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An Experiment on Monomeric and Polymeric Silica Precipitation Rates from Supersaturated Solutions

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ABSTRACT

Experimental solutions initially supersaturated with amorphous silica were allowed to polymerize while being pumped through a column packed with silica gel. The concentrations of silica monomers and polymers in the solutions were monitored at the inlet and outlet of the column. Results of experimental runs conducted at 50°C with pure water and saline solutions (0.1 M, 0.2 M, 0.3 M and 0.4 M NaCl) showed shorter induction time and faster polymerization with increasing salinity consistent with theory and past studies. In all runs, initial level of monomeric silica dropped to saturation for amorphous silica in the column. In contrast, the concentration of polymerized silica changed little before and after the column.

A solution of 0.3 M NaCl at 90°C also showed lesser tendency for polymeric silica than monomeric silica to precipitate on the surface of the silica gel in the packed column. However, higher temperature and salinity allowed polymers to grow large enough to deposit in the source tank. In the column, some of the polymeric silica lost either by precipitation or filtration from solution in the void spaces of the column. The experiment demonstrates that amorphous silica scaling from geothermal brine can be mitigated by allowing dissolved silica in excess of amorphous silica solubility to polymerize provided that factors affecting polymerization rate and polymer deposition rate are known.

1. INTRODUCTION

Harnessing geothermal energy entails overcoming the difficulties encountered in its various stages of development. Whereas geothermal projects are spurred forward after establishing the heat source and permeability, addressing problems associated with the chemical composition of the geothermal fluids is as critical for successful exploitation. Geothermal water undergoes cooling and degassing during the process of extracting the heat. These changes favor the formation of different scales along the fluid path, which are often detrimental to geothermal operations. Amorphous silica is one of the major and most common scaling problems as its solubility decreases with decreasing temperatures. Depending on the conditions, amorphous silica scales may form anywhere from the production wells, surface facilities to downstream of injection wells. Injecting the fluids back to the reservoir is either an integral part of field management and/or compliance to environmental regulations. As spent geothermal waters are injected, silica may precipitate to cause mild to severe decline in injectivity of wells. High costs both in drilling wells and treatment to restore well injectivity make it important to maintain injection well capacities in a sustainable period. The scale formation, which deteriorates the injectivity of the wells, provided the motivation to investigate the precipitation rates of the different silica species in a controlled experiment. Angcoy (2006) provides a comprehensive report for more details and discussion.

2. BACKGROUND

The term silica is a short convenient form of silicon dioxide (SiO_2) and may refer to any of its nine natural or engineered earth system forms (polymorphs). In studying geothermal fluids, the silica phases of most interest are quartz, chalcedony and amorphous silica. Quartz is the most stable and common form in nature and is invariably present as secondary mineral of most geothermal systems. Reaction of quartz with aqueous solution can be expressed as:

$$SiO_{2,quartz} + 2H_2O \Leftrightarrow H_4SiO_{4,aqueous} \qquad (1)$$

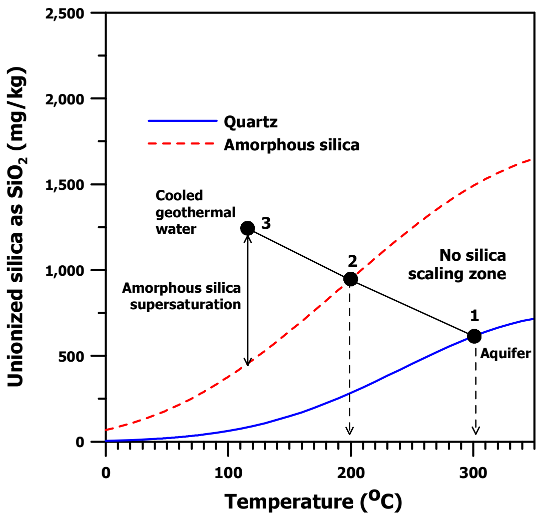

Figure 1: Solubility curves of quartz and amorphous silica as a function of temperature.

In most high-temperature reservoirs, aqueous silica concentrations are controlled by quartz solubility. Quartz solubility is temperature dependent. Accordingly, aqueous silica concentrations in geothermal reservoirs are determined by the reservoir temperature (point 1 on Figure 1). As the reservoir water rises to the surface, it boils by depressurization and cools down and in the process it gives off heat to the steam that forms. Steam formation increases the silica concentration in the water. This causes the water to become quartz supersaturated. But experience shows that quartz precipitation from supersaturated solution is very slow. Silica only precipitates at appreciable rate if the effects of cooling and steam formation are sufficient to produce amorphous silica supersaturated solution (point 2 on Figure 1). To prevent deposition of amorphous silica in geothermal installations it is common to keep its temperature above that corresponding with saturation for amorphous silica. This limits the amount of heat that can be extracted from the fluid discharged from production wells. Thus, it is common to cool the water past the saturation levels (point 3 in Figure 1) making it supersaturated with respect to both quartz and amorphous silica. Quartz and amorphous silica solubilities have been investigated numerous times over a wide range of temperatures, pressures, and solution compositions which are summarized in the works of Chan (1989) and Gunnarsson and Arnórsson (2000).

Dissolved silica in typical conditions of geothermal reservoir waters (<600°C, 6-8 kbar) were determined by Zotov and Keppler (2002) to be all on monomeric form (monosilicic acid), $H_4SiO_4^0$. A monomer may also be written as $Si(OH)_4^0$ showing a central Si atom with 4 separate bonded –OH , or silinol, groups. The silinol groups between two monomers form the Si-O-Si bonding into dimers, an initial step called a condensation reaction towards formation of higher molecular weight polymers:

$$Si(OH)_4^0 + Si(OH)_4^0 \Leftrightarrow (HO)_3Si - O - Si(OH)_3 + H_2O \quad (2)$$

When monomeric concentration exceeds amorphous silica saturation level, the growth of polymers and scale deposition are functions of combined chemical and physical processes following two dominant and essentially competing pathways: (1) molecular deposition upon solid surfaces and (2) particle deposition which follows homogenous nucleation and growth of suspended particles. The two mechanisms compete for the supply of excess $Si(OH)_4$ in solution such that the dominant one tends to slow down the other.

Molecular deposition involves not only chemical bonding of dissolved silica directly to solid surfaces like pipe walls, forming hard, dense, difficult to remove, vitreous, and often dark-colored scale. It also refers to the mechanism in which the growing polymer surface is a solid to which the monomer and silicate ions migrate by circulation and diffusion (heterogenous nucleation). This mechanism is a slow process and dominant at supersaturation ratio (silica concentration/equilibrium solubility at the given condition) <2 or at high flow velocity such that nucleation occurs further downstream. In particle deposition, the starting process is termed homogenous nucleation since the polymers develop spontaneously in solution. The decline of monomeric silica concentrations in solution (from initial supersaturation to saturation level) as analyzed by the molybdate method has been the principal method of studying polymerization processes. The rate of decline of monomeric silica is a strong function of initial supersaturation such that it is often instantaneous or very rapid if the ratio is >2.5 but exhibits a plateau called induction period which can last from minutes to hours if the ratio is <2.5. Induction period and polymerization rate are subjects of a lot of studies (Chan, 1989; Gunnarsson and Arnórsson, 2005). In general, at a given supersaturation level, induction will be shorter at a lower temperature, higher salinity, and higher pH (except in very basic solution when solubility of amorphous silica is high). Most authors agree that polymerization continues until the monomeric silica concentration falls to the solubility of amorphous silica.

Polymers continue to grow until they reach a critical size (<50 Å) for them to be considered colloidal particles. If the solution is static or flowing very slowly, the colloids may coagulate and form flocs which could either precipitate or remain suspended as semi-solid material. In some cases, the colloids are very stable in solution and do not precipitate (Klein, et al., 1991). The colloids may deposit to a solid surface driven by transfer processes such as diffusion, flow turbulence and gravity. When the colloids are deposited along with monomeric silica (Iler, 1979), deposition rate are much faster than deposition involving monomers only and the deposits are much more dense and hard than those formed by coagulated colloids only. Simultaneous deposition of colloids and monomeric silica creates worse scaling problems than deposition of monomeric silica only as the depositing colloids are cemented together by the monomers (Weres and Apps, 1982).

Similar studies on silica chemistry have been carried out similar to those of the present study. Bohlmann et al. (1980) simulated geothermal brines under controlled conditions at specified supersaturation, pH, temperature and salinity and passed through columns with various substrates. They observed that (1) once thoroughly coated with silica, the deposition behavior was identical and independent of the type of substrate and (2) more than half the silica removed from solution was deposited as monomers. Polymerized silica had little tendency to deposit. Amorphous silica precipitation behavior was investigated by Carroll et al. (1998). They observed slower rates in laboratory tests than in field experiments. The cause was considered to be due to chemical impurities in the geothermal brine. Mroczek and McDowell (1990) found that with rapidly polymerizing brine, deposition rate across gravel beds were lesser compared to brine containing only monomeric silica.

3. SILICA EXPERIMENT

3.1 Experimental Design

The objective of the experiment was to obtain data on relative precipitation rates of monomeric versus polymeric silica from amorphous silica supersaturated solution. Two sets of experiment were carried out. The first set was conducted at fixed temperature (50°C), atmospheric pressure, initial silica concentration (500 mg/kg) and pH of 6-7 but salinity was varied by adding 5 M NaCl solution to the initial test solution (0 M, 0.1 M, 0.2 M, 0.3 M and 0.4 M). The second set of experiments was conducted at 90°C, atmospheric pressure, initial silica concentration of 500 mg/kg, 0.3 M NaCl and pH of 6-7.

The experimental runs were performed using an oven set at experimental temperature (Figure 2). The silica-supersaturated solution was pumped from a container across a column packed with washed silica gel. The solution was pumped against gravity to prevent channeling in the column. Pumping across the column from an experimental solution was continuous for at least 30 minutes before sampling the discharge. The same column was used in other experimental solutions. After the column, a three-way valve was manipulated to direct the outlet solution either for sampling or for pH measurement. The solution did not come into contact with any glass material to prevent leaching of silica. Residence time in the column was fixed by regularly monitoring the flow rate at 1 ml/min. The determination of residence time was conducted using an inert visual tracer after completing all experimental runs. The initial and final weights of the dried column were measured.

The procedures in preparing the solutions and reagents were taken from another silica polymerization experiment (Gunnarsson and Arnórsson, 2005). Silica stock solution was prepared by dissolving silica gel in 0.1 N NaOH and filtered using 0.2 µm cellulose acetate filter paper at room temperature. In all runs, 1 liter experimental solution with target concentration of 500 mg/kg SiO_2 was prepared by diluting the stock solution with deionized water and adding variable amounts of 5 M NaCl solution depending on the desired salinity. The experimental solution after these steps was very basic (pH≈11). At this pH, all silica species present in the solution were molybdate active and undersaturated with respect to amorphous silica. The undersaturated solution was kept inside the oven at the experimental temperature for at least 12 hours. The pH of the thermally stabilized experimental solution was lowered to target value of 6.97 by adding concentrated HCl to oversaturate it with respect to amorphous silica. Prior to acidification, the experimental solution was buffered with TRIS, $(HOCH_2)_3CNH_2$, to stabilize its pH. Polymerization of the silica-supersaturated solution proceeded in the source tank as the solution was pumped across the column. The solutions at the inlet and outlet of the column were monitored for molybdate active and total silica concentrations to determine the relative amount of monomeric and polymeric silica in solution.

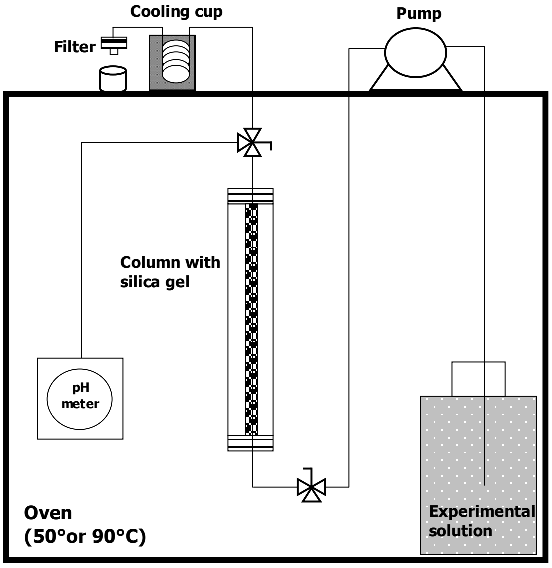

Figure 2: Set-up of silica experiment.

3.2 Sampling and Analytical Methods

Sample from inlet of the column was extracted from the experimental solution container using a 10 ml syringe while sample at outlet of the column was collected into a small vial after passing it through a 0.2 µm cellulose acetate filter. For analysis of monomeric silica concentration, the samples were immediately brought to room temperature through a cooling spiral and aliquots were drawn using a pipette. The entire sampling procedure was completed less than 30 seconds to minimize the effect of cooling to polymerization. For analysis of total dissolved silica, all samples were diluted at least 10 times and acidified with concentrated HNO_3. In the first set of experiments (50°C), all samples were passed through 0.2 µm cellulose acetate filter while in the second set of experiments (90°C) a run was conducted where filtered samples were duplicated with unfiltered ones.

Monomeric silica concentration was determined using the yellow molybdate method. The absorbance was measured at 410 nm using a Cary, 1E UV-visible spectrophotometer. In theory, the molybdic acid will react only with monomeric silica in the solution. However, since the samples in the analytical procedure are diluted to become undersaturated with respect to amorphous silica, some of the monomers forming the yellow molybdosilicic complex may have also been formed from the breakdown of silica dimers and trimers (Iler, 1979). Thus in this study, all monomeric silica are referred to as molybdate active silica. Total dissolved silica concentration was measured using Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES). Solution pH was measured with buffer-calibrated pH meter.

3.3 Experimental Results

Representative results of the experiment are presented in Figures 3-6 (complete results in Angcoy, 2006). After completing all the experimental runs, the retention time of the solution in the column was visually determined to be ~9 minutes using a colored tracer. The first run conducted in 90°C showed almost equal total and monomeric silica levels of the inlet solution through time. To determine whether this is a result of the polymers actually depositing in the tank or growing to sizes large enough to be filtered by the 0.2 µm cellulose acetate filter membrane, the experiment was repeated and the filtered samples were duplicated with unfiltered samples (Figs. 5-6). The initial and final dry weights of the column containing the silica gel did not differ significantly.

4. DISCUSSION

The results show that monomeric silica concentrations after the column were always at the same reduced concentration relative to initial level. This indicates that monomeric silica easily precipitates on the surface of the silica gel in the packed column. However, the concentration levels approached correspond at temperatures significantly lower than the experimental temperatures. Since it is unlikely that a more stable silica polymorph other than amorphous silica has precipitated in the column, the results are taken to indicate that cooling of the outlet solution occurred with the result that amorphous silica equilibration was attained at the lower temperature. The column was kept at the oven temperature except during sampling of the inlet solution. Thus, it is unlikely that the solution cooled across the column. Significant cooling only occurred when the sample was brought to room temperature to ensure accuracy of the volumes measured by the pipettes. Probably due to larger temperature difference, the monomeric silica level in the outlet solutions approached saturation of amorphous silica at lower temperatures in the 90°C runs (73°C) than in the 50°C runs (45°C). In contrast to the monomers, the polymerized silica formed in the inlet solutions and pumped across the column has little tendency to precipitate in the column. Most of it remained in solution when pumped through the column. In the experiments at 90°C and saline solution, the analyses of the filtered samples indicated that the polymers grew to a large enough size to be filtered from solution by the 0.2 µm cellulose acetate filter membrane as confirmed by the analyses of the duplicate unfiltered samples. In the experiment at 90°C, analyses of unfiltered samples indicated some polymeric silica (20 mg/kg maximum) was lost either by precipitation or filtration in the void spaces of the column (Figure 6). But compared to the losses of monomeric silica across the column, the amount of polymeric silica retained in the column is significantly less. Thus it is important that polymerization of the excess monomers is fast to use the advantage of polymeric silica observed in the experiment.

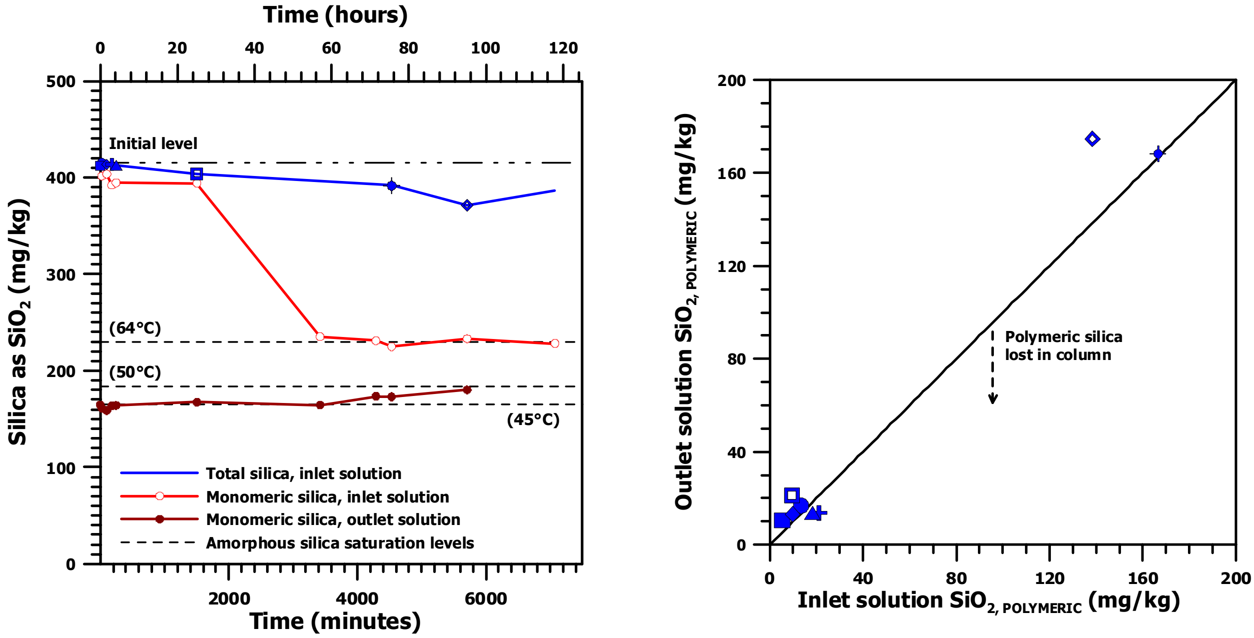

Figure 3: Experiment results at 50°C, 1 atm, pure water, pH ~7.00, 9 minutes retention time, filtered samples.

The experiment confirms the results of previous studies that at about constant degree of supersaturation, pH (buffered solutions) and temperature, polymerization of monomeric silica in excess of amorphous silica saturation is a strong function of salinity. Experiments carried out at 50°C show that increasing salinity increases silica polymerization rate in the tank solution (Figure 4). The monomers polymerized about 10 times faster in the 0.3 and 0.4 M NaCl saline solutions than in pure water. Silica polymerization rate is also a strong function of supersaturation. In the 50°C run, the 0.1 M NaCl solution was inadvertently prepared with a lower supersaturation (~165 ppm) than the solution in pure water (~220 ppm). The effect of salinity was offset by the low level of supersaturation such that the two solutions exhibited almost the same induction time but longer time was required to closely approach amorphous silica saturation for the 0.1 M NaCl solution. At the salinity of 0.3 M NaCl (50°C and 90°C), it was anticipated that increased polymerization rate due to higher temperature will also be counteracted by the higher saturation level of amorphous silica. Thus, supersaturation was increased in the 90°C, 0.3 M NaCl run by starting at a higher initial silica level to achieve a reasonable onset of polymerization of the excess monomers after about 5 hours.

The experiment demonstrated that precipitation of amorphous silica from supersaturated solutions is decreased if the monomers in excess of saturation are allowed to polymerize. However, the successful application of this method to mitigate silica scaling requires a balance between both silica polymerization rate and deposition rate. Silica polymerization is regarded as a precursor to the precipitation of silica gel (Iler, 1979). At pH ~7, the growing polymers in pure water tend to repel each other because of their negatively charged surfaces. But in saline solutions, the presence of ions reduces the repulsive forces allowing the polymers to aggregate and gel (Figure 7). In the experiment, increased salinity increases both silica polymerization and deposition rates. In all saline solutions of the experiment, the total silica concentration of the inlet solutions slightly declined from the initial silica levels indicating that some polymers have grown large enough to deposit in the tank. Growth and precipitation of the silica polymers is enhanced by the presence of electrolytes in solution. Marshall (1980) observed that the nature of cation and not the anion has greater effect. The decreasing effect of cations is $Mg^{2+} > Ca^{2+} > Sr^{2+} > Li^{+} > Na^{+} > K^{+}$ (Chan, 1989).

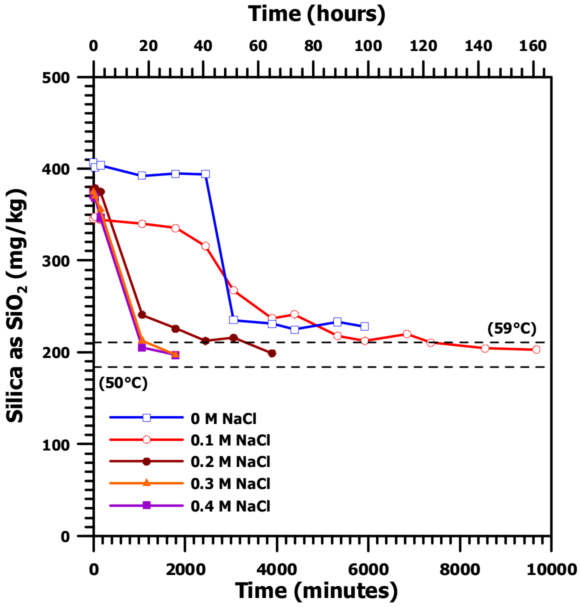

Figure 4: Polymerization of tank solutions (starting solutions) at 50°C, 1 atm, pH ~7.00, varying salinities and filtered samples.

Preventing solutions to oversaturate with respect to amorphous silica mitigates silica scaling. But in this experiment, it showed that silica oversaturation may be probably tolerated as long as the excess silica is in the form of polymers. Successful application of the method demonstrated by the experiment require (1) very fast silica polymerization such that no induction period is observed and (2) conditions that allow the polymerized silica not to precipitate or if precipitated, remain suspended in solution (i.e., do not deposit). For brine with slight supersaturation ratio (<2), rapid polymerization of the brine is possible by increasing the level of oversaturation by either brine flashing to low pressure or rapid cooling. Either way, it opens opportunities to cascade the energy of the brine for further utilization before final injection. If cooling the brine is not an option due to adverse impact to field management, heterogenous nucleation may be induced by seeding or brine transit through fluidized or packed beds with the objective of stripping the excess silica monomers from solution before injecting the brine.

The experimental procedure needs to be improved so as to allow direct sampling and analyses of samples without cooling. Analyses of monomeric silica concentrations may also be carried out using the more sensitive blue molybdate method. After these improvements, silica polymerization and deposition rates may be investigated with more confidence at various conditions. Laboratory tests need to be confirmed by field tests to validate the results. For instance, since the silica polymers in saline brine are likely to precipitate by gravity, field tests will help gauge the increased risk of deposition. Polymerization and deposition rates may further be complicated by the influence of trace amounts of iron, aluminium and manganese in the brine (Gallup, 1998).

5. SUMMARY

An experiment in the laboratory showed that polymeric silica has lesser tendency than monomeric silica to precipitate from the solution in a column packed with silica gel. Thus allowing the monomers in excess of the amorphous silica saturation level to polymerize before injection will possibly mitigate the declining injectivity of wells. Successful application of this method should consider the conditions that will allow deposition of polymeric silica precipitated due to dissolved salts in the solution.

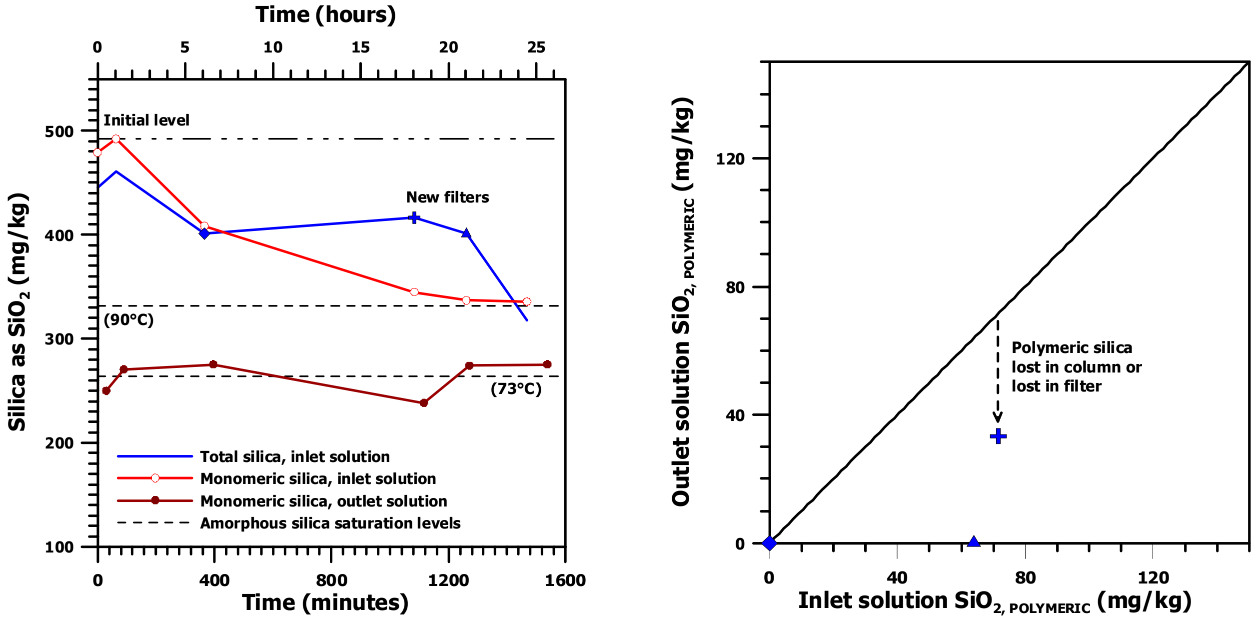

Figure 5: Experiment results at 90°C, 1 atm, 0.3 M NaCl, pH ~7.00, 9 minutes retention time, filtered samples.

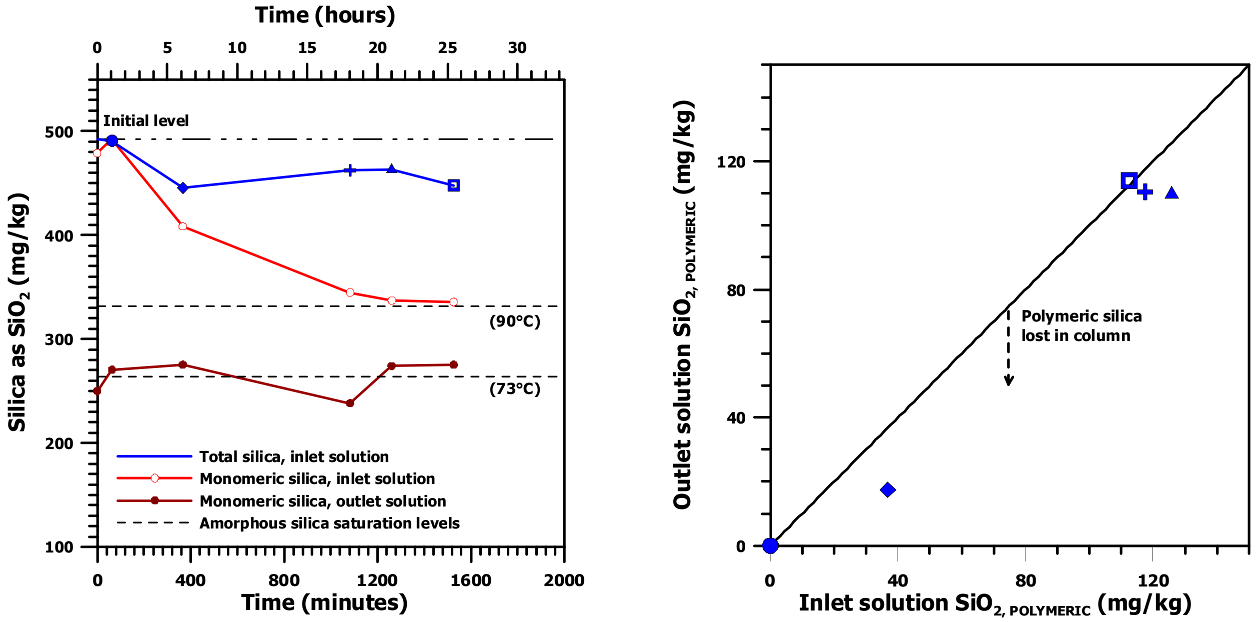

Figure 6: Experiment results at 90°C, 1 atm, 0.3 M NaCl, pH ~7.00, 9 minutes retention time, unfiltered samples.

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