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Characterization of Silica Precipitation at Geothermal Conditions

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ABSTRACT

Geothermal fluids in high enthalpy geothermal systems are often strongly enriched with dissolved silica, because these waters quickly ascend from hot geological formations and are, therefore not at chemical equilibrium on the surface. Especially the dissolved silica concentration would still resemble the amount of silica dissolved the reservoir thus being highly oversaturated at surface conditions. This silica might precipitate uncontrolled at various locations in the geothermal plant, in the reinjection well, or in the reservoir at the injection site thus causing severe damages of the plant or the reservoir. To prevent such uncontrolled silica precipitation, this study aims to understand the precipitation process by characterizing both the solid silica precipitates (using geochemical and mineralogical methods) and the polymerization of silica in solution at well-defined lab conditions (using measurements of ultrasonic velocity). Precipitation reactions have been investigated in dependence of temperature, pH value and ionic strength. The results can be used for understanding the polymerization and precipitation process as well as to develop methods that can be applied at geothermal sites for for controlled and accelerated silica precipitation in ponds or vessels before fluid re-injection. This eventually would prevent silica precipitation at the reinjection site which would severely damage the reservoir by permeability reduction.

1. INTRODUCTION

At high enthalpy geothermal systems silica (SiO_2) scaling is a common challenge for operating binary plants (ECFA, 2010; Guerra et al., 2012; Grassiani, 1999). While at reservoir conditions, at given high temperatures dissolved silica of the brine would be in equilibrium with the host rock thus containing up to several hundred mg/L dissolved silica, the brine would be highly oversaturated at surface conditions. Precipitation of silica however, might be kinetically inhibited and takes often not place immediately, but retarded and uncontrolled in the injection well. This would be of special concern for power plant operation, because a precipitation of silica in pores of the reservoir rock would reduce rock permeability and thus the injectivity of the well. Eventually this could provoke irreversible reservoir damage and thus operation stop. In general silica precipitation depends not only on temperature but also on solution pH, ionic strength and other components in solution (Rothbaum et al., 1979; Yokoyama et al., 1989; Zotov and Keppler, 2002; Tobler et al., 2008b). Therefore it is essential to understand the process of silica precipitation and the effect of solution parameters.

In order to prevent or control silica precipitation the complex behavior of silica molecules in solution have to be considered. In under saturated solutiosn silica occurs as monomeric SiO_4 tereder (silic acid). With increased saturation the monomers start to agglomerate forming first dimeric than trimeric, tetrameric- etc acids. These oligomers can prevail as aqueous large molecules (polymers) without precipitation. The addition of crystal seeds or changes of solution conditions such as a pH value decrease would result in the precipitation of these polymers forming typically amorphous silica.

Solid silica can occur both, as crystalline or amorphous phase. At least eleven different silica phases with diverse crystalline structure are found in natural and engineered earth systems in various forms such as quartz, opal or amorphous silica (Dove and Rimstidt, 1994). The silica structure consists of a network, where oxygen and silicon ions are bound in siloxane bridges (Si-O-Si). The fundamental structure is described as tetrahedron element, a silicon ion surrounded by four oxygen ions. The degree in which a silica network is crystalline, determines how reactive the specific network is. A network that is a less crystalline will have a larger specific surface area and as a result it will have greater reactivity than a more crystalline network. Moreover, the more amorphous a network is the more defects it will have and the greater the probability to form a silanol bound, which is vulnerable to alkali-silica reactions (Crucq, 2005).

Understanding silica precipitation and polymerization reactions is crucial for the operation of geothermal plants (Gunnarsson & Arnorsson, 2005). By changing the solution equilibrium silica could be removed from the brine. At a geothermal plant this process could be induced in certain equilibration pools before the reinjection well (Gallup, et al., 2003). This study aims to characterize both, the silica polymerization process and the mineralogical characteristics of the precipitates formed under well-defined lab conditions in dependence of pH-value, temperature and ionic strength. To monitor silica polymerization and precipitation the ultrasonic velocity of synthetic brines has been measured at various conditions. So far polymerization has been usually measured by spectroscopic methods which are however difficult to apply at in situ conditions. In contrast the ultrasonic probe can be directly inserted in reaction vessels at in situ conditions and changed in ultrasonic velocity can be monitored online. This study aimed to apply this method to identify and monitor silica polymerization. Additionally, chemical properties of the silica solution were compared with the mineralogical appearance of the formed silica precipitates.

2. MATERIAL AND METHODS

2.1 Monitoring silica polymerization by ultrasonic measurements

Ultrasonic velocity was measured in silica solutions prepared by diluting ultrapure silica standard solutions (1000 ppm) with deionized water. To prevent evaporation and maintain temperature stability, experiments were performed in autoclaves to which the ultrasonic probe (LiquiSonic40-14) was attached in the lid along with a pressure gauge, pressure safety valve, and a sampling port so that the desired conditions could be maintained while online measurement and sampling could be simultaneously undertaken. The ultrasonic velocity and temperature were measured with an immersion sensor connected to a controller (Controller 50). The solutions were continuously stirred with a magnetic stirrer to acquire homogeneous conditions.

The measurement of ultrasonic velocity is based on the change of compressibility and density of a solution. At constant density, the compressibility is affected by concentration of ions according to equation 1 and 2 (Allam & Lee, 1966).

$$\boldsymbol{v} = \sqrt{\frac{\mathbf{1}}{\boldsymbol{\beta\rho}}} \quad (1)$$

$$\beta = \beta 0\ (1 - S\frac{n2}{n1}) \quad (2)$$

Where v is ultrasonic velocity, β is compressibility, ρ is density, S is solvation number, $n1$ and $n2$ are numbers of moles of solvent and solute present, respectively.

To determine the effect of various pH values on the ultrasonic velocity at constant temperature (30 °C), various amounts of HNO_3 were added to the initially alkaline (pH 12) silica solution. The effect of ionic strength on ultrasonic velocity at 30 °C was measured by adding NaCl to the silica solution to obtain concentrations of 0.5, 0.124, and 0.024 M. Afterwards silica oversaturation was obtained by adjusting the pH to 7 by adding HNO_3. In all experiments subsamples were collected over the time (after 1, 2, 3, 4, 5, 6, and 24 h).

The effect of temperature was measured in 490 ppm silica solutions in presence and absence of additional hematite (Fe_2O_3) powder (1 g/L) acting as crystallization seed. These solutions were heated to 150 °C. Afterwards the pH was adjusted to pH seven by adding some HNO_3. During the cooling process at each temperature step (150, 125, 100, 75, and 50 °C) subsamples were collected after 1 hour equilibration time. In collected samples, immediately monomeric SiO_2 was measured photometrically by the silicomolybdate method at 385 nm (Tanaka & Takahashi, 2000). All experiments were performed in glass-free containers (polyethylene or Teflon) to avoid Si contamination.

2.2. Characterization of precipitates formed at various conditions

A 1 M sodium silicate stock solution was prepared by dissolving silica gel in 0.5 M of sodium hydroxide at 65 °C (pH 12). Silica precipitation was afterwards obtained by adjusting the solution pH to values between 7 and 10 in Bola A240-08, PTFE digestion vessels heated in the oven between 30 and 90 °C for 24 hours. Ionic strength was adjusted to 1.5 M in some samples by adding NaCl. The supernatant was discarded after measuring the pH value (pH100 non-glass electrode) and the precipitate was washed with distilled water, dried in the oven (90 °C), and the mass of each sample was determined by weighing.

The synthesized silica precipitates were characterized for their crystallinity by X-ray powder diffraction (XRD), on a Bruker AXS D8 X-ray operated at 40 kV, with a CuKα (λ = 1.54 Å) in the range 4.8-84.9° 2Θ with step size of 0.013° 2Θ and step size 2 s. Molecular bonding structures were measured by Fourier transform infrared (FTIR) spectroscopy on KBr pellets (ratio KBr to sample: 450:1). Selected samples were evaluated in detail by scanning electron microscopy (SEM) with a model Ultra 55 Plus (Carl Zeiss SMT). Samples were covered with silver paint (G3692 Acheson Silver DAG 1415), a dispersion of flake silver that produces a flexible silver coating of high electrical conductivity. The secondary electron images were obtained at 20kV in various magnifications (e.g. 400 and 500X).

3. RESULTS AND DISCUSSION

3.1. Effect of solution parameters on the liquid phase

Measuring ultrasonic velocity in liquids depends on solution density and compressibility. Since compressibility is inversely proportional to ion concentration at constant temperature and density, the measurement of ultrasonic velocity can indicate changes of silica concentration and thus give information on polymerization and precipitation process.

It was found, when measuring ultrasonic velocity in silica solutions (500 ppm silica) at various pH values, that with decreasing pH, also the ultrasonic velocity decreased (Fig. 1) which could indicate silica polymerization. In general, the area between saturation and nucleation is defined as “metastable zone” of a solution. In this zone, here between pH 6 and 9 (Fig.1), no precipitation occurred during back and forward titration although the solution was silica oversaturated. In this case, the range of ultrasonic velocity of the metastable zone (1513-1514.5 m/s) would correlate with the amount of polymeric silica.

It is known that with increasing ionic strength silica solubility decreases. This “salting out” effect can be explained by salt molecules attracting water molecules thus lowering the solvation of the silica thus inducing enhanced silica oversaturation (Tanaka & Takahashi, 2001). However, ultrasonic velocity itself is strongly depended on ionic strength since this parameter affects solution density. This is very obvious from Fig. 2 where hardly any changes of ultrasonic velocity due to decreasing silica concentration can be observed. Instead, the ultrasonic velocity is mostly determined by the overall ionic strength (Fig. 2a).

The effect of temperature on ultrasonic velocity was investigated by cooling down an oversaturated silica solution from 150 to 20 °C. It was found, that with decreasing temperatures the silica concentration slightly (from 490 to 460 ppm) decreased (due to polymerization or precipitation) and ultrasonic velocity increased (Fig. 2a). This indicates that ultrasonic velocity measurements are

a strong tool to determine even slight solution changes. However, the overall silica precipitation is a very slow process which is little affected by pH-value (Fig. 1) or temperature (Fig.2b).

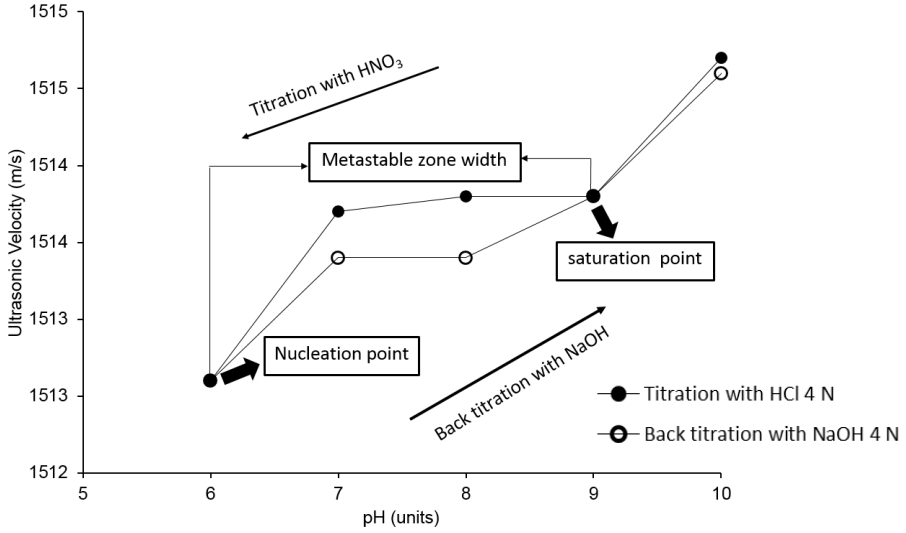

Figure 1: Ultrasonic velocity measured in 500 ppm silica solutions in dependence of pH values at 30 °C.

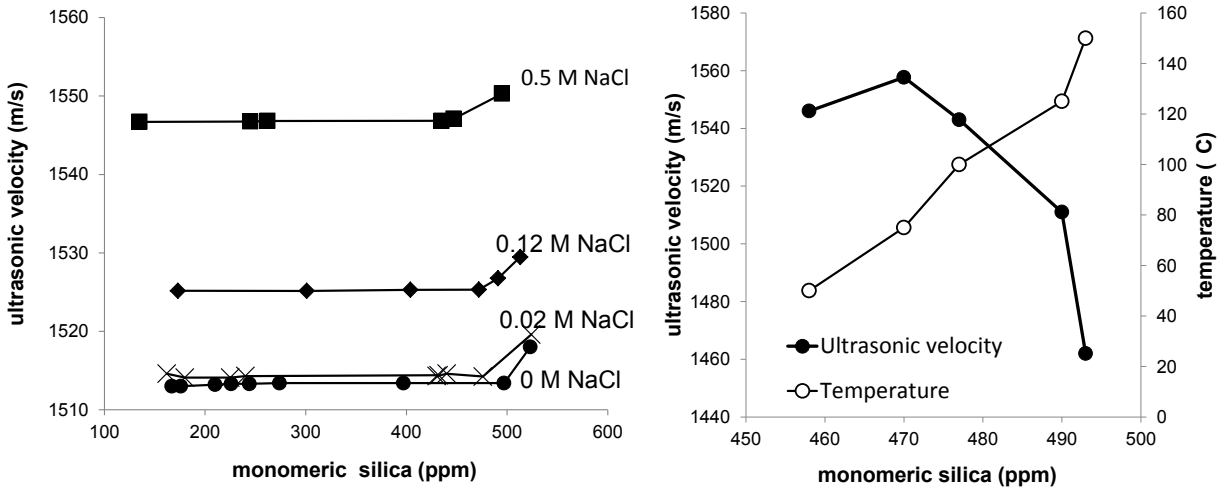

Figure 2: Ultrasonic velocity at a) various NaCl concentrations in 500 ppm silica solutions at 30 °C (left) and b) measured during cooling of a 490 ppm silica solution with of 1 g/L hematite at pH 7 (right).

3.2 Effect of solution parameters on the solid phase

Solid silica observed in this study and elsewhere (Brown, 2011) usually forms aggregates and gels which increase in size with increasing temperature independently of pH value and ionic strength. Scanning electron microscopy identified no distinct crystal shapes. In some samples conchoidal fractures were observed (Fig. 3) that is particularly characteristic for amorphous material. They occur when bonds between atoms are approximately the same in all directions within the solid, and result in breakage along smooth, curved surfaces such as obsidian, and are also common in quartz, chert and glass (Goude, 2003).

As expected, the highest amount of precipitates had formed at neutral pH, where silica solubility is lowest (Fig. 4, Iler, 1979). At pH 11 to 12, the amount decreased (Fig. 4), which is explained by the fact that in strongly alkaline solution monosilicic acid does not polymerize, thus reducing the amount of silica precipitation (Tarutani, 1989). For a NaCl content of 1 M, an increase in the mass of the silicate precipitate was observed (Fig. 4). Gunnarsson and Arnórsson (2005) have shown that at a pH value above and around 7, silica polymers have negative surface and as a result the individual polymers repel each other. These repelling forces are reduced significantly when the ionic strength is increased because cations as Na^+ decrease their negative surface charge and enhance the growing of polymers in size and eventually become so big that they precipitate. The presence of NaCl seems to enhance the precipitation of silica, as for pH values ranging from 7.49 to 10.45, an average increase of 0.3 g is observed with respect to precipitates in the absence of NaCl.

For the range of temperatures investigated in this study (30 to 90 °C), the amount of silica precipitation was highest at 30 °C (Fig. 4). The presence of NaCl enhanced silica precipitation in all experiments. For pH values between 7.49 and 10.45, an average mass increase of 0.3 g was observed in the absence of NaCl. At highly alkaline pH (pH = 10.72) and at the 50 °C. Without added NaCl

significantly less silica precipitated. This result confirms solution measurements showing a strong impact of temperature, salinity and pH value on the rate of silica polymerization.

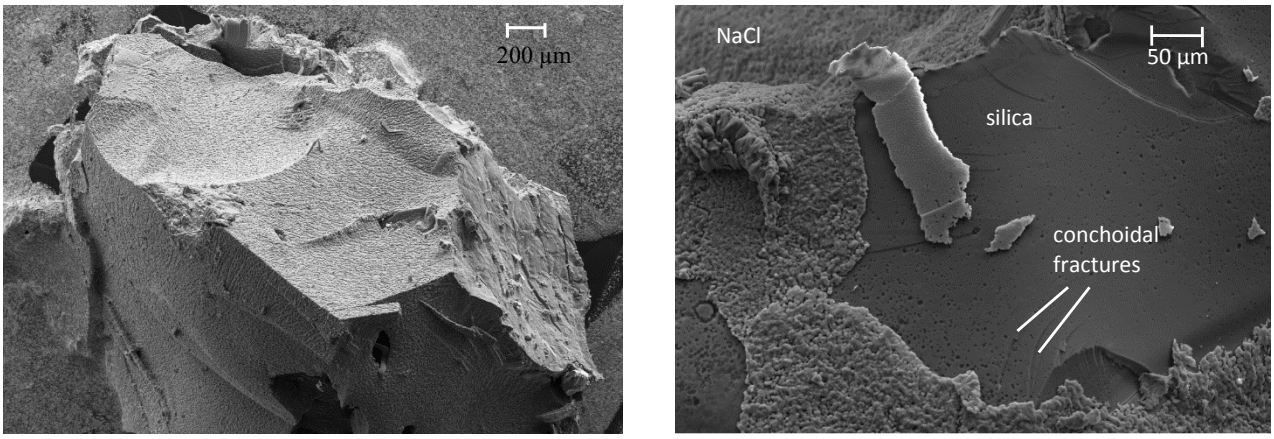

Figure 3: Scanning electron micrograph of a typical silica precipitate prepared at 70 °C and pH 10 in two different enlargements. At higher resolution (right) conchoidal fractures and NaCl encrustation are visible on the smooth silica surface.

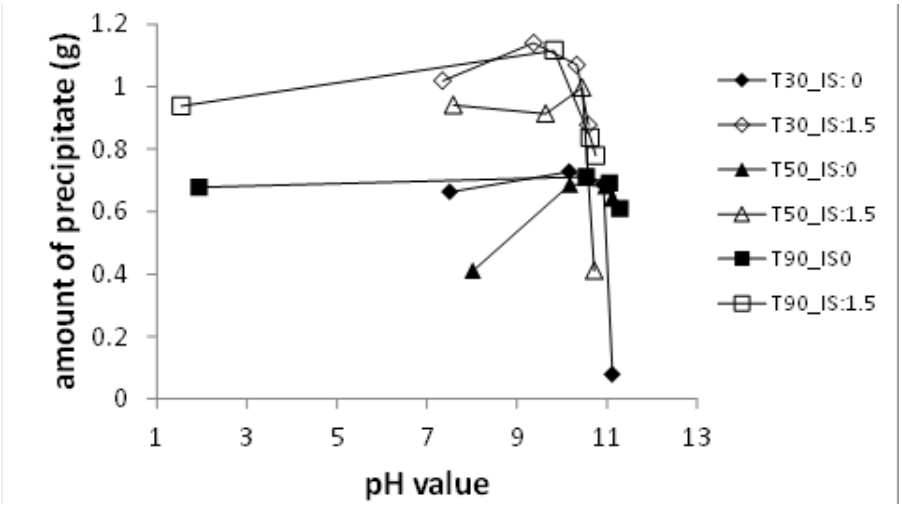

Figure 4: Amount of silica precipitation in dependence of temperature, pH and ionic strength (IS).

Crystallinity was investigated by XRD measurements on silica samples precipitated at various temperatures (30 to 90 °C). It was found that all precipitates were amorphous marked by just one peak at 23° 2Θ (Fig. 5).

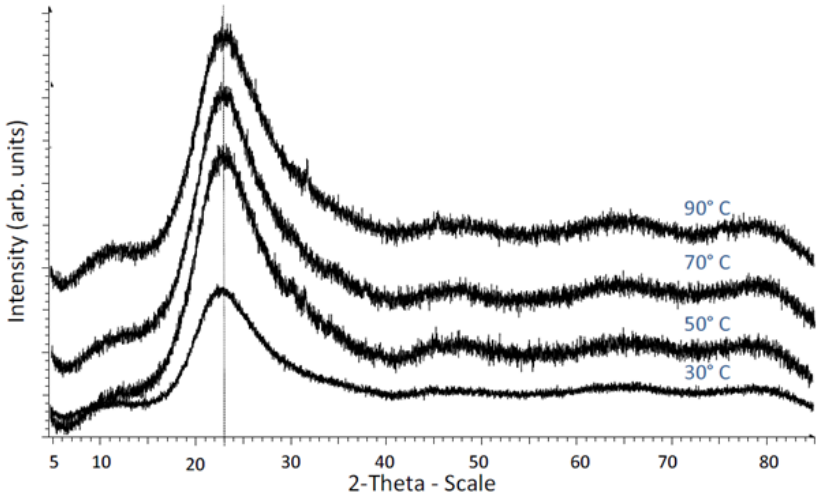

Figure 5: XRD of SiO_2 precipitated at various temperatures.

FTIR spectra of substances can give information of molecular bonding structures of solids and liquids. Due to the amorphous properties of produced silica, we aimed in this study to identify some shifts in the spectra which would indicate changes on the molecular structure of silica. All samples precipitated at various conditions (pH, ionic strength, and temperature) were measured by FTIR, however, the spectra of all synthetic silica precipitates are similar with no clear trends in dependence on the investigated parameters. They show SiO_2 vibrations typical for amorphous silica, which are characterized by a multi-component broad absorption band between 3500 and 2900 cm^{-1} and a sharp peak at 3500-3450 cm^{-1} (Figure 6; Music et. al., 2011). These bonds correspond to the OH stretching vibration of hydrogen bonded of water (Adamo et al., 2010; Hamelmann et al., 2005; Music et al., 2011). In some cases a shoulder at 3300 cm^{-1} is present that can be assigned to the stretching vibrations of the silanol functional groups (Si-OH) in the structure of amorphous SiO_2, which are proved as bonded water (Music et al., 2011). The very strong and broad IR band at 1070 cm^{-1} with a shoulder at 1200 cm^{-1} in some samples is usually assigned to the TO (transversal) and LO (longitudinal) modes of the Si-O-Si asymmetric stretching vibrations, whereas the peak at 940 cm^{-1} can be assigned to silanol groups or $Si\text{-}O^-$ stretching vibrations in the case of alkali silica glasses, and the observed IR band at 800 cm-1 to Si-O-Si symmetric stretching vibration (Music et al., 2011). The two strong bands 1070 and 800 cm^{-1}, related to the fundamental vibration Si-O, are common to all silicates with tetrahedrally coordinated silicon (Adamo et al., 2010). Finally, the weak peak at 670 cm^{-1} corresponds to Si-H wagging vibration in $O_xSi\text{-}H$ bonds configuration (Hamelmann et al., 2005). The vibrations from amorphous silica spectrum are produced basically from the SiO_4 tetrahedron and O_2- and cation (e.g. Na^+) interaction.

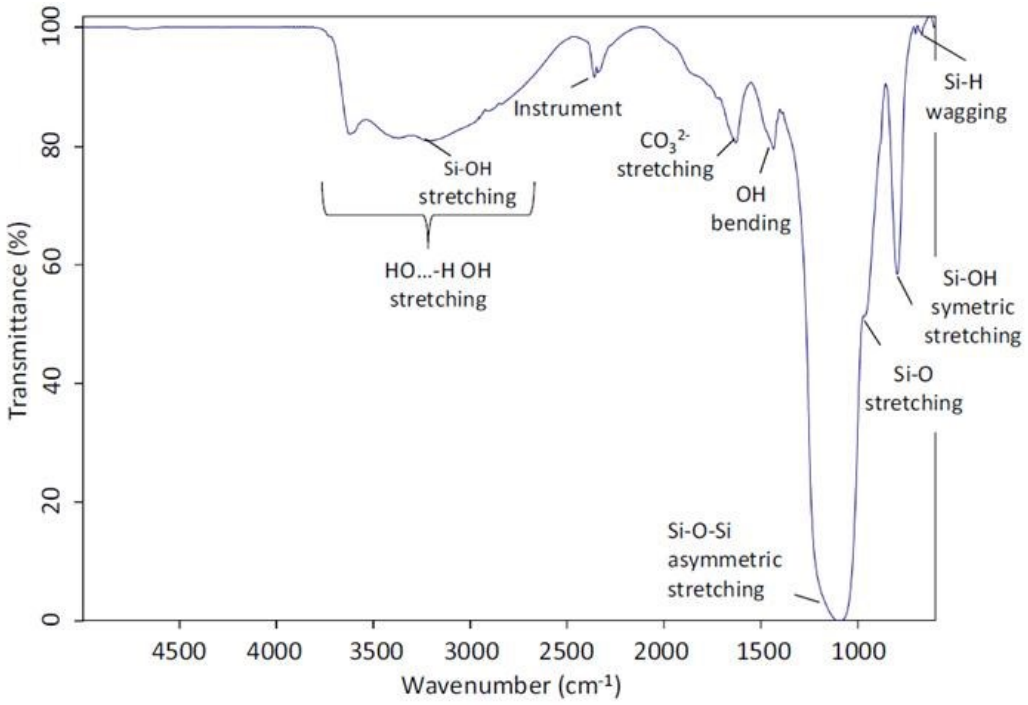

Figure 6: FTIR spectrum of a typical silica sample.

4. CONCLUSION

Understanding the processes of silica precipitation and the parameters that affect the process in terms of quantity and properties of the solid phase is crucial when methods are required plant to remove silica from solution at a geothermal site, for example in scaling ponds.

In this study, geothermal conditions which might occur at binary plants of high enthalpy geothermal sites were simulated in lab experiments by adjusting silica solutions to certain well-defined parameters. Both, the mass and properties of the solid phase and the precipitation process in the liquid phase were characterized. It was found that the method of ultrasonic velocity measurements to monitor silica polymerization and precipitation is very sensitive and can only be applied at constant ionic strength.

All silica precipitates that formed under given conditions (similar as expected in cooling geothermal brines at binary plants) are amorphous and do not change structurally in dependence of pH-value, ionic strength and temperature (< 90 °C). However, the amount of precipitates and the velocity of the process were strongly affected by these parameters. At around neutral pH value, with increasing salinity and decreasing temperature the amount of precipitates was highest.

However, the total amount of precipitates that formed at various conditions was relatively low as compared to the silica content still in solution which remained usually oversaturated. In future, the effect of other additives so silica polymerization and or precipitation reaction should be investigated to find a method that more strongly accelerates the precipitation process.

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