

## Silica precipitation from geothermal fluid and synthetic solutions: salts effects on kinetics and mechanisms

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### ABSTRACT

Hot geothermal fluids generally contain various dissolved species which can form scale deposits during their cooling and lead to a loss of efficiency for geothermal power plants. Despite various studies on the silica precipitation from hot geothermal water and aqueous solutions, the understanding of the phenomenon remains incomplete probably due to the great number of parameters involved.

In this study, we investigated the effect of five salts (NaCl, MgCl<sub>2</sub>, AlCl<sub>3</sub>, FeCl<sub>3</sub> and CaCl<sub>2</sub>) on the kinetics of silica precipitation in neutral pH (pH ~ 7) aqueous solutions with initial silica concentrations of 600 mg L<sup>-1</sup> at 80°C. Experimental kinetic data were modeled with a 2-order kinetic law previously proposed in Dixit et al. (2016) for Bouillante geothermal water and the computed rate constants  $k_2$  were used to quantify and discuss the salt effects on silica precipitation.

Results show that, except FeCl<sub>3</sub>, the salts tested accelerated the decrease of silica concentration in this order: AlCl<sub>3</sub> > MgCl<sub>2</sub> > CaCl<sub>2</sub> > no salt. In the presence of Fe<sup>3+</sup> and Ca<sup>2+</sup>, the reaction begins with an induction period that significantly decreases the kinetics of silica polymerization.

Comparison between kinetic modeling on Bouillante geothermal water and a synthetic fluid with nearby composition indicates that laboratory experiments on synthetic solutions can help for improving our knowledge on the kinetics and mechanisms of silica precipitation in natural geothermal waters, under different exploitation conditions.

A chemical and physical characterization of the particles formed along the kinetic experiments by electron microscopy (SEM and TEM), X-Ray diffraction, BET method and light scattering method, in order to better understand the polymerization mechanisms, is currently on going. Preliminary SEM and XDR results show that the precipitates contain mainly amorphous silica with the presence of small quantities of sodium, magnesium and calcium in some samples.

### 1. INTRODUCTION

Extraction of heat from high-temperature (>200°C) geothermal fluids for electricity production is an interesting alternative to fossil fuels particularly in the current context of global warming. However, these hot fluids generally contain various dissolved species (Si, Zn, Pb, Ag, As, etc.) which can form scale deposits during their cooling and cause serious problems on geothermal power plants. Silica deposit is a common problem observed and studied in many geothermal plants (White et al., 1956; Makrides et al., 1980; Carroll et al., 1998; Potapov et al., 2001; Gallup et al., 2003; Sanjuan et al., 2010; Demir et al., 2014). The extraction of geothermal fluids is accompanied by a decrease in both temperature and pressure, resulting in supersaturation with respect to amorphous silica. This can lead either to precipitation of dissolved silica directly onto a solid surface (silica scaling), or to polymerization of the silica into larger molecules that eventually coalesce to form silica colloids (silica gel) (Iler, 1979; Rothbaum and Rohde, 1979; Weres et al., 1981; Chan, 1989; Gunnarsson and Arnórsson, 2008; Alekseyev et al., 2010). It is crucial to well understand the mechanisms and parameters involved in silica precipitation in order to limit it and increase the efficiency in the use of high-temperature geothermal resources. Various studies showed the main parameters influencing the precipitation of amorphous silica are the degree of supersaturation with respect to amorphous silica, pH, temperature, and others ions in solution such as salts. Few of these studies have treated on the effects of salinity or ionic strength (Marshall and Warakowski, 1980; Icopini et al., 2005; Gorrepati et al., 2010; Celik et al., 2017; André et al., 2017; Kley et al., 2017; Spinthaki et al., 2018).

In this paper, we propose to investigate the effects of five salts (NaCl, MgCl<sub>2</sub>, AlCl<sub>3</sub>, FeCl<sub>3</sub> and CaCl<sub>2</sub> at different concentrations) on the kinetics of silica precipitation for an initial silica concentration of 600 mg L<sup>-1</sup>, at pH 7 and 80°C. We have chosen to work both on synthetic solutions representatives of geothermal waters encountered in volcanic context and on natural geothermal water from Bouillante geothermal plant (Guadeloupe, French West Indies). In Dixit et al. (2016), we already presented a detail study on the effect of temperature and pH on the kinetic of silica polymerization during the cooling of the Bouillante geothermal fluid.

Our main objective in this work is to evaluate quantitatively the change in the rate of silica precipitation in the presence of salts by modeling kinetic data. These models are also useful to estimate kinetic parameters suitable to various geothermal fluids compositions and then better predict and prevent silica deposition in a wide range of geothermal areas.

We are also interested in the effects of salts on the mechanisms by which silica colloids grow and precipitate. So we have collected the particles formed along the kinetic experiments in order to observe their evolution in size and shape using light scattering technique. The analyses still are in progress and will be presented in the poster linked to this paper. Physical and chemical characterizations of these particles, performed by electron microscopy (SEM), X-Ray diffraction (XDR) and BET method, are also ongoing. However preliminary results obtained on the precipitates collected at the end of the kinetic experiments are presented in this paper.

## 2. MATERIALS AND METHODS

### 2.1 Materials

#### 2.1.1 Synthetic fluids

We presented in this paper results from 11 synthetics solutions with different chemical compositions (Table 1).

**Table 1. Characteristics and compositions (in mg L<sup>-1</sup>) of the synthetic solutions (SYNT) and the natural geothermal water from Bouillante (BOU).  $k_2$  represents the rate constant (in mol m<sup>-2</sup> s<sup>-1</sup>) for a 2-order reaction law obtained from kinetic modeling (see sections 2.2.3 and 3)**

Name	pH	T (°C)	SiO <sub>2</sub>	Na	Mg	Fe	Al	Ca	$k_2 \times 10^{-8}$ (mol m <sup>-2</sup> s <sup>-1</sup> )	
SYNT0	7	80	600	0	0	0	0	0	0.35	
SYNT1				970					1.16	
SYNT2				2600					2.36	
SYNT3				9700					5.71	
SYNT4				9700					2	7.30
SYNT5				2					0.98	
SYNT6				20					1.52	
SYNT7				60					21.7	
SYNT8				20					0.172	
SYNT9				0					0	20
SYNT10	0	0	0	20	0.39					
BOU	7.3	80	640	6400	2	0.2	0.02	2200	7.90	

One initial silica concentration of 600 mgL<sup>-1</sup> closed to SiO<sub>2</sub> concentration in Bouillante separated water and representative of middle silica initial concentration was used.

Five salts at various concentrations were tested: sodium chloride (NaCl, assay  $\geq$  99.99%, Sigma-Aldrich); magnesium chloride (MgCl<sub>2</sub>, assay  $\geq$  98%, Sigma-

Aldrich); as well as aluminum chloride (AlCl<sub>3</sub>, assay  $\geq$  99.99%, Sigma-Aldrich), iron(III) chloride hexahydrate (FeCl<sub>3</sub>·6H<sub>2</sub>O, assay  $\geq$  99.99%, Sigma-Aldrich) and calcium chloride dihydrate (CaCl<sub>2</sub>·2H<sub>2</sub>O, assay  $\geq$  99%, Honeywell). We have chosen to prepare solutions than permit us to investigate in a first step the effect of the different salts separately. We used three different concentrations for Na<sup>+</sup> and Mg<sup>2+</sup> whereas the others cations Ca<sup>2+</sup>, Fe<sup>3+</sup> and Al<sup>3+</sup> were tested for one concentration. In SYNT6, SYNT8, SYNT9 and SYNT10, the salts except NaCl were at a same concentration in order to study the effect of the salt kind.

Only the sample SYNT4 combines the effects of Na<sup>+</sup> and Mg<sup>2+</sup>.

Synthetic solutions were prepared by dissolving Na<sub>2</sub>SiO<sub>3</sub>·5H<sub>2</sub>O in a beaker of ultra-purified water under magnetic stirring, using the appropriate product weight. The salts were dissolved separately in another beaker of ultra-purified water under magnetic stirring. Thereafter the two solutions were mixed under magnetic stirring to obtain synthetic solutions at the wanted concentrations. pH solution is closed to 11 so silica precipitation is not favored (Tarutani, 1989).

#### 2.1.2 Separated water from Bouillante geothermal plant

In this study, we used Bouillante geothermal water (Guadeloupe, FWI) as a reference for validating experimental protocols and kinetic results on synthetic solutions. The Bouillante high-temperature (250-260 °C) geothermal field is located on the west coast of the volcanic island of Guadeloupe. A high pressure (HP) steam-water separator separates the extracted geothermal fluid, at 167 °C and 6-7 bars, into approximately 20% steam and 80% water that is termed separated water. Part of the fluid is also separated at close to 110°C in a low-pressure (LP) phase separator. It is well established that the deep geothermal fluid collected from the wells is a Na-Cl brine (TDS = 25 g L<sup>-1</sup>) comprising 58% seawater and 42% freshwater that has attained a chemical equilibrium at 250-260 °C. The separated geothermal water is characterized by a near neutral pH of 6.8, a silica concentration of about 600 mg L<sup>-1</sup> (Sanjuan et al., 2010; Dixit et al., 2016). Its chemical composition is given in Table 1.

Dixit et al. (2016) investigate on site the kinetics of silica precipitation as a function of temperature and pH. Only silica polymerization was observed, with the formation of colloidal particles in suspension in the solutions. Modeling the experimental data indicates that the silica polymerization up to the state of equilibrium is characterized by a 2<sup>nd</sup>-order kinetic that could indicate that the polymerization is controlled mainly by the formation of dimers. Under the investigated experimental conditions, they show that the kinetics of silica precipitation is affected more strongly by pH than by temperature change.

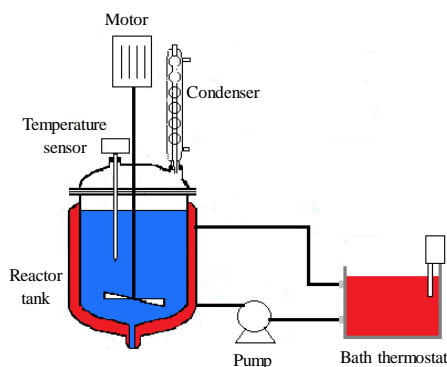
The experimental protocol used to sample Bouillante geothermal water is described in Dixit et al. (2016). The

separated water was sampled in 250 mL polyethylene bottles from a fixed fluid sampling point located after the HP separator phase. The sample BOU was obtained directly at the relevant working temperatures (80°C) using a suitable cooling system composed of a tank with a small submerged streamer. A thermostatic water bath was used to maintain the working temperature ( $\pm 1^\circ\text{C}$ ) for the entire duration of the kinetic experiment. The natural pH of the separated water was 7.3.

## 2.2 Methods

### 2.2.1 Experimental protocol

To study the kinetic of scales deposits we use a continuous stirred tank chemical reactor (Figure 1).



**Figure 1. Experimental apparatus**

This reactor is composed of a closed container made of glass and consisted of two layers, a mixing motor (mechanical stirrer) and a temperature probe. Cold water heated at the working temperature (80°C) from a thermostatic water bath ( $\pm 1^\circ\text{C}$ ) is introduced between the container layers and removed by a circulation device (pump), allowing to heat the solution inside the container by conduction. The mixing motor allows a uniform stirring of the solution. In this study we worked at atmospheric pressure.

For kinetic experiments, 2L of the tested solution is introduced in the main reactor container with hot water circulating in the second layer at the working temperature. When the solution reached the working temperature, pH was adjusted to pH 7 by addition of ~5 ml of 25% HCl solution in order to initiate silica precipitation.

To monitor the change in dissolved silica concentration over time, 1 mL of solution was taken with a syringe, filtered at 0.45  $\mu\text{m}$  and diluted at least 100 times by weight with ultra-purified water to avoid silica polymerization. Thereafter the  $\text{SiO}_2$  concentration was measured using the method described in section 2.2.2. The measurements were made every 10 min during the first hour, every 20 min during the second hour and finally every hour up to 7-8 h. Each experiment was repeated at least twice for a reliable dataset.

The particle suspensions in solution were recovered along and at the end of the experimental runs by filtering under vacuum. Their analyses by light scattering experiments, X-ray diffraction (XRD),

scanning and transmission electron microscopy (SEM and TEM), and BET gas adsorption must permit to detect any change in particle size and shape, crystallinity, morphology/chemical composition, and surface area, respectively.

### 2.2.2 Analysis of the dissolved silica

The decrease in dissolved silica concentration with time was monitored by spectrophotometry using the molybdenum blue method. With this method, the sample reacts with ammonium molybdate over 10 min to give a blue complex species (silicomolybdic acid) whose absorbance is measured at 650 nm using a MERCK spectrophotometer. The uncertainty with this method is typically about 5%.

In principle, only low-molecular-weight silica polymers, including monomers, dimers, trimers, and longer chained polymers, can be complexed with molybdate. But the real species measured with this method are still not well defined (Iler, 1979; Rothbaum and Rohde, 1979; Icopini et al., 2005). For the present study, we assumed that the measured molybdate-reactive silica concentration included only monomers  $[\text{H}_4\text{SiO}_4]$ . This assumption is based on the fact that the polymers (dimers, trimers, tetramers) must depolymerized before reacting with the molybdate reagent and that this step, under our experiment conditions, is probably too slow to influence the measurements (Makrides et al., 1980; Carroll et al., 1998).

### 2.2.3 Kinetic modeling

The rate of silica precipitation  $r$  ( $\text{mol L}^{-1} \text{s}^{-1}$ ) was calculated using the equation [1] proposed in Dixit et al. (2016):

$$r = -\frac{dC_{\text{SiO}_2(\text{am})}}{dt} = -k_2 \cdot A_s \cdot \left(1 - \frac{C_t}{C_{eq}}\right)^2 \quad [1]$$

where  $k_2$  is the rate constant ( $\text{mol m}^{-2} \text{s}^{-1}$ ) for a 2-order reaction law,  $C_t$  is the concentration of dissolved silica at a given time  $t$  ( $\text{mol L}^{-1}$ ),  $C_{eq}$  is the amorphous silica solubility at a given temperature  $T$  ( $\text{mol L}^{-1}$ ), and  $A_s$  is the surface area of silica particles ( $\text{m}^2 \text{L}^{-1}$ ).

This kinetic law is derived from Lasaga (1981) work and has been successfully tested on geothermal separated water from Bouillante. We used for these calculations, the geochemical code PHREEQC (Parkhurst and Appelo, 1999) and the associated LLNL (Lawrence Livermore National Laboratory) thermodynamic chemical database, following the method described in details in Dixit et al. (2016).

$C_{eq}$  was calculated at  $T = 80^\circ\text{C}$  using Gunnarsson and Arnórsson relation (2000) given in equation [2].

$$\log C_e = -8.476 - 485.24 \times T^{-1} - 2.268 \times T^2 + 3.068 \times \log T \quad [2]$$

$A_s$  was estimated from the measured specific surface area,  $S_{BET}$  (in  $\text{m}^2 \text{g}^{-1}$ ), using equation [3].

$$A_s = S_{BET} \cdot (C_t - C_{eq})_T \cdot 60.0848 \quad [3]$$

where  $C_i$  and  $C_{eq}$  are respectively the initial concentration of dissolved silica ( $\text{mol L}^{-1}$ ) and the amorphous silica solubility ( $\text{mol L}^{-1}$ ) at a given temperature  $T$ .

The  $k_2$  parameter for each kinetic dataset were adjusted to fit the measured  $\text{SiO}_2$  concentrations as a function of time. An estimation of the error on the model  $\varepsilon$  was computed using equation [4].

$$\varepsilon = \sqrt{\frac{\sum_{i=1}^N (C_{exp} - C_{cal})^2}{\sum_{i=1}^N (C_{exp})^2}} \quad [4]$$

We considered a model to be valid if  $\varepsilon$  is lower than 10%.

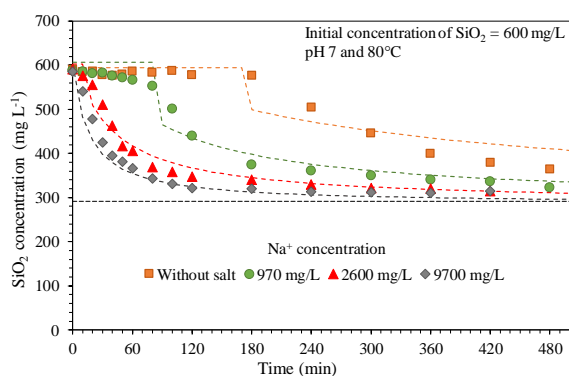
### 3. RESULTS AND DISCUSSION

#### 3.1 Salt effects

Salt effect on the silica precipitation was investigated in presence of sodium, magnesium, iron, aluminium and calcium ions at different concentrations. Experiments were performed from neutral supersaturated silica solution with silica content of  $600 \text{ mg L}^{-1}$  at  $80^\circ\text{C}$ .

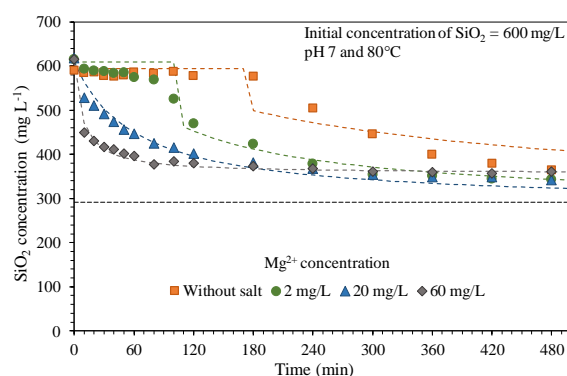
Figure 2 shows the evolution of the measured silica concentration as a function of time for three  $\text{Na}^+$  concentrations (corresponding to 0.42; 0.11 and  $0.042 \text{ mol L}^{-1}$ ).

Monomeric silica concentration decreases with the  $\text{Na}^+$  concentration increase to reach equilibrium between 4 to 6h. In the absence of salt and for the lowest concentration, a transition period for up to 3h, during which the concentration of silica does not significantly vary, is observed.



**Figure 2:** Evolution of the monomeric silica concentration as a function of time for silica solution (pH ~ 7 and  $80^\circ\text{C}$ ) and for three  $\text{Na}^+$  concentrations. Dashed gray line corresponds to the amorphous silica solubility at  $80^\circ\text{C}$  (i.e.  $291 \text{ mg L}^{-1}$ ) Dashed color lines correspond to kinetic modeling of the experimental data represented in the same color.

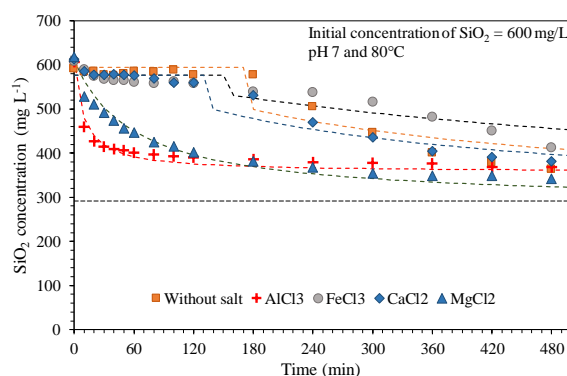
Figure 3 represents experiments at different  $\text{Mg}^{2+}$  concentrations. We can make the same observations as for the sodium ions except that the equilibrium reached is much higher than the calculated solubility.



**Figure 3:** Evolution of the monomeric silica concentration as a function of time for silica solution (pH ~ 7 and  $80^\circ\text{C}$ ) and for three  $\text{Mg}^{2+}$  concentrations. Dashed color lines correspond to kinetic modeling of the experimental data represented in the same color.

The effect of the different salts except  $\text{NaCl}$ , considered separately but at the same concentration, on the precipitation kinetics of silica is shown in Figure 4. Overall, the  $\text{Al}^{3+}$  and  $\text{Mg}^{2+}$  ions accelerate the decrease of the silica concentration while the  $\text{Ca}^{2+}$  and  $\text{Fe}^{3+}$  ions appear to have much less effect. Experiments in presence of  $\text{Fe}^{3+}$  and  $\text{Ca}^{2+}$  exhibit a transition period as in absence of salt. After this period, the decrease of silica concentration is slow and the equilibrium is not reached after 8h.

For  $\text{Al}^{3+}$  ions, the concentration of dissolved silica rapidly decreases without induction period but the equilibrium reached is not corresponding to the silica solubility calculated at  $80^\circ\text{C}$ .



**Figure 4:** Evolution of the monomeric silica concentration as a function of time for silica solution (pH ~ 7 and  $80^\circ\text{C}$ ) and for four cationic species ( $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Al}^{3+}$  and  $\text{Fe}^{3+}$ ) at  $20 \text{ mg L}^{-1}$ . Dashed color lines correspond to kinetic modeling of the experimental data represented in the same color.

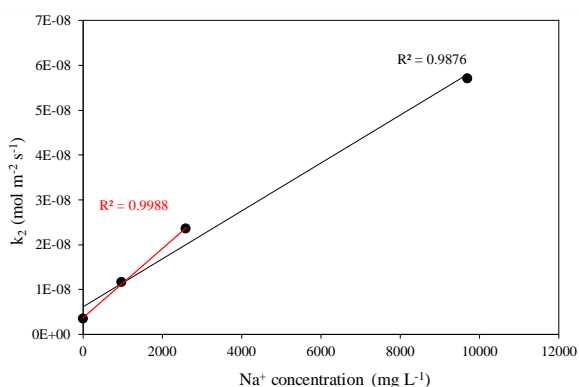
The combined effect of  $\text{Na}^+$  and  $\text{Mg}^{2+}$  is observed with SYNT4 solution and discuss below with result on BOU solution (see Figure 6).

To summarize, all the kinetic experiments show that, in the presence of salt, the concentration of monomeric silica decreases over time even if an induction period is observed and the decrease depends on the type and the concentration of salt.

The rate constants  $k_2$  (in  $\text{mol m}^{-2} \text{s}^{-1}$ ) computed using the second-order reaction given in Equation [1] are presented in Table 1 and the models are represented in the previous figures 2, 3 and 4. Note that in presence of an induction period, the model adjustment begins at the end of it.

We used  $k_2$  kinetic parameter to quantify and discuss the effect of salt on silica precipitation. Over the entire dataset, the rate constant  $k_2$  ranges from 0.17 to 21.7  $10^{-8} \text{ mol m}^{-2} \text{ s}^{-1}$  and model errors  $\varepsilon$  were smaller than 6 %. The smaller  $k_2$  value corresponds to sample SYNT8 (2  $\text{mg L}^{-1}$  of  $\text{Fe}^{3+}$ ) and the higher one to SYNT7 (60  $\text{mg L}^{-1}$  of  $\text{Mg}^{2+}$ ).

Table 1 show that  $k_2$  values vary with salt type and concentration. Concerning NaCl effect, figure 5 shows a linear trend between the  $k_2$  and the concentration of  $\text{Na}^+$  ions for concentrations up to 2600  $\text{mg L}^{-1}$  ( $R^2 = 0.9989$  against 0.9876 for the entire dataset)



**Figure 5: Plot of constant rate  $k_2$  vs.  $\text{Na}^+$  concentration for 3 and 4 concentrations of  $\text{Na}^+$ .**

For  $\text{Mg}^{2+}$ , the concentration range tested is too narrow to conclude on the evolution of  $k_2$  with  $\text{Mg}^{2+}$  concentration. Additional concentrations have to be tested.

By comparing  $k_2$  values for the four other salts tested at a same concentration of 20  $\text{mg L}^{-1}$ , it seems that these salts accelerated the precipitation rate according to the following order:  $\text{AlCl}_3 > \text{MgCl}_2 > \text{CaCl}_2 > \text{no salt}$ , at 80°C and pH 7. With a  $k_2$  value ( $0.17 \cdot 10^{-8} \text{ mol m}^{-2} \text{ s}^{-1}$ ) largely smaller than the one obtained on sample without any salt ( $0.35 \cdot 10^{-8} \text{ mol m}^{-2} \text{ s}^{-1}$ ), we considered that  $\text{FeCl}_3$  has a weak decelerating effect by comparison to the other salts tested. It is difficult to include NaCl to this classification since the concentrations used in this study are largely higher. Additional experiment at the same concentration has to be done.

Previous studies on salt effects on silica precipitation (Crerar et al., 1981; Gorrepati et al., 2010; Brown, 2011) showed that a high ionic strength accelerates the silica precipitation (kinetics and silica nanoparticle formation). This is due to cations adsorption on the negatively charged silica that leads to a reduction of the electrostatic repulsion and the revelation of van der Waals attraction. However, these studies do not agree on the degree of effect for the different kind of salt and

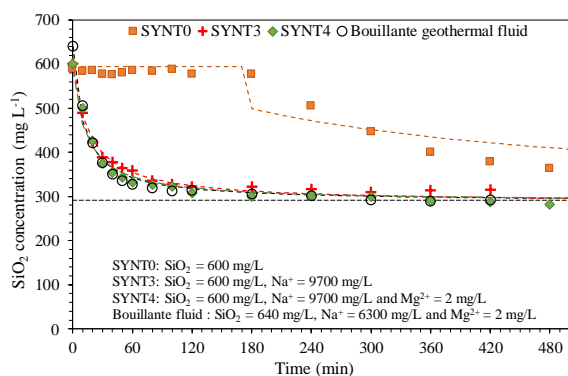
the classification proposed are different. Gorrepati et al. (2010) who worked at low pH conditions found the order:  $\text{AlCl}_3 > \text{CaCl}_2 > \text{MgCl}_2 > \text{NaCl} > \text{no salt}$ , partially in agreement with Crerar et al. (1981) results in neutral solution:  $\text{CaCl}_2 > \text{MgCl}_2 > \text{NaCl}$ . Other authors have found the opposite trend in mildly acidic to basic conditions.

According to Brown (2011), small amounts of highly charged ions such as  $\text{Al}^{3+}$  and  $\text{Fe}^{3+}$ , greatly increase the deposition rate of silica since the negative surface charge of  $\text{SiO}_2$  attracts these cations in solution acting as a bridge between neighboring colloid particles and bonding them together. If our results are in agreement for  $\text{Al}^{3+}$ , it is not the case for  $\text{Fe}^{3+}$ . Additional experiments with higher concentrations must be performed to conclude on  $\text{Fe}^{3+}$  effect.

André et al. (2017) used an integrative approach based on experiments and modeling to study the Mg effect on the silica precipitation rate. They demonstrated that the basic thermodynamic and standard kinetic approaches, what is presented in this study, are not sufficient to comprehensively describe the properties of the solution as pH variations. We will therefore apply their method (*i.e.* take into account the silica solid surface complexation reactions and the protonation reactions of the silanol sites outcropping of silica surface) to our data, for magnesium and other salts, to improve the modeling results and our analysis on the effect of the cations studied on kinetics.

An induction period was also observed at the beginning of some experiments, the longest being in the absence of salt. The decrease in the transition period after small addition of NaCl,  $\text{FeCl}_3$  or  $\text{CaCl}_3$  suggests that salt addition significantly affects the first stage of particle formation. This tendency, noted by other authors (Makrides et al., 1980; Weres et al., 1981; Icopini et al., 2005) could be attributed to a silica solubility reduction by salt addition.

One objective of our study is to generalize the kinetic model established for geothermal water of Bouillante presented in Dixit et al. (2016) to other fluids in volcanic context. Since is not easy to access to others natural geothermal waters to lead our experiments, we proposed to use synthetic solutions to test our model. Figure 6 shows a comparison between the kinetic data obtained from the Bouillante separated water BOU and three synthetic solutions: SYNT0, SYNT3 and SYNT4. SYNT4 is the synthetic solution having the closest composition to BOU solution. We can observe that the models for SYNT4 and BOU are very close which is confirmed by the  $k_2$  values of rate constant:  $7.9 \cdot 10^{-8}$  and  $7.3 \cdot 10^{-8} \text{ mol m}^{-2} \text{ s}^{-1}$  respectively. Figure 6 also demonstrates that the both presence of  $\text{Na}^+$  and  $\text{Mg}^{2+}$  cations in solution has to be taking into account to predict correctly the kinetic of silica precipitation in geothermal water: the  $k_2$  value for SYNT4 (presence of  $\text{Na}^+$  and  $\text{Mg}^{2+}$  cations) is clearly closer to  $k_2$  value for BOU than SYNT3 (only  $\text{Na}^+$  cations) and SYNT0 (no salt). Experiments on the combined effect of salt have to be continued.



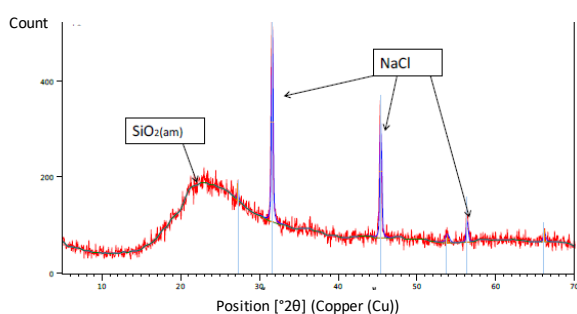
**Figure 6: Evolution of the monomeric silica concentration as a function of time at pH ~ 7 and 80°C for Bouillante geothermal fluid and the synthetic solutions SYNT0, SYNT3 and SYNT4.**

Moreover, the use of synthetic solutions can help to understand and model the kinetic of silica precipitation under various conditions (pH, T, ...), at least for Bouillante geothermal water.

Extended experiments and comparison to others natural geothermal waters have to be lead to conclude on the effectiveness of synthetic solutions to reproduce the precipitation of silica in complex waters such as hot geothermal fluids.

### 3.2 Precipitate analysis

Physical and chemical characterizations of the colloidal suspensions extracted at the end of these experiments, performed by electron microscopy (SEM), X-Ray diffraction (XDR) and BET method, still are ongoing. Preliminary SEM and XDR results show that the precipitates contain mainly amorphous silica (Figure 7). The chemical elemental analysis shows the presence, in small quantities, of sodium, magnesium and calcium in some samples.



**Figure 7: Example of XRD patterns of polymerized silica extracted at the end of kinetic experiment on sample SYNT4.**

To improve knowledge on silica precipitation, these kinetic experiments have been supplemented by a study on the precipitation mechanisms. In Dixit et al. (2016), we showed that the initial stage of precipitation, fast silica precipitation follows a 4th-order reaction law, probably due to the formation of large oligomers (silica tetramers). Thereafter, with a lower silica supersaturation, the monomers react to form smaller oligomers (dimers) in great quantity. To continue these

investigations, dynamic light scattering technique are ongoing in order to observe, in situ, the early stages of silica precipitation from synthetic solutions in the presence and absence of salt. These analyses also concerned Bouillante geothermal water that will allow a comparison to synthetic solutions.

Kley et al. (2017) applied similar approach to investigate the 3-step silica polymerization from supersaturated dilute aqueous solutions. Very interesting results were obtained from their analyses on the impact of alkaline earth cations on the formation process of silica particles. The study reveals that salt addition increase/accelerate formation of nuclei/particles but seems to have no effect on growth kinetics. Moreover, the salt presence allows to shift the silica concentration level for particles agglomeration from ~ 2000 mg L<sup>-1</sup> to a range between 500 and 750 mg L<sup>-1</sup>.

## 4. CONCLUSION

The aim of the study presented in this paper was to investigate the effect of five different salts (NaCl, AlCl<sub>3</sub>, FeCl<sub>3</sub>, MgCl<sub>2</sub> and CaCl<sub>2</sub>) on the silica precipitation from neutral silica solutions with silica content of 600 mg L<sup>-1</sup> at 80°C. Preliminary results show that on the one hand, silica precipitation rates increases with increasing ionic strength. On the other hand, the salts accelerate the decrease of the monomeric silica concentration in the following order: AlCl<sub>3</sub> > MgCl<sub>2</sub> > CaCl<sub>2</sub> > no salt. FeCl<sub>3</sub> seems has no effect or a weak decelerating effect at least.

Kinetic modeling was used to compute rate constant  $k_2$  and to better quantify the salt effect for the different synthetic solutions tested. Like so we show that  $k_2$  linearly increase with Na<sup>+</sup> concentrations under our experimental conditions.

Moreover, a comparison between the kinetic model obtained on the natural geothermal water from Bouillante and on synthetic solution with nearby chemical composition, under similar experimental conditions, shows the possibility to reproduce the complex behavior of silica precipitation from aqueous solutions.

In a wider perspective, we can therefore consider applying the knowledge acquired on the kinetic modeling of silica precipitation in the context of the Bouillante field to other high temperature geothermal fields in volcanic context, thanks to experiments carried out on synthetic fluids in laboratory.

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