

Polymeric Silica Scale Inhibitors: Computational Predictions and Experimental Studies on Inhibitor Efficiencies

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ABSTRACT

In the present work we present experimental and computational results on the efficacy of two simple polymers, polyethylene glycol (PEG) and polyvinyl alcohol (PVA) on silica scale inhibition. The aim of this study is to compare the experimental and computational approaches, in order to explain why PEG is an effective silica inhibitor, while PVA is not. Based on the computational studies, PVA prefers to form interactions between the polymeric chains and not between the polymeric chains and the silicic acid molecules. In contrast, PEG does induce stabilizing interactions between the polymeric chains and the silicic acid molecules. These computational predictions are confirmed by experimental scale inhibition studies, which prove indeed that PEG is an efficient silica scale inhibitor, whereas PVA is not.

Key words: silicic acid, inhibition, polyethylene glycol, polyvinyl alcohol, polycondensation

INTRODUCTION

Inorganic scaling and fouling are undesirable processes occurring in process waters that are supersaturated with respect to scaling cations and anions.¹ Mineral scaling is the result of nucleation and crystal growth phenomena that follow predictable pathways. This is because the mineral scales are composed of well-defined crystalline salts, the most common being calcium carbonate, calcium sulfate dehydrate (gypsum), metal sulfides, depending on the particular water chemistry and operational parameters (eg. temperature).² Among inorganic foulants, colloidal (amorphous) silica is a unique case for the following reasons: (a) it is not a crystalline phase because it is not composed of discrete cations and anions, (b) it is essentially an inorganic polymer constructed of Si-O-Si bonds, (c) it has unique surface chemistry due to its surface silanol (-Si-OH) groups, (d) “traditional” scale inhibitors (eg. phosphonates or anionic polymers) are not effective in its control. Although colloidal silica can be a useful material for a plethora of applications,³ it is still an undesirable issue in water treatment.

Silica scale formation is an intricately complex process.⁴ Existing data reveal that silica solubility is essentially independent of pH in the range of 6 to 8. Silica exhibits “normal” solubility characteristics, its solubility increasing proportionally to temperature. Silica formation is actually a polymerization event,

not a cation-anion association based on electrostatic attraction. When silicic acid polymerizes, a plethora of structural motifs are created, including rings of various sizes, cross-linked polymeric chains of different molecular weights, oligomeric structures, etc. The resulting “silica scale” is a complex and amorphous solid (colloidal silica).

Prevention of silica-silicate fouling in industrial water systems is based on the following approaches:⁵

- Inhibition of silica formation with chemical additives.
- System operation at low silica-silicate levels (< 200 ppm).
- Silica removal before it enters the system.
- Silica dispersion.
- Control of other scales in order to avoid co-precipitation or composite fouling.
- Maintain effective corrosion control to avoid silica deposition on corroded surfaces.
- Maintain system pH below ~ 8.5 to avoid metal-silicate precipitation.

The silicate polymerization process, from monomeric silicic acid to silica particles, involves several, ill-defined steps (Figure 1). Previously, we reported that certain water-soluble polymers, with neutral chemical functional groups can be effective silica scale inhibitors. Among these, the polyethylene glycols (PEGs) are notable (Figure 2).⁶ PEGs can stabilize silicic acid, and delay its polymerization through hydrogen bonding interactions between the silanol groups (-Si-OH) and the ether oxygens on the polymeric PEG backbone. Inspired by the efficiency of PEGs as silica inhibitors, we put forth the hypothesis whether other neutral polymers, capable of forming hydrogen bonding interactions with silicic acid, could act as silica inhibitors. One such polymer is polyvinyl alcohol (PVA, Figure 2), having hydroxyl (-OH) groups on the polymer backbone (instead of ether Os, in the case of PEGs).

In this paper, we investigate the inhibitor efficacy of PEG and PVA in silica formation, and attempt a viable explanation of why PEG is an efficient silica inhibitor, whereas PVA shows no inhibitory activity at all. We present experimental results for both inhibitors, as well as computational results on the hydrogen bonding interactions between the polymer oxygen atoms and silicic acid.

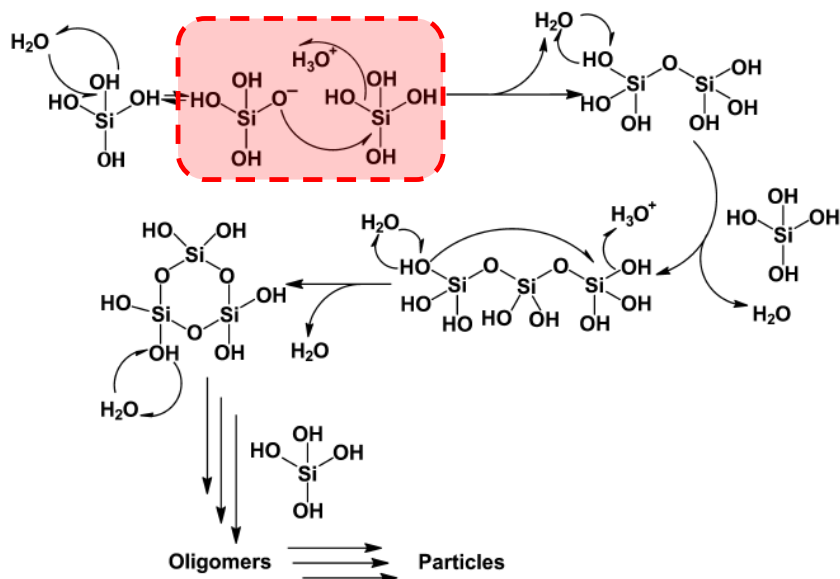


Figure 1: Polycondensation of monosilicic acid to form colloidal silica particles.

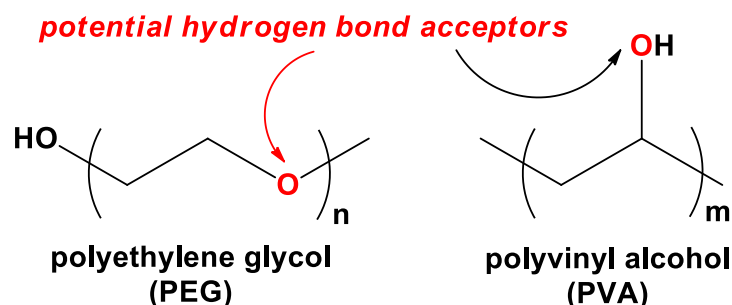


Figure 2: Schematic structures of polyethylene glycol (PEG) and polyvinyl alcohol (PVA).

EXPERIMENTAL PROCEDURE

Instruments

The measurements of soluble (reactive) silica were performed either on a HACH 890 spectrophotometer or on a HACH 1900 spectrophotometer from the Hach Co., Loveland, CO, USA.

Reagents

Sodium silicate $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$ was from EM Science (Merck). Ammonium molybdate $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$, oxalic acid $(\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O})$ were from EM Science (Merck). Sodium hydroxide (NaOH) was from Merck, hydrochloric acid 37% was from Riedel de Haen. Acrodisc filters (0.45 μm) were from Pall-Gelman Corporation. In-house, nanopure water was used for all experiments. This water was tested for soluble silica and was found to contain negligible amounts.

Additives

PEG and PVA were from Alfa Aesar. The molecular weights of the PEG additives ranged from 1,550 to 20,000. The molecular weights of the PVA additives were in three ranges: low (average MW 11,000-31,000) medium (average MW 57,000-66,000) and high (average MW 88,000-97,000).

Solution Preparation

A solution containing 500 ppm silicate (as SiO_2) was prepared by dissolving 4.4 g of $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$ in 2.5 L nanopure water. Similarly, stock solutions of 400, 300, and 200 ppm silicate (as SiO_2) was prepared. 1 % (10,000 ppm) stock solutions of the inhibitors in water were also prepared by making the appropriate dilution with nanopure water in case the inhibitor was in solution, or by dissolving 0.1 g of the solid inhibitors in 10 mL nanopure water. The following solutions were prepared for the silica analytical test: (a) 10 g of ammonium molybdate were dissolved in 100 mL water and its pH was adjusted between 7 – 8 with NaOH to avoid precipitation of ammonium molybdate, (b) HCl 1+1 is prepared by mixing one volume 37% HCl with equal volume water, (c) 8.75 g of oxalic acid was dissolved in 100 mL water. All solutions were kept in plastic containers (glass containers must be avoided in order to minimize silicate leaching).

“Control” and inhibitor screening tests

All screening tests were performed at room temperature. 100 mL from the 500 ppm SiO_2 stock solution was placed in a plastic beaker which contained a teflon – covered magnetic stir bar. The pH of this solution was initially ~ 11.8 and adjusted to 7.00 ± 0.1 by addition of HCl and NaOH (the change in the resulting volume was about 3 %). Then the beaker was covered with plastic membrane and set aside without stirring. The solution were checked for soluble silicate by the silicomolybdate method. For inhibitor screening, 100 mL portions of the 500 ppm SiO_2 stock solution were placed in plastic containers charged with teflon[®] – covered magnetic stir bars. In each container different volumes of inhibitor (10,000 ppm stock solution) were added to achieve desirable inhibitor concentration. After that the same procedure for the control test was followed.

Determination of soluble (reactive) silica

Soluble silica was measured using the silicomolybdate spectrophotometric method.⁷ Silica measurements were performed immediately after sampling. According to this method 2 mL filtered

sample, with 0.45 μm syringe filter, from the test solution is diluted to 25 mL in the cell, with light path 1 cm. 1 mL ammonium molybdate stock solution and 0.5 mL 1 + 1 HCl are added to the sample cell, the solution is mixed well and left undisturbed for 10 min. Then 1 mL oxalic acid solution is added and mixed again. The solution is set aside for 2 min. After the second time period the photometer is set at zero absorbance with water. Finally the sample absorbance is measured at 452 nm as “ppm soluble silica”. The detectable concentrations 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 the molybdophosphoric acid leaving silicomolybdate intact, and thus eliminating any color interference from phosphates. It must be mentioned that this method measures “soluble” silica species, mainly the monomer and the dimer.

Computational details

All calculations were performed using the GAMESS (General Atomic and Molecular Electronic Structure System) electronic structure package. The geometries were fully optimized with the 6-31G Basis Set. Then a reaction cell containing 8 $\text{Si}(\text{OH})_4$ molecules, 8 polymer molecules and 200 water molecules, was created by using Packmol. The simulation environment was fixed via ASE (Atomic Simulation Environment). Afterwards, a data and an input files were created. Some parameters, like bond- and angle-related force field parameters and charges, in the data file were edited to achieve more accurate results. The input file was used in order to set some parameters related to the simulation, like temperature, pressure, time step and total simulation time. After an initial mixing of 0.5ns the normal run of the simulation lasted 5ns, resulting in a total 5.5ns of simulation. The time step was set at 1fs so a tape of 5500000 snapshots was created in an output file. This output file was inserted in OVITO, which is a visualization and analysis software for output data generated in molecular dynamics, and the results were visualized.

Another tool that was utilized was the VMD (Visual Molecular Dynamics) program. It provided the ability to calculate and record diagrams of radial pair distribution between two types of atoms. This function was used to create diagrams of the average distances between monosilicic acid molecules through each simulation.

RESULTS

Silica inhibition chemistry

PVA as silica inhibitor

PVA was tested as a potential silica inhibitor at pH 7.0. The results for a range of inhibitor dosages (460 ppm to 1260 ppm) are shown in Figures 3 and 4. The dashed line in the graphs has been added to aid the reader and corresponds to molybdate-reactive silica left in solution after 24 hours, in the absence of inhibitor (control). Based on these results it becomes apparent that PVA is an ineffective silica inhibitor, even at extremely high dosages. No differentiation from the “control” was observed within the experimental error of the measurement method. No molecular weight effects were noted. Lower dosages of PVA were not evaluated and it was assumed that PVA is still an inactive inhibitor at dosages < 400 ppm.