

## **Review of the State of the Art of Siliceous Scale Management in Industrial Systems**

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### **ABSTRACT**

Fouling of equipment surfaces by siliceous materials in industrial water systems is a problem associated with high silica laden waters. The complexity of siliceous deposits formation stems from the limited solubility of amorphous silica and metal silicates. Once formed, these deposits are difficult to remove and often requires the use of chemical and/or mechanical approaches. This paper presents mechanisms of siliceous deposits formation and reviews various approaches attempted to control these deposits in industrial systems. Comparative performance data on a variety of polymeric, non-polymeric, and formulated products as siliceous deposit control agents are presented. Additionally, information on morphology of various siliceous deposits formed is discussed.

**Key words:** siliceous, scale, mitigation, antiscalant type, efficacy, precipitate characterization

### **INTRODUCTION**

Fouling of equipment surfaces by siliceous salts such as silica, metal silicates, coprecipitated silica with mineral salts such as calcium carbonate, calcium sulfate, etc., is a serious challenge facing the technologists in the efficient operation of industrial systems. Severe fouling at times results in premature expensive equipment replacement, early shutdown, increase in operating pressure of pumps, and enhance the probability of corrosion damage. In many cases, the removal of foulants leads to discontinuous operation of the system, resulting in higher operating costs. In geothermal applications, siliceous scale typically occurs when brine is cooled in the course of brine handling and energy extraction. Factors contributing to siliceous scale formation include variable fluid

composition, fluctuating plant operating conditions, and the complex nature of silica formation.<sup>1</sup> Siliceous scale is tenuous and once formed it is particularly difficult to remove, and in some cases fouled equipment must be removed.<sup>1</sup> Both chemical and mechanical methods are used to remove siliceous scale. However, strong chemical cleaners (e.g., ammonium bifluoride, hydrofluoric acid) pose serious environmental challenges and require care to avoid damaging equipment whereas mechanical cleaning is labor intensive.<sup>1</sup> In brackish water reverse osmosis systems (RO) membrane surfaces and spacers are particularly susceptible to fouling by siliceous deposits, easily coagulated by small amounts of cations such as Ca, Mg, Fe, and Al.<sup>2</sup> The deposition of siliceous materials in RO systems cause reduced permeate production rates resulting in pressure increase, poor permeate quality, and more frequent membrane cleaning. In evaporative cooling water systems, water technologists must maintain silica at acceptable level (usually <180 mg/L in the absence of antiscalant) to avoid the formation of siliceous scale. The difficulties in using high silica water in cooling systems or in geothermal applications are further aggravated by the presence of iron and phosphate.<sup>3</sup>

### Silica Species

Orthosilicic acid,  $\text{H}_4\text{SiO}_4$ , the simplest soluble form of silica is a weak acid. Silicon atom is tetrahedrally coordinated to four hydroxyl groups,<sup>4</sup> and is found in almost all types of natural waters at concentration levels of a few ppm. The main equilibria in aqueous media are described by the equations:



Apparently, the equilibrium described by Equation (1) is the most significant. The speciation over the pH range between 2.5-9.5 is shown in Figure 1.

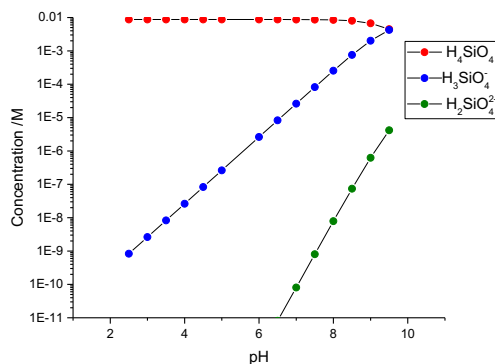


**Figure 1: Equilibrium speciation in a solution containing 525 mg/L sodium silicate and 0.15M NaCl; 40°C**

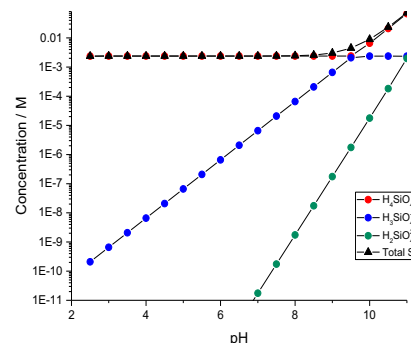


**Figure 2: Solubility of amorphous silica in a solution containing 525 mg/L of sodium silicate and 0.15M NaCl; 40°C.**

In aqueous solutions the presence of silica concentrations, at levels exceeding solubility of several possible solids may result to precipitate formation and deposition on surfaces of critical importance (pipes, membranes, heat exchangers etc.). In a typical silicate solution as the one shown in Figure 1 the silica solids likely to precipitate are amorphous silica, and the crystalline forms of  $\text{SiO}_2$  chalcedony and cristobalite. During precipitation

from aqueous media, as a rule amorphous SiO<sub>2</sub> is formed. The dependence of the solubility of amorphous silica as a function of pH is shown in Figure 2. Figure 3 shows the speciation of silica solutions at equilibrium with amorphous silica as a function of pH.

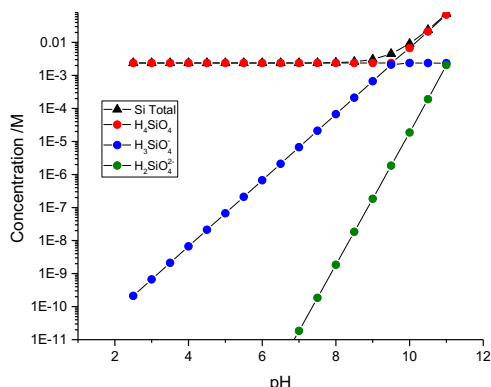


**Figure 3: Solubility of amorphous silica in a solution containing 525 mg/L of sodium silicate, 0.15M NaCl, 200 mg/L Ca<sup>2+</sup>, 57.5 mg/L Mg<sup>2+</sup>, 40°C.**

Because of the lack of complexes between calcium, magnesium and silicate species, the concentration, of which is very low, except for pH values exceeding 7.0, it seems that the solubility of amorphous silica is not affected significantly.

### Mechanisms of Siliceous Scale Formation and Inhibition

It has been proposed that the precipitation of silica from supersaturated solutions proceeds through condensation of silica species with silicic acid, which as already shown is the predominant species in solution.<sup>6</sup> The precipitation of silica from aqueous supersaturated solutions is described by Equation (3):



The thermodynamic driving force for the precipitation of silica is the saturation ratio,  $\Omega$ , defined as:

$$\Omega = \frac{\alpha_{\text{SiO}_2(\text{s})} \alpha_{\text{H}_2\text{O}}^2}{\alpha_{\text{H}_4\text{SiO}_4}} \quad (4)$$

A fourth order dependence of the rate of precipitation of silica on  $\Omega$  has been suggested.<sup>7</sup> The rate constant was found to depend both on the ionic strength and on the solution pH. It is believed that silica formation in the supersaturated aqueous media, proceeds through the formation of a critical size nucleus, according to the classical nucleation theory, with four silica groups participating in the critical nucleus formation<sup>7</sup>. Protons in solution, are suggested that they interact with the silica particles forming up to pH 7, past which the formation rate is reduced, due possibly to silica polymerization. The presence of other ions like Mg<sup>2+</sup>, Ca<sup>2+</sup>, Fe<sup>3+</sup>/Fe<sup>2+</sup>, depending on their concentrations favor metal silicates scale formation at alkaline pH values (exceeding 8.5) while at neutral or acid pH values the formation of amorphous silica is favored. The presence of cations has a decreasing effect on amorphous silica solubility according to the order: Mg<sup>2+</sup> > Ca<sup>2+</sup> > Sr<sup>2+</sup> > Li<sup>+</sup> > Na<sup>+</sup> > K<sup>+</sup>.<sup>8</sup> This order would imply higher relative supersaturation and enhancement of the

rate of precipitation. Similar effect has been shown for anions (bound with sodium) in the order  $I^- > Br^- > Cl^-$ .<sup>8</sup>

### **Siliceous Scale Control Strategies**

Siliceous fouling in industrial water systems fall into two categories: a) precipitation fouling and b) particulate fouling.<sup>9</sup> Precipitation fouling occurs when monomeric silica (or silicic acid) polymerizes and/or magnesium silicate precipitates on the heat exchanger or RO membrane surfaces. Particulate fouling is the accumulation of the colloids, formed during silica polymerization and/or suspended matter. During the past three decades the precipitation and control of silica and metal silicates in industrial systems such as cooling waters, geothermal, desalination, etc., has been the subject of numerous investigations. It is generally understood that the siliceous scale formation is a very complex phenomenon and to combat this problem a number of approaches have been proposed including:<sup>10</sup>

- Reducing feed water silica concentration e.g., by precipitation processes using Al, Fe, Mg salts. This approach involves extra steps to remove soluble silica.
- Operating system at low silica-silicate concentration. This option is not attractive as it consumes large amounts of water.
- Inhibiting siliceous scales with additives.
- Effective inhibition on carbon steel corrosion (<3MPY).
- Dispersing precipitated siliceous scales. This strategy strongly depends on the selection of effective dispersant(s) for siliceous particles, silt, clay, and precipitated mineral scales.
- Maintaining system <pH 8.3 to avoid metal-silicate precipitation.
- Effective control of other scales e.g., calcium phosphate, calcium carbonate. If other mineral scales are not controlled, silica may co-precipitate with crystalline mineral scales.

### **Factors Affecting Silica Inhibitor/Dispersant Performance**

The performance of silica scale inhibitor/dispersant is dependent on several factors including: characteristics of the additive, water chemistry, pH, temperature, hardness level, supersaturation of scale forming salts including silica, type and ionic charge of functional group of the inhibitor molecules, molecular weight, thermal stability, interactions with components of water treatment formulations, biocides, etc. High temperature as well as elevated pressure can cause degradation of inhibitor. In high ionic strength waters, the anionic charge density is reduced and inhibitor performance tends to diminish.<sup>9</sup> The low levels of coagulating/flocculation agents may reduce the inhibitory performance of the additive. In summary, the above mentioned, factors must be considered to develop a strategy to meet water treatment program objectives.

### **Inhibitor Evaluation Process**

During the last three decades a large variety of new polymeric and non-polymeric additives have been developed for use in developing new and improved formulations for handling complexed scaling issues in industrial water systems. Water technologists use different tests to evaluate the efficacy of new additives for their ability to control corrosion, scale, and to disperse suspended matter. These tests include: simple static jar test, fast controlled precipitation method, critical pH method, turbidity test, conductivity, dynamic test using heat exchanger and/or reverse osmosis membrane, and dynamic tube blocking test.

The progress of precipitation inhibition is calculated as follows:

$$\text{Percent Inhibition (\%I)} = \frac{[\{A\}_a - \{A\}_f]}{[\{A\}_i - \{A\}_f]} \times 100 \quad (5)$$

Where  $\{A\}_i$  and  $\{A\}_f$  indicate initial and final concentrations of scaling species ion in the absence of inhibitor at 0 hr and 20 hr, respectively and  $\{A\}_a$  refers to scaling species ion concentration in the presence of inhibitor at known time. Higher %I value denotes better inhibitor performance. It is worth mentioning that static tests, although produce fast results and are good for initial inhibitor screening, often exhibit poor correlation with field data due to several factors including variation in pH, temperature, pressure, fluid dynamics, suspended matter, and equipment metallurgy.

The next step after selecting the best inhibitor (s) on cost performance basis, involves pilot testing of formulated product(s). The pilot testing enables water technologists to evaluate the performance of formulated product under small-scale simulated field conditions. Following pilot testing water technologist select suitable customer site for final evaluation and confirmation of water treatment program.<sup>9,10</sup>

## PERFORMANCE OF ANTISCALANTS

Industrial water technologists use a variety of additives to control scaling, corrosion, microbiological growth, and deposition of unwanted materials on equipment surfaces. The additives selection largely depends upon several factors including water chemistry, system metallurgy, system operating conditions, and additive compatibility with other formulation components as well as metal ions (i.e., Ca, Mg, Fe, Al) present in recirculating water or in brine. In addition, oxidizing and nonoxidizing biocides used. The following sections present discussion on the evaluation of a variety of additives e.g., non-polymeric, phosphonates, natural, bio- and hybrid polymers, and synthetic polymers with different molecular structure, as silica inhibitors for cooling, geothermal, and RO applications.

### Phosphonates and Boric Acid Performance

Organophosphorous compounds form a family of compounds which find application in a variety of industrial processes including crude oil production, pigment dispersion, electroplating, pulp and paper slurries, industrial water treatment and scale removal. Although there are many phosphonates available, six of the most commonly used phosphonates in water treatment formulations are: hydroxyphosphono acetic acid, HPA; aminotris(methylenephosphonic acid), AMP, 1-hydroxyethylidene 1,1-diphosphonic acid, HEDP, 2-phosphonobutane 1,2,4-tricarboxylic acid, PBTC; and polyamino polyetherphosphonic acid, PAPEMP. Figure 4 presents silica inhibition data collected in the presence 25 and 100 mg/L of phosphonates. It can be seen that none of the phosphonates tested show any efficacy for silica inhibition. It is worth noting that whereas these phosphonates show good to excellent inhibitory activity for  $\text{CaCO}_3$ ,<sup>11</sup>  $\text{BaSO}_4$ ,<sup>12</sup>  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ,<sup>13</sup> etc., exhibit poor inhibitory activity for silica precipitation. Data presented in Figure 4 suggest that phosphonate groups do not influence silica polymerization reaction. Figure 4 also shows inhibition data for 25 and 100 mg/L of boric acid (BA). It is evident under the conditions employed BA is an ineffective silica inhibitor. The application of BA and /or its water-soluble salts to prevent silica scaling in cooling water systems operating at 250-300 mg/L silica has been reported. It has been suggested that silica inhibition presumably originates from the ability of borate to condense with silicate to form