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# Silica precipitation kinetics: the role of solid surface complexation mechanism integrating the magnesium effects from 25 to 300°C

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## Abstract

The results presented in this paper allow identifying and integrating the role of magnesium in the kinetic rate of silica precipitation. The basic thermodynamic and kinetic approaches are not sufficient to comprehensively describe the kinetic rate of silica precipitation as well as the simultaneous changes of the solution properties such as pH variations. Trial-error modelling tests reveal that it is necessary to take into account the silica solid surface complexation reactions, in particular the protonation reactions of the silanol sites outcropping of silica surface, in the kinetic law to reproduce measured properties (pH, dissolved silica concentrations, etc.). This newly developed kinetic law is able to correctly describe silica precipitation in presence of magnesium as well as chemical changes in the aqueous phase up to high temperatures (300°C).

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*Keywords:* silica; nanoparticles; modelling; precipitation and aggregation kinetic rates

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## 1. Introduction

Silica deposits are encountered as a problematic of industrial practices dealing with water, oil, and geothermal energy, leading to economical impairing and industrial and technological challenges. Obviously, the vector of silica deposits is always liquid water. The silica concentration in feeding waters including drinking ones is between 1 to 100-1000 ppm depending on the effective water temperature, pH, origin and evolution of the water and the concomitant solid phases (silica rocks, industrial/manufactured materials, etc.).

Understanding the precipitation of silica in complex waters is always a challenge since many parameters can impact simultaneously this process. An integrative approach based on experiments and modelling is developed to determine how Mg is sorbed at the surface of SiO<sub>2</sub> nanoparticles as this mechanism is crucial to explain the silica

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precipitation rate in presence of Mg. First experiments are done to characterize the surface properties of the SiO<sub>2</sub> nanoparticles, mimicking the nucleus of SiO<sub>2</sub> formed during the silica precipitation. As few data are available on Mg sorption onto SiO<sub>2</sub> nanoparticles are available in the literature, new experiments are performed. These results are then used to develop a surface complexation model simulating Mg speciation at the surface of SiO<sub>2</sub> nanoparticles.

In this study, we are going further by integrating the role of Mg in the kinetic rate of silica precipitation. We therefore demonstrate that the basic thermodynamic and “standard” kinetic approaches are not sufficient to comprehensively describe the properties of the solution as pH variations. It is necessary to introduce the silica solid surface complexation reactions, in particular the protonation/deprotonation reactions of the silanol sites outcropping of silica surface. The newly developed kinetic law including surface complexation model is able to describe silica precipitation and the aqueous solution pH.

The extended numerical kinetic approach is tested and validated on solutions containing silica and MgCl<sub>2</sub> for a large temperature interval (25 – 300°C). Experimental results are numerically reproduced thanks to this new model. This comprehensive model is able to establish detailed aqueous and solid surface complexation speciation in solution (including silica and magnesium), the pH and the mass of precipitated minerals.

## 2. Measurements of surface charge density of SiO<sub>2</sub> nanoparticles and Si precipitation kinetic rates

The experiments are done on silica nanoparticles Klebosol K30R12 from Clariant. The granulometry of nanoparticles (size, distribution, minimal concentration observable) is characterized according to solid concentration with Dynamic Light Scattering. The structure of nanoparticles (NPs) is observed with MET PHILIPS-CM20. Porosity and specific surface area of NPs is estimated by N<sub>2</sub> adsorption/desorption. The mean diameter of a single SiO<sub>2</sub> nanoparticle is about 12.4±1.2 nm, with particle diameters ranging between 7 and 30 nm. The highest diameters are too high for single SiO<sub>2</sub> nanoparticles and suggest that the SiO<sub>2</sub> NPs are partially aggregated.

Titration experiments have been done to determine surface charge density ( $\sigma$ ) of SiO<sub>2</sub> NPs at various pH (3.5 < pH < 8.5) and four different MgCl<sub>2</sub> concentrations (from 0.001 to 0.1 M). These experiments are brought to 25°C within the few minutes following the sampling. The pH of the suspension is modified by adding small volumes of NaOH solution. More than 100 adds are performed from pH 3.5 to pH 8.5 for each MgCl<sub>2</sub> concentration (Fig. 1b). At each add, surface charge density is estimated.

As shown in Fig. 1b, the surface charge density of silica ( $\sigma$ ) begins to drastically decrease at pH > 6. This decrease is amplified when salinity increases. Note that the measurements of surface charge were corrected relative to the value measured at pH 3.4. This value has been chosen as it is close to the point of zero charge estimated for silica (about 3.5 according to Sverjensky, 2005).

Precipitation experiments consist initially in a solution containing only dissolved Si at ambient temperature. Then solution is heated up to the temperature of interest. When temperature is stabilized, the MgCl<sub>2</sub> solution is injected into the enriched Si solution and pH, silica and magnesium concentrations are followed according to time.

## 3. Modeling approach of silica precipitation

### 3.1. Surface complexation model

The 1-pK Basic Stern model (BSM) is the most suitable electrostatic surface complexation model to predict the electrochemical properties of the amorphous silica/water interface (Leroy et al., 2013). The 1-pK model provides a sufficiently accurate description of the acid-base titrations of amorphous silica in most chemical conditions. Indeed, the singly Si-coordinated groups outcropping from the mineral surface can be present as negatively-charged or uncharged surface species over a broad pH range.

In order to reproduce correctly titration experiments, we have to account for protonation reactions and Mg surface complexes. Although some surface complexation models have been developed in the literature to simulate protonation reactions at the SiO<sub>2</sub> surface (Hiemstra et al., 1989; Sverjensky, 2005), we do not use the model parameters defined for equilibrium constant of the protonation reaction proposed in these models as they were obtained for macroscopic particles of SiO<sub>2</sub>. In the present study, we therefore determine the values of the equilibrium constants of the protonation reaction:



where the symbol “>” refers to the mineral framework. An equilibrium constant  $K$  (at the standard state) is associated with the surface adsorption of protons.

For this purpose, we fit the titration experiments performed by Dove and Craven (2005), which are done on a suspension of  $\text{SiO}_2$  nanoparticles in a NaCl solution (Fig. 1a). In these simulations, we also take into account Na surface complexes in order to explicitly simulate the effect of salinity (ionic strength) on the protonation reactions. We also use this experiment in order to calibrate the value of the capacitance ( $C_1$ ).

After this first step, we fit our own experiments (Fig. 1b). We describe the sorption of Mg at the surface of  $\text{SiO}_2$  NPs according to the two reactions proposed by Dove and Craven (2005):



$$K_{>\text{SiOMg}^+} \cong \left( \frac{a_{>\text{SiOMg}^+}}{a_{>\text{SiO}^-} a_{\text{Mg}^{2+}}} \right) \cong \left( \frac{\Gamma_{>\text{SiOMg}^+}}{\Gamma_{>\text{SiO}^-} a_{\text{Mg}^{2+}}} \right) = \left( \frac{\Gamma_{>\text{SiOMg}^+}}{\Gamma_{>\text{SiO}^-} a_{\text{Mg}^{2+}}^w} \right) \exp\left(-\frac{ze\phi_\beta}{k_b T}\right) \quad \text{with } \phi_\beta = \phi_d \quad (3)$$



$$K_{>\text{SiOMgOH}} \cong \left( \frac{a_{>\text{SiOMgOH}} a_{\text{H}^+}}{a_{>\text{SiO}^-} a_{\text{Mg}^{2+}} a_{\text{H}_2\text{O}}} \right) \cong \left( \frac{\Gamma_{>\text{SiOMgOH}} a_{\text{H}^+}}{\Gamma_{>\text{SiO}^-} a_{\text{Mg}^{2+}} a_{\text{H}_2\text{O}}} \right) = \left( \frac{\Gamma_{>\text{SiOMgOH}} a_{\text{H}^+}^w}{\Gamma_{>\text{SiO}^-} a_{\text{Mg}^{2+}}^w a_{\text{H}_2\text{O}}} \right) \exp\left(-\frac{e\phi_\beta}{k_b T}\right) \quad (5)$$

Our approach enables us to determine the equilibrium constants of the two Mg surface complexes ( $\text{Log } K_{>\text{SiOMg}^+}$  and  $\text{Log } K_{>\text{SiOMgOH}}$ ). These values are coherent with the values found for Mg adsorption onto macroscopic silica (Sverjensky, 2006).

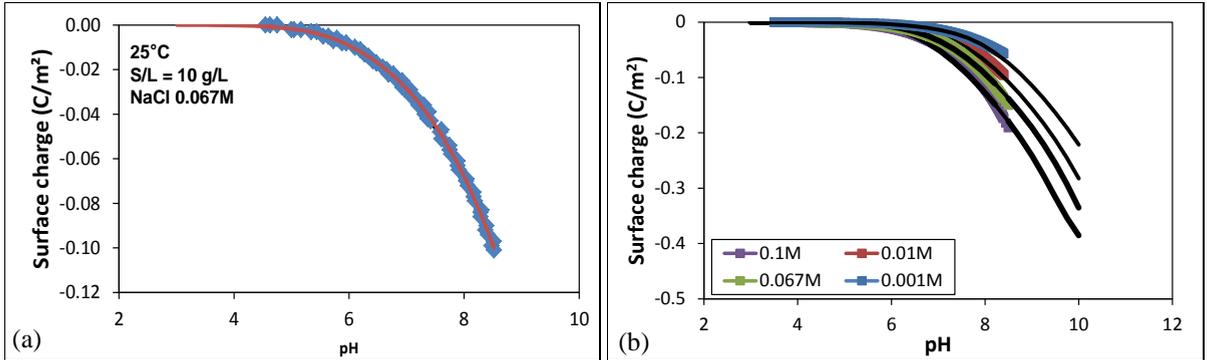


Fig. 1. a) Evolution of surface charge ( $Q_0$ ) of silica nanoparticles according to pH. Red curve corresponds to model results estimated from NaCl solutions (Dove and Craven, 2005); b) Variation of surface charge density of silica NPs (KLEBOSOL K30R12) in four  $\text{MgCl}_2$  solutions (from 0.001 to 0.1 M) according to pH. The four black curves correspond to model results

### 3.2. Kinetic model of silica precipitation in Mg-bearing solutions

The chosen modelling approach for silica precipitation is inspired from existing laws issued from literature (Rimstidt and Barnes, 1980). However, we modify this law to include the protonation reaction and the complexation reactions with Mg.

The calculated kinetic constant used to reproduce our experimental results is  $k_{\text{prec}}(25^\circ\text{C}) = 3.8 \times 10^{-10} \text{ mol m}^{-2}$  at  $25^\circ\text{C}$ . This value is in coherence with the value estimated by Rimstidt and Barnes (1980). For the calculations performed in this paper, this constant is re-calculated according to temperature conditions with the Arrhenius equation and an activation energy of 49800 J/mol (Rimstidt and Barnes, 1980).

In order to be coherent with X-ray and SEM measurements made on solid phases sampled at the end of experiments of Si precipitation, the kinetic rate is calculated according to the  $Q/K$  ratio considering a magnesium silicate mineral. At last, the kinetic law integrates a dependence to surface complexation mechanisms through the concentrations of two Mg surface complexes, which are determined at each time step of the simulation of the precipitation reactions. These concentrations depend on pH and Mg concentration.

Calculations are made with the PHREEQC-v3 code (Parkhurst and Appelo, 2013), a geochemical program widely used by the geoscientist community. The kinetic law is coded in PHREEQC integrating the different equilibrium constant determined in this project, particularly the complexation constants with Mg.

### 3.3. Modelling results

Fig. 2 compares the experimental results with the modelling results. The model is able to reproduce precisely the decrease of dissolved silica and consequently the silica precipitation in presence of  $MgCl_2$  at 120 and 220°C (Fig. 2). The final Si concentration is very close to the measured values. Only the kinetic rate at 220°C is probably too high but we have a limited number of experimental points in the first minutes of the experiment to constrain the model.

The model allows also defining the Mg concentration and is able to deal with the important decrease when additive is added to the solution. This is due to the precipitation of the magnesium silicate mineral.

Concerning the pH of the solution, it is reproduced with accuracy at the end of the experiment (i.e. after 3.5 hours). We can just remark some discrepancies at 120°C with low values of pH not reproduced.

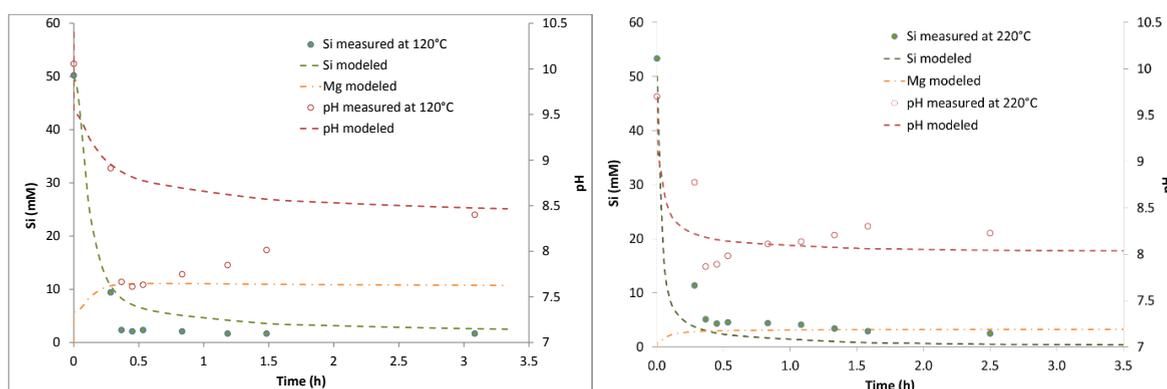


Fig. 2. Modelling results of silica precipitation at 120°C (left) and 220°C (right). Symbols are experimental values measured in this work. Curves are the model results.

## 4. Conclusions

The results presented in this paper allow identifying and integrating the role of magnesium in a new comprehensive kinetic rate of the silica precipitation. We demonstrated that the basic thermodynamic and “standard” kinetic approaches are not sufficient to comprehensively describe the properties of the solution as pH variations. It is necessary to introduce the silica solid surface complexation reactions, in particular the protonation reactions of the silanol sites outcropping of silica surface and the Mg surface complexation reactions.

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