greywacke (Greywacke 2) from another geothermal field, scaling rate was observed to be a quarter of the 18.4 mg day⁻¹ previously measured when Brine 1 was reacted in Greywacke 1. The decrease in silica concentration was also small at <50 mg kg⁻¹, whereas no change in calcium concentration was observed and brine pH only increased by ~1 unit higher (Figure 6, left). Greywacke 2 has no measurable calcite but has <0.5% pyrite.

Iron and hydrogen sulfide concentrations increased in the brine, however, there was no change in calcium and CO₂ was below detection limit. As such, the increase in the brine pH is attributed to pyrite dissolution rather than calcite dissolution. SEM examination of the reacted rock for this experiment shows only a small amount of amorphous silica scale at the bottom of the REACTOR and little to no amorphous silica at the top.

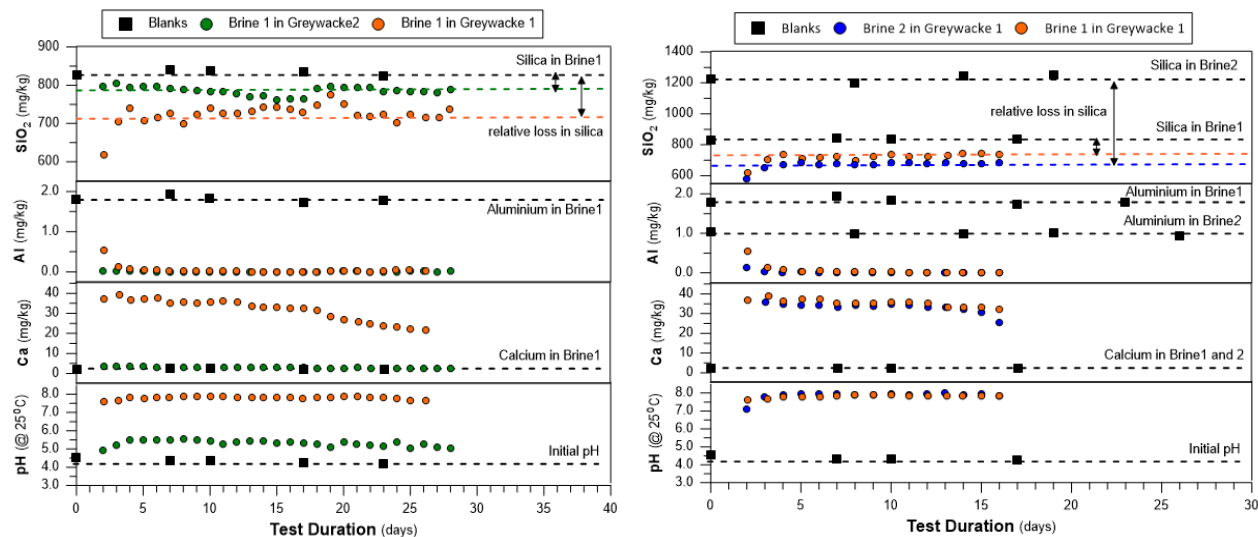


Figure 6: Plot of selected parameters monitored during the formation-brine matrix experiments: (left) Brine 1 passing through different greywacke substrates and (right) Brine 2 passing through the same greywacke.

The addition of chemical inhibitors to the acid-dosed brine did not result in any significant reduction in the scaling rate when compared to the control experiment. Figure 7 shows that silica concentration in the brine decreased by about 150 ppm even after the addition of the chemical inhibitor. The aluminum concentration in the brine is below detection limit and is evidenced by the deposition of aluminous amorphous silica in the greywacke rock formation. The same increases in pH and calcium concentration were observed consistent with the neutralization process seen in earlier experiments associated with calcite dissolution.

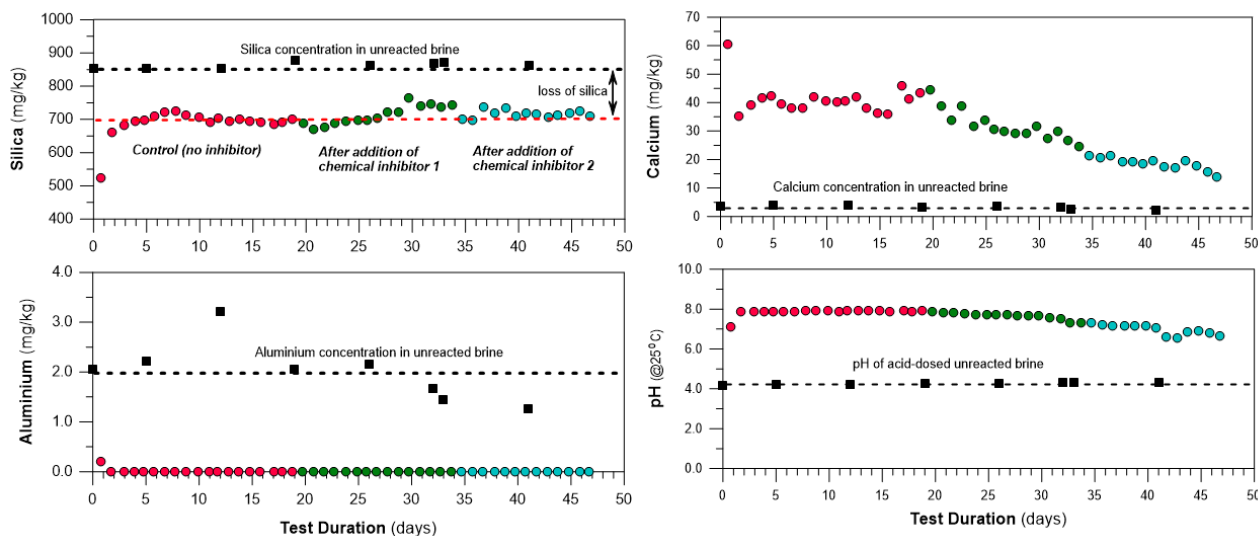


Figure 7: Plot of selected parameters monitored during the experiment using silica inhibitors.

Table 2 shows the scaling rates calculated based on silica loss after the acid-dosed brine passed through the greywacke formation in the autoclave REACTOR. The results show that there is no observable change in scaling rate relative to the control after the addition of the two chemical inhibitors.

Table 2: Comparison of scaling rates before and after addition of chemical inhibitors.

	Control	Chemical Inhibitor 1	Chemical Inhibitor 2
Average Silica Conc (mg/kg)	689 ± 20	713 ± 29	716 ± 12
Average Scaling Rate (mg/day)	18.5 ± 3.8	16.2 ± 3.5	15.9 ± 1.6

When neutral-pH, silica-depleted brine was passed through the greywacke formation at 110°C, there was no significant silica scale deposition observed in the rock. Moreover, a partial dissolution of previously deposited silica scale formed earlier in Stage 1 experiment (refer to Section 2.2.4) was observed as the silica-depleted brine passed through the greywacke and heated up to 110°C.

Figure 8 shows this increase in silica concentration at start of Stage 2, from an initial 250 ppm in the unreacted silica-depleted brine to about 400 ppm, which occurs when fluid interacts with the formation and approaches amorphous silica saturation at 110°C. The kinetics of this process is slow at this temperature, however, and the silica concentration eventually decreases back to 250 ppm. This

is lower than the control stage where the silica concentration decreased from 850 ppm to 400 ppm before stabilizing at about 600 ppm. The pH of the silica-depleted brine also remained unchanged at 8.0-8.3 whereas in Stage 1, the pH has increased from 4.6 to 8.0 consistent with rapid neutralization by calcite dissolution. The increase in calcium concentration in both Stage 1 and Stage 2 of the experiment supports the dissolution of calcite present in the Greywacke formation. The relative difference is dictated by the solubility as a function of both the pH and temperature of the brine.

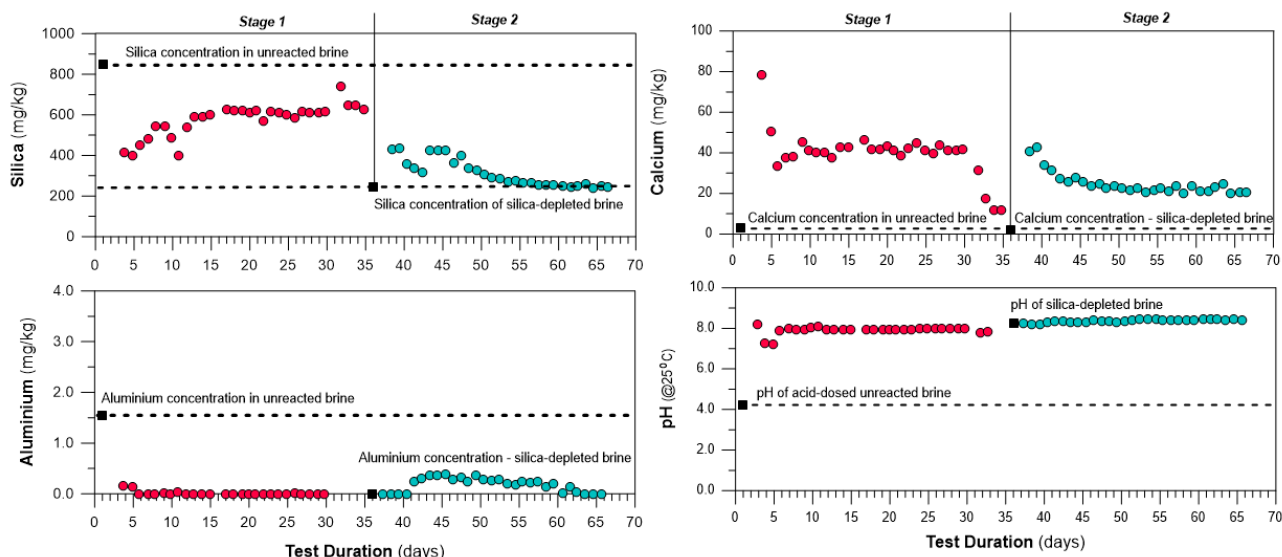


Figure 8: Plot of selected parameters monitored for the silica-depleted brine experiment.

Scanning electron microscopy (SEM) confirmed the presence of a continuous layer of amorphous silica scale at the bottom of the REACTOR after Stage 1 (Figure 9). The scale contains significant amount of aluminum. The standard deviation of the silica concentration from the Energy Dispersive Spectroscopy (EDS) analysis is relatively low relative when compared to the median concentration. This indicates a continuous coating, relatively constant in composition covering the greywacke substrate. EDS analyses from the top of the REACTOR show a lower median and a much higher standard deviation indicating the presence of silica scale-free rock minerals (quartz, feldspar, illite, etc.) rather than a continuous silica scale.

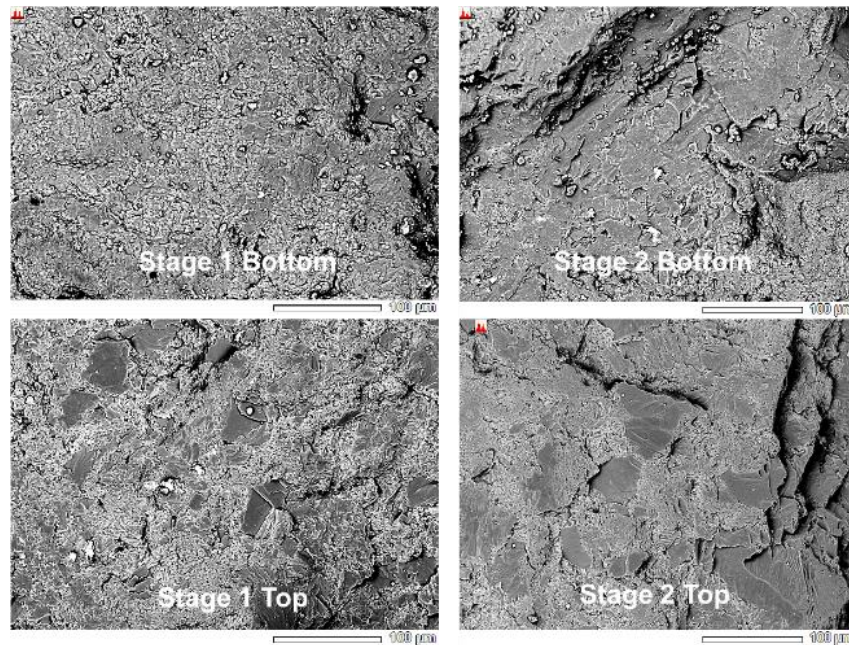
After Stage 2, there was no evidence of further silica scale formation in the REACTOR vessel. The silica scale found at the bottom is composed of a smooth surface, is still continuous, but lacks the granular texture compared to the scale found after Stage 1. This is attributed to partial dissolution of earlier deposited silica scale formed during Stage 1.

4. SUMMARY AND CONCLUSION

Laboratory autoclave experiments were conducted to investigate the mechanism of silica scaling in the near-wellbore formation. The results of the experiments show that:

- Scales found covering the greywackes substrates are composed entirely of aluminous amorphous silica.
- Neutralization of acid-dosed brine occurs and can be attributed to presence of reactive minerals in the formation. It is driven mainly by fast dissolution kinetics of calcite, causing an increase in the silica scaling rate due to increases in brine pH
- Injection of acid-dosed brine into a formation with little to no calcite mineral will potentially reduce the problem of silica scaling
- Injection of a highly oversaturated brine into a formation with abundant calcite will increase scaling rate and can result in severe scaling
- Injection of a brine with undersaturated or close to equilibrium saturation level with respect to amorphous silica will potentially eliminate the problem of silica scaling

The laboratory experiments served as basis in assessing management options addressing the scaling problem, as well as to guide technical decisions to sustain performance of injection well. The knowledge of the type of scale formed, where it formed, and extent of scaling outside of the wellbore and in the formation can be useful in designing well interventions such as mechanical clean-out and acid treatment. Knowing the relative influence between fluid saturation level and formation characteristics can provide an indication of the best way forward to manage problems associated with silica scaling.



	Stage 1				Stage 2			
	Bottom of Reactor		Top of Reactor		Bottom of Reactor		Top of Reactor	
	Median wt. %	Std. Dev. wt. %	Median wt. %	Std. Dev. wt. %	Median wt. %	Std. Dev. wt. %	Median wt. %	Std. Dev. wt. %
Na ₂ O	0.8	0.9	5.1	3.9	1.2	0.9	3.1	4.4
MgO	0.1	0.1	0.9	1.2	0.2	0.1	0.7	1.4
Al ₂ O ₃	4.8	2.5	16.8	6.7	6.0	2.5	14.2	7.4
SiO ₂	93.4	3.3	72.2	11.1	91.8	3.7	74.8	11.6
K ₂ O	0.5	0.2	0.2	0.1	0.4	0.1	0.3	0.6
CaO	0.2	0.3	0.4	0.2	0.1	0.1	0.4	0.4
FeO	0.3	0.3	3.9	5.5	0.4	0.4	1.2	3.6

Figure 9: Comparative SEM-EDS analysis of formation in the autoclave reactor after Stage 1 and Stage 2 of the silica-depleted brine experiment.

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