

Investigating Alternative Mechanisms for Metal-Silicate Scale Formation: Do Metal Hydroxides Play a Role?

Michaela Kamaratou

Crystal Engineering, Growth and Design Laboratory, Department of Chemistry, University of Crete
Voutes Campus
Heraklion, Crete, GR-71003
Greece

Konstantinos D. Demadis

Crystal Engineering, Growth and Design Laboratory, Department of Chemistry, University of Crete
Voutes Campus
Heraklion, Crete, GR-71003
Greece

ABSTRACT

Colloidal silica is one of the most undesirable deposits in industrial water treatment. It is rare, compared to other more common mineral scales, such as CaCO_3 , but its formation and deposition onto critical equipment surfaces can be problematic. Control approaches usually include: (a) removal of “soluble” and colloidal silica before entering the water system, and (b) use of chemical scale inhibitors/dispersants. Nevertheless, silica scale inhibition is not easy because of the chemical nature of colloidal silica. Silica is a random, three-dimensional polymer that forms by propagation of Si-O bonds, which form by polycondensation of monosilicic acid. The amorphous nature of silica precludes use of the “traditional” scale inhibition approaches (usually phosphonate additives and polyacrylate-based polymers) that are principally applied for mineral scales. Silica formation is further complicated by the presence of metal hydroxides (commonly iron, aluminum, and magnesium hydroxides). The scope of the present study is to explore the effects of the presence of such hydroxides in a process system on silica formation.

Key words: silicic acid, metal hydroxides, polycondensation, magnesium silicate, aluminum silicate

INTRODUCTION

The polycondensation of silicate to form colloidal silica is a well-known process. Silica formation takes place through an S_N2 -like mechanism that involves an attack of a mono-deprotonated silicic acid molecule on a fully protonated one. Thus, monomeric silicate species produce silicate dimers, and oligomers, and eventually form colloidal silica particles.¹ Nevertheless, this straightforward silica chemistry can be profoundly affected by the presence of certain metal cations, such as calcium,²

magnesium,³ aluminum,⁴ and iron.⁵ When such cations are present in a process water they enhance the rate of polymerization of silicate ions and induce the formation of metal silicate precipitates.

The effects of soluble Mg^{2+} and Al^{3+} species on the autocondensation of silicate have been recently studied by our group.^{6,7} Notably, these effects are strongly pH-dependent, and are maximized at the pH values of ~ 10 (for Mg^{2+}) and ~ 7 (for Al^{3+}). These are the pH regimes that also induce *in situ* formation of $\text{Mg}(\text{OH})_2$ and $\text{Al}(\text{OH})_3$. Hence, the involvement of $\text{Mg}(\text{OH})_2$ or $\text{Al}(\text{OH})_3$ in the polymerization of silicate cannot be ruled out.

In this paper we investigate the role of $\text{Mg}(\text{OH})_2$ and $\text{Al}(\text{OH})_3$ in the polymerization of silicate. Since these hydroxides are insoluble in water, only the effects of surface chemistry can be taken into account.

EXPERIMENTAL PROCEDURE

Instrumentation

ATR-IR spectra were collected on a Thermo-Electron NICOLET 6700FTIR optical spectrometer. Determinations of soluble silicic acid (molybdate-reactive silica) were carried out using a HACH 1900 spectrophotometer from the Hach Co., Loveland, CO, USA. SEM images were collected on a scanning electron microscope LEO VP-35 FEM.

Reagents and materials

Sodium silicate $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$, ammonium molybdate $[(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}]$, sodium hydroxide (NaOH), and oxalic acid dihydrate ($\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$) were from EM Science (Merck). Aluminum chloride hexahydrate ($\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$), magnesium chloride hexahydrate ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) and hydrochloric acid 37 % were from Riedel de Haen. Ethylenediamine tetraacetic acid (EDTA, tetrasodium salt) and Eriochrome Black T were from Alfa Aesar. sulfuric acid (95–97%), ascorbic acid (99%) were from Sigma-Aldrich. Magnesium hydroxide ($\text{Mg}(\text{OH})_2$) and aluminum hydroxide $\text{Al}(\text{OH})_3$ hydrate (particle size < 45 microns) were either from Sigma-Aldrich or laboratory-made. Alumina (Al_2O_3) was from Merck and the blend of amorphous aluminum hydroxide and bohmite ($\gamma\text{-AlO}(\text{OH})$) was laboratory made. Aluminum nitrate $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was from Alfa Aesar and sodium acetate was from Fluka. Acetic acid (glacial) was from Scharlau and Eriochrome cyanine R was from Merck. All reagents were used as received from the suppliers. Acrodisc filters (0.45 μm) were from the Pall-Gelman Corporation. In-house deionized (DI) water with an electrical conductivity 0.05 $\mu\text{S}/\text{cm}$ was used for all experiments. This water was tested for soluble silica, magnesium and aluminum ions and was found to contain negligible amounts.

Stock solution preparation

The sodium silicate stock solution (**solution A**) used in all experiments was prepared by dissolving 4.080 g of $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$ in 2 L DI water. The mixture was stirred for at least 24 h to ensure complete dissolution. This stock solution contains 500 ppm “Si” (8.33 mM), expressed as “ppm SiO_2 ”. A 1 % w/v (10,000 ppm in Al^{3+}) solution (**solution B**) was prepared by dissolving 8.948 g of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ in 100 mL DI water. A 1% w/v (10,000 ppm in Mg^{2+}) solution (**solution C**) was prepared by dissolving 8.360 g of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ in 100 mL DI water. The ammonium molybdate solution (**solution D**, stored in the refrigerator) used in the silicomolybdate test was prepared by dissolving 10 g $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ in 100 mL DI water, to which 24 pellets of solid NaOH were added under vigorous stirring, followed by pH adjustment to 7.7 - 7.8. A 1 + 1 HCl stock solution (**solution E**) was prepared by mixing equal quantities of concentrated HCl (37 % w/v) and DI water. The oxalic acid solution (**solution F**) was prepared by dissolving 8.750 g of solid dihydrated oxalic acid ($\text{C}_2\text{O}_4\text{H}_2 \cdot 2\text{H}_2\text{O}$) in 100 mL DI water. Sulfuric acid (H_2SO_4) 0.02 N (**solution G**) was prepared as follows. 25 mL of pure sulfuric acid were first diluted in 25 mL of DI H_2O , resulting in a 1:1 sulfuric acid solution. From this solution, 0.053 mL were diluted in DI H_2O to a final volume of 50 mL. A buffer solution was prepared by dissolving 68 g sodium acetate trihydrate ($\text{NaOOCCH}_3 \cdot 3\text{H}_2\text{O}$) in 200 mL deionized water, then adding 1.144 mL acetic acid (**solution H**). The solution was then diluted with DI water to a final volume of 500 mL. The ascorbic acid solution (**solution I**) was prepared (daily) by the dissolution of 25 mg of $\text{C}_6\text{H}_8\text{O}_6$ in 25 mL of DI H_2O . Eriochrome cyanine R, ECR, (**solution J**) was prepared by dissolving 0.015 g of ECR in 5 mL of

DI H₂O. The solution pH was adjusted to 2.9 by using acetic acid, 1:1 with water. DI water was then added until a final volume of 100 mL. A 0.01M Na₄EDTA solution (**solution K**) was prepared by dissolving 1.900 g of Na₄EDTA in 500 mL DI H₂O. A 1% w/v Eriochrome Black T solution (**solution L**) was prepared by dissolving 0.30 g of C₂₀H₁₂N₃NaO₇S in 30 mL ethanol.

General precipitation protocols

All experiments were carried out at room temperature. Precipitation reactions were carried out at pH values of 7.0, and 10.0. Polyethylene (PET) containers (200 mL maximum volume) were exclusively used to avoid silicate leaching from the glass. Molybdate-reactive (soluble) silicic acid was determined by using the "yellow" silicomolybdate spectrophotometric method.⁸ Reproducibility was excellent, with all measured values being within a $\pm 5\%$ error margin. The solution pH was checked after every sampling, but no major fluctuations were observed. In general, the pH was adjusted only when it was off by more than 0.2 pH units. Details are described in the protocol below.

Protocol for precipitate formation in the presence of metal ions (Mg²⁺ or Al³⁺) or metal hydroxides and oxides (Mg(OH)₂, Al(OH)₃, Al₂O₃ or a blend of amorphous Al(OH)₃ and γ -AlO(OH)) and silicic acid

The required quantity of **solution B or C** was placed in a PET container, such that the final either Mg²⁺ or Al³⁺ concentration was 200 ppm (expressed as Mg and Al, respectively). In the same way of thinking, the required quantity of **solid metal hydroxides and oxides Mg(OH)₂, Al(OH)₃, Al₂O₃ or blend of amorphous Al(OH)₃ and γ -AlO(OH)** were placed in a PET container, such that the final either metal hydroxide or oxide concentration was 100, 200, 300, 500, 1000, 2000, 3000 and 4000 ppm (expressed as Mg and Al, respectively). The desired volume of **solution A** was placed in the container and the desired pH value was adjusted by the addition of 1 M solutions of HCl and NaOH, as needed. The volume of the combined **solutions A + B, A + C or A + Solid** was made up to 50 mL. The final working solution contained 200 ppm silicic acid (as SiO₂) and the aforementioned variable concentrations of soluble metals (Mg²⁺ or Al³⁺) or metal hydroxides and oxides (Mg(OH)₂, Al(OH)₃, Al₂O₃ or blend of amorphous Al(OH)₃ and γ -AlO(OH)). Finally, the container was covered with a plastic membrane and set aside under quiescent conditions. The solutions were checked for soluble silicic acid by the silicomolybdate yellow method (see below) at the first 30 minutes, 1st, 2nd, 4th, 8th and every 24 hours for the next three days after the final pH adjustment (t = 0). In all results presented below the concentration of molybdate-reactive silica is expressed as "ppm SiO₂" and the concentration of magnesium and aluminum, as "ppm Mg and Al", respectively.

Quantification of "soluble (molybdate-reactive) silica"

"Soluble" or "reactive" silica actually denotes any silicon species that is reactive towards molybdate to form a yellow-colored complex. The majority (~ 90 %) is silicic acid, together with a minor component (~ 10 %) of di-silicic acid. Therefore, the terms "soluble", "reactive", or "molybdate-reactive silica" include both acid forms. According to this methodology, 2 mL of working solution is filtered through a 0.45 μ m syringe filter (to remove any turbidity), and diluted to 25 mL in the cell, with a light path 1 cm. 1 mL of **solution D** and 0.5 mL of **solution E** are added to the sample cell, the solution is mixed well and left undisturbed for 10 min. Then 1 mL of **solution F** is added and mixed again thoroughly. The solution is set aside for 2 min. After the second period the photometer is set to zero absorbance with DI water. Finally, the sample absorbance is measured at 452 nm as "ppm soluble silica". The detectable concentration range is 0–75.0 ppm. In order to calculate the concentration in the original solution a dilution factor is applied. The silicomolybdate method is based on the principle that ammonium molybdate reacts with reactive silica and any phosphate present at low pH (about 1.2) and yields heteropoly acids, yellow in color. Oxalic acid is added to destroy any molybdophosphoric acid presence (due to the possible presence of phosphate in the water), leaving silicomolybdate intact, and thus eliminating any color interference from phosphates. According to the definition of Icopini et al. (2005) "molybdate-reactive silica" includes all three species, namely, monomeric (monosilicic acid, H₄SiO₄), dimeric (disilicic acid, H₆Si₂O₇), and possibly trimeric (H₈Si₃O₁₀) silica. However, since trimeric silica has not been detected in any of present and past experiments, the term "molybdate-reactive" silica refers to a mixture of monosilicic acid (primarily) and disilicic acid, with the first being dominant under our