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**A New Antifoulant
for Controlling Silica Fouling
in Reverse Osmosis Systems***

**Zahid Amjad, John F. Zibrida, and Robert W. Zuhl
*Lubrizol Advanced Materials, Inc.***
9911 Brecksville Road, Cleveland, OH 44141**

Lubrizol



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** Formerly BFGoodrich Performance Materials.

ABSTRACT

In many parts of the world including the western United States, Hawaii, Puerto Rico, Mexico, the Middle East, and Southeast Asia, the use of water in reverse osmosis (RO) applications is limited by the solubility of silica. Where silica is present, the recovery rates of RO systems are typically limited because the solubility of silica in water is exceeded at about 150 mg/L. This can result in the precipitation and deposition of amorphous silica and silicates with consequential RO membrane fouling and loss of efficiency. Once formed, silica scale is very difficult and costly to remove.

Several water short areas of the world have poor quality ground or surface waters where RO technology would be ideally suited if it were not for high silica content that limits RO system recovery to well below 75%. From a practical viewpoint, the challenge is how do we exceed the range of silica solubility to facilitate the use of RO systems in areas where the available feedwaters have high silica concentrations.

Silica solubility is well known to be both pH and temperature dependent. We have studied the polymerization and precipitation of amorphous silica at various supersaturation conditions. Prevention of silica polymerization and dispersion of precipitated silica species were both found to play a role in effective control of silica fouling. We also investigated the chemical structure and activity relationships of both existing and experimental products as silica control agents. This led to the development of a new chemical technology for the control of silica in aqueous systems and RO systems in particular.

This paper presents the results of laboratory evaluations of the silica fouling problem and the use of various products for extending silica solubility. A new product was found to provide excellent properties for preventing silica polymerization and dispersing particulate matter. Field evaluations of the new silica control technology for RO systems are currently underway. The observations from a pilot RO test study are discussed.

INTRODUCTION

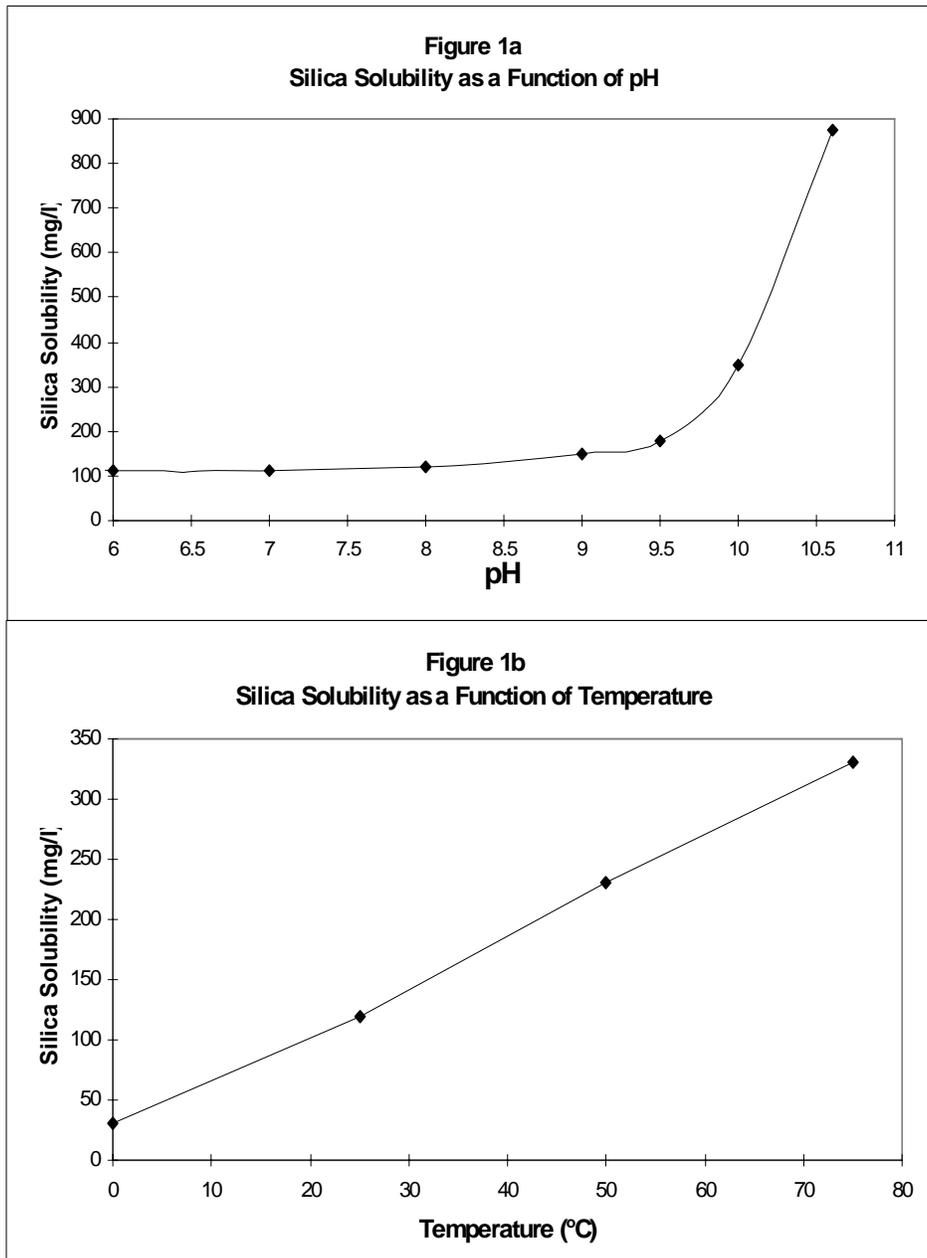
In many parts of the world including the western United States, Hawaii, Puerto Rico, Mexico, and Southeast Asia, the efficient use of water in cooling, boiler, and reverse osmosis (RO), and geothermal applications is limited by the solubility of silica. Water supplies in these geographic areas have silica levels from 30 to 120 mg/l. For example, 80 mg/L silica is typical of Mexico City water. Conventional operation of water treatment systems limits the concentration of silica to 150 mg/L due to the limited solubility of amorphous silica and silicates. Exceeding silica solubility can cause silica precipitation and deposition thereby leading to loss of equipment efficiency, premature shut down, and in some cases irreversible damage. Cleaning of silica fouled RO membranes is costly and time consuming. Repeated cleaning of RO membranes causes performance to decline and eventually replacement.

Accordingly, in order to prevent silica deposition and avoid downtime, cleaning, etc., the RO industry is forced to operate water treatment systems less efficiently and is reluctant to exceed 150 mg/L silica in water systems. For example, RO systems must limit system recovery thereby causing excessive RO feedwater requirements and large wastewater discharge volumes. The absence of proven silica control technology limits the growth rate and opportunities for RO technology and limits water conservation. The rapid growth of RO technology, particularly in water short areas of the world, is increasingly challenged by high silica water sources thereby creating a growing need for effective silica/silicate control technology.

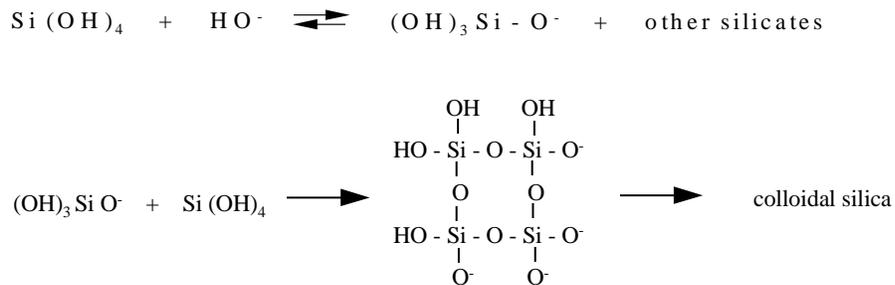
Silica solution chemistry is very complex and difficult to predict. In RO feedwaters, silica can exist in three different forms as follows:

- Monomer silica or silicic acid, Si(OH)_4 , is commonly referred to as ‘soluble’ (a.k.a., dissolved) or ‘reactive’ silica.
- Polymeric silica commonly referred as ‘colloidal’ or ‘unreactive’ silica that results from polymerization of silicic acid.
- Granular silica or ‘particulate’ silica.

The solubility of silica as a function of solution pH and temperature is shown in Figure 1a and Figure 1b (Iler, R.K., *The Chemistry of Silica*, John Wiley and Sons, New York, NY, 1979), respectively.



The potential of silica scaling occurs when the dissolved silica level in an RO system concentrate (i.e., reject stream) exceeds the solubility limit (≈ 120 to 150 mg/L at ambient temperature) for amorphous silica. Exceeding this saturation level in cold water ($< 10^\circ\text{C}$) is not as serious a problem as silica polymerization is a very slow process at lower temperatures. However, silica in excess of 180 mg/L presents a potential problem at any temperature.[1] Colloidal silica formed during the silica polymerization can foul the membrane surface and plug the membrane feed channel spacer. Additionally, polyvalent metal ions (i.e., iron, aluminum, calcium, magnesium, etc.) present in the feedwater stream can absorb or complex silica and catalyze the precipitation (ASTM Standard D-4993-89). The mechanism of polymerization of amorphous silica follows a pattern of the breakdown of the soluble silica unit and the growth of the silicate anion into a larger macromolecule via anionic polymerization as shown in the reactions below.



The development and application of silica control technology in aqueous systems has been the subject of many research efforts and numerous technical papers.[2-6] The literature and current technical approaches have been directed at several approaches including:

- Inhibiting silica polymerization [2]
- Increasing the silica solubility as it forms [7,8]
- Dispersion of precipitated silica and silicate compound using polymeric dispersants [5,9]

Another type of silica deposit commonly encountered in RO systems is magnesium silicate. The precipitation of magnesium silicate strongly depends on solution pH and temperature. In RO systems operating above pH 9, magnesium silicate is very likely to form due to the presence of magnesium hydroxide and silicate ions. Although other hydroxide salts such as calcium, strontium, and sodium, can react with silicate ion, but the resulting products are much more soluble and hence less likely to foul the membrane. [10]

In the past two decades, the precipitation of silica and magnesium silicate in industrial water systems has attracted the attention of several investigators. Amjad and Yorke in their evaluation of polymers reported that cationic-based copolymers are effective silica polymerization inhibitors.[2] Similar conclusions were also reported by Harrar et al. in their investigation on the use of cationic polymers and surfactants in inhibiting silica polymerization under geothermal conditions.[11] Although these cationic-based homo- and copolymers showed excellent performance in terms of inhibiting silica polymerization, they offered poor silica/silicate dispersancy activity.

Another approach that has been attempted with limited success to control silica/silicate scaling in cooling water systems involves the use of dispersants. Momozaki et al. reported the use of a polyacrylamide-based treatment program to control silica problem in recirculating cooling water systems.[12] Gill et al., in another study conducted using high silica water at $\text{pH} > 9$, documented that a blend of phosphonate and

a copolymer of acrylic acid and 2-acrylamido-2-methylpropane sulfonic acid can effectively extend the operating limits for SiO_2 from 150 to 300 mg/L.[4] The performance of a formulated product containing hydroxyphosphonoacetic acid and a copolymer of acrylic acid and allyl hydroxy propyl sulfonate ether as a silica dispersant has been reported.[9] The inspection of heat exchangers using water containing high hardness, high alkalinity (pH 8.2), and 250 mg/L SiO_2 showed essentially no deposit in the presence of a formulated product compared to heavy silica and silicate deposits in the control (no treatment).[9]

The use of boric acid and/or its water soluble salts to control silica based deposits in cooling water systems operating at 250 to 300 mg/L silica has been reported. Silica inhibition presumably originates from the ability of borate to condense with silicate to form borate-silicate complexes that are more soluble than silica.[3]

The use of a polymeric dispersant to control silica/silicate in RO systems has recently been investigated.[13] The results of a pilot RO study showed that deposition of silica and magnesium silicate on membrane surface can be prevented by the use of a polymeric dispersant. The following guidelines were proposed for using a polymeric dispersant for silica control based on three pilot plant studies: [13]

1. Maintain silica below 240 mg/L as SiO_2
2. For pH < 7.5: Maintain Mg x Si < 220,000
For pH > 7.5: Maintain Mg x Si < 110,000
(where Mg is expressed as CaCO_3 , Si is expressed as SiO_2)
3. Iron and aluminum levels must not exceed 0.05 mg/L in the feedwater.

Another investigator recently discovered that, if all multivalent cations are removed from the feedwater stream and the RO system is operated at high pH (pH 10 to 11), silica concentrations of up to 450 mg/L can be tolerated without the use of dispersants or inhibitors.[14] However, this technique is limited to those systems that can be successfully operated at > pH 10.

The use of borate-based inhibitors to increase silica solubility is limited because of the high use levels for boron-based compounds as well as the associated costs and environmental impacts (effluent discharge limitations on boron). Polymeric additives have been shown to be effective in certain operating windows for controlling the deposition of precipitated silica and silicate compounds. However, there is no established chemical treatment program currently commercially available that is designed to inhibit the polymerization of silica by controlling the formation of amorphous silica on membrane and heat exchanger surfaces.

Certain polymers have been shown to be capable of dispersing fine particles of amorphous silica once they have formed.[4,5,6] These polymeric dispersants are often used when the potential for particulate silica fouling exists. Although these dispersants may minimize the impact of the fouling, they do not address the root problem of controlling silica polymerization. With this goal in mind, the current investigation was initiated to find a polymeric additive that minimizes or controls the effect of silica polymerization. It should be noted that in all the treatment approaches discussed above there is no treatment commercially available which can effectively control silica polymerization at high supersaturation (> 550 mg/L SiO_2) as well as disperse colloidal matter.

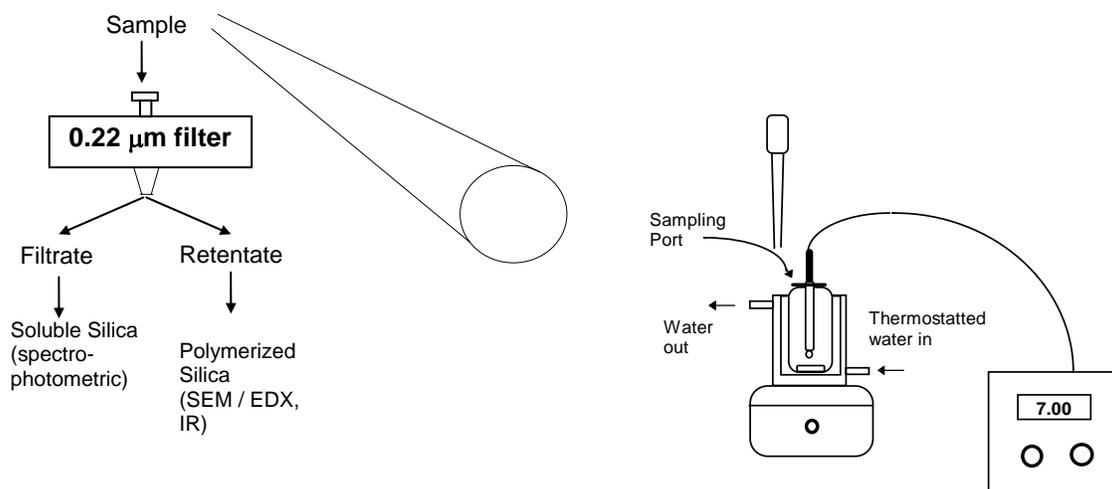
EXPERIMENTAL

Reagent grade chemicals and distilled water were used throughout this study. Silica stock solutions were prepared from sodium metasilicate, standardized spectrophotometrically, and were stored in polyethylene bottles. Calcium and magnesium chloride solutions were prepared from calcium chloride dihydrate and magnesium chloride hexahydrate, and were standardized by EDTA titration. The inhibitors, polymeric and non-polymeric, used in this study were selected from the range of experimental and commercial materials. All experimental results are reported on a 100% active inhibitor basis for comparative purposes.

Silica polymerization experiments were performed in a polyethylene container placed in a double-walled Pyrex cell maintained at 40°C. The supersaturated solutions were prepared by adding a known volume of sodium silicate solution to a known volume of water in the polyethylene container. After allowing the temperature to equilibrate, the silicate solution was quickly adjusted to pH 7.0 using dilute hydrochloric acid (HCl). The pH of solution was monitored using Brinkmann / Metrohm pH meter equipped with combination electrode. The electrode was calibrated before the start of each experiment with NIST standard buffers. After pH adjustment, a known volume of a calcium chloride and magnesium chloride stock solution was added to the silicate solution. The solution was adjusted to pH 7.0 with dilute HCl and/or NaOH and was maintained constant throughout the silica polymerization experiment. Experiments involving inhibitors were performed by adding inhibitor solutions to the silicate solution before adding the calcium and magnesium solution.

Figure 2 illustrates the experimental setup. The reaction vessel is capped and kept at constant temperature and pH during the experiment. Silica polymerization in these supersaturated solutions was monitored by analyzing the aliquots of the filtrate from 0.22 μm filter paper for soluble silica using the standard colorimetric method as previously reported.[2]

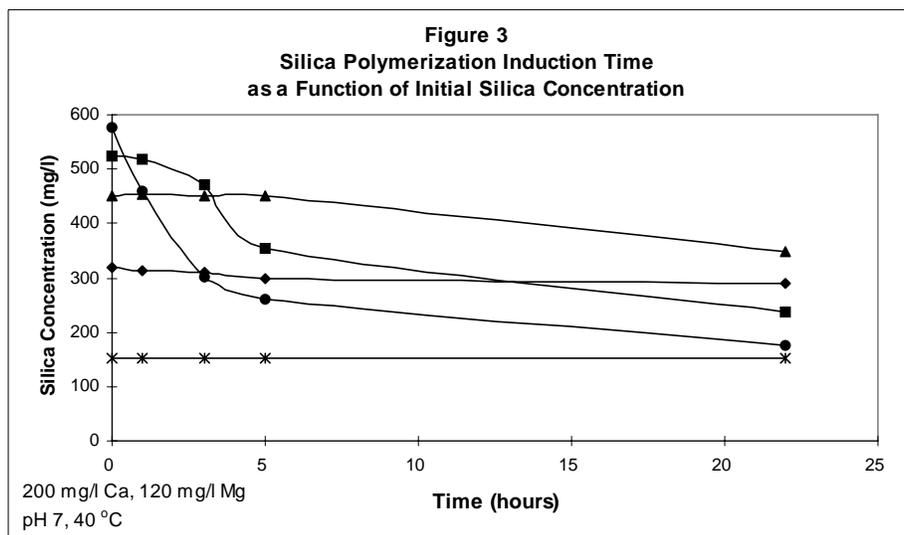
Figure 2
Setup Used for Studying Silica Polymerization



RESULTS AND DISCUSSION

Effect of Silica Supersaturation

Using the experimental set up described and shown above, a series of experiments were conducted at various silica supersaturation (SS) conditions. Figure 3 shows profiles of soluble silica concentration as a function of time for various silica SS solutions. Figure 3 shows that 600 mg/L silica in solution reacts instantaneously, whereas, lower silica concentrations react at a much slower rate. At low degrees of supersaturation, a decrease in silica concentration is preceded by a slow polymerization reaction (induction time, i.e., β). During this time, the concentration of soluble silica does not change significantly. However, once polymerization is underway, solution silica begins to decrease. Figure 3 illustrates that the β values for various SS solutions are 3 hours for 525 mg/L, 8 hours for 450 mg/L silica, and > 20 hours for 300 mg/L silica compared to < 5 minutes for the high supersaturation (600 mg/L silica) solutions. The base saturation level appears to be approximately 150 mg/L silica, which is consistent with previously reported silica equilibrium concentrations. For the study presented herein, we chose high supersaturation conditions (i.e., 600 mg/L) as a means to evaluate the effect of polymeric and non-polymeric inhibitors on silica polymerization instead of the effect of inhibitors on induction time.



The structures of the inhibitors evaluated for silica polymerization are summarized in Table 1. These products were chosen to test the effect of the various functional groups (e.g., carboxylic acid, sulfonic acid, phosphonate, borate, etc.) on silica polymerization. The products tested include several polymeric-based (Products A through G) and several non-polymeric based (Products H through J) inhibitors.

Table 1
 Products Evaluated: Name, Structure, and Designation

<u>Name</u>	<u>Structure</u>	<u>Designation</u>
poly(acrylic acid)	$\text{-(CH}_2\text{-CH)}_n\text{-}$ $\begin{array}{c} \\ \text{COOH} \end{array}$	Product A
poly(maleic acid)	$\text{-(CH - CH)}_n\text{-}$ $\begin{array}{cc} & \\ \text{COOH} & \text{COOH} \end{array}$	Product B
poly(acrylic acid:2-acrylamido-2-methyl propane sulfonic acid)	$\text{-(CH}_2\text{-CH)}_n\text{-(CH}_2\text{-CH)}_m\text{-}$ $\begin{array}{cc} & \\ \text{COOH} & \text{CO} \\ & \\ & \text{NH} \\ & \\ & \text{CH}_3\text{-C-CH}_3 \\ & \\ & \text{CH}_2\text{SO}_3\text{H} \end{array}$	Product C
AQUAFEED® 800 Antiscalant	Proprietary	Product D
AQUAFEED 1000 Antiscalant	Proprietary	Product E
New Noveon Product *	Proprietary	Product F
Hypersperse™ SI 300 Antiscalant	Proprietary	Product G
1-hydroxyethylidene-1,1-diphosphonic acid	$\begin{array}{c} \text{OH} \\ \\ \text{H}_2\text{O}_3\text{P - C - PO}_3\text{H}_2 \\ \\ \text{CH}_3 \end{array}$	Product H
2-phosphonobutane-1,2,4-tricarboxylic acid	$\begin{array}{c} \text{CH}_2\text{ - COOH} \\ \\ \text{H}_2\text{O}_3\text{P - CH - COOH} \\ \\ \text{CH}_2 \\ \\ \text{CH}_2\text{ - COOH} \end{array}$	Product I
Boric Acid	H ₃ BO ₃	Product J

AQUAFEED® is a registered trademark of Noveon, Inc.
 Hypersperse™ is a trade name of BetzDearborn (formerly Argo Scientific).
 *Patent Pending.

Effect of Inhibitor Concentration

Figure 4 shows the silica concentration as a function of time for Product F (New Noveon proprietary product). The data in Figure 4 indicate that dosage strongly affects the ability of Product F to inhibit silica polymerization.

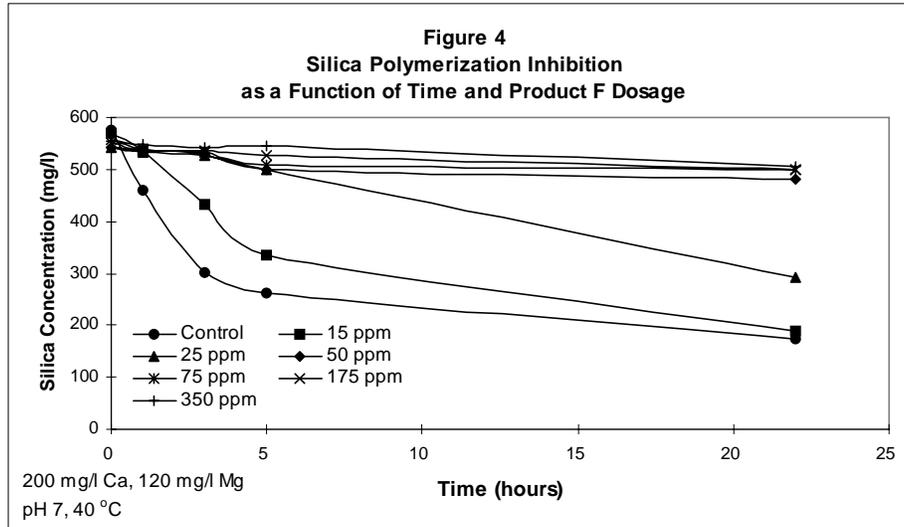
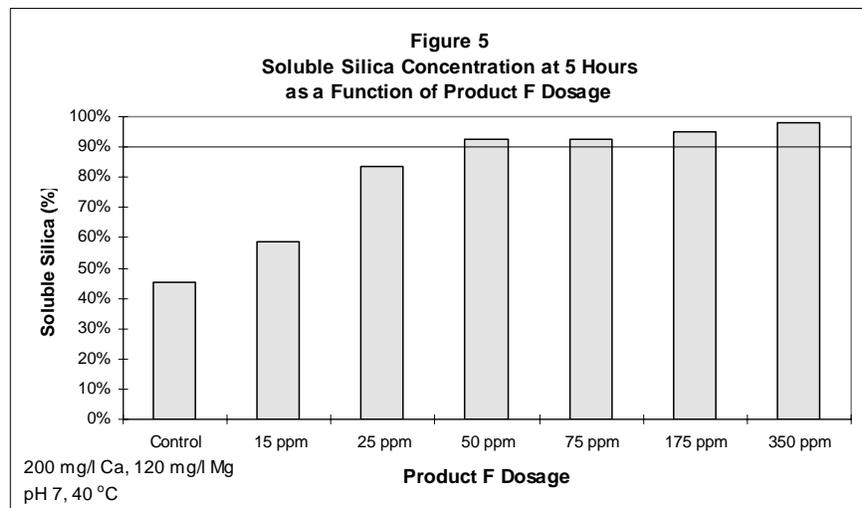
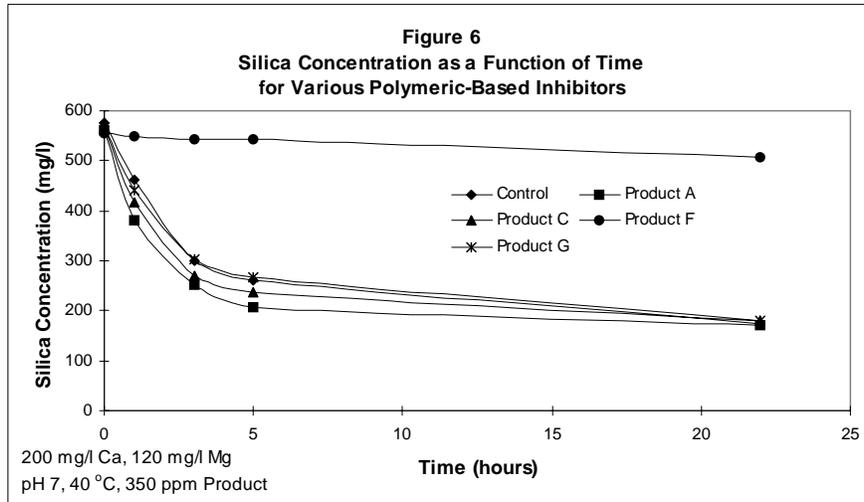


Figure 5 examines a portion of the data presented in Figure 4, specifically the inhibitory effect of Product F at 5 hours. At a dosage of 15 ppm, Product F shows poor inhibitory activity (e.g., 65% soluble silica). However at a 50 ppm dosage, Product F performance is substantially improved, and maximum inhibition (> 90%) is obtained. This suggests that at high SS conditions (i.e., 600 mg/L), a 1:12 ratio of inhibitor-to-silica provides protection for at least 5 hours (for lower SS conditions, it is likely that the inhibitor-to-silica ratios for effectively inhibiting silica polymerization will be lower). Therefore, in RO systems where residence times are much shorter than 5 hours, Product F should prevent silica polymerization.



Polymeric Inhibitors

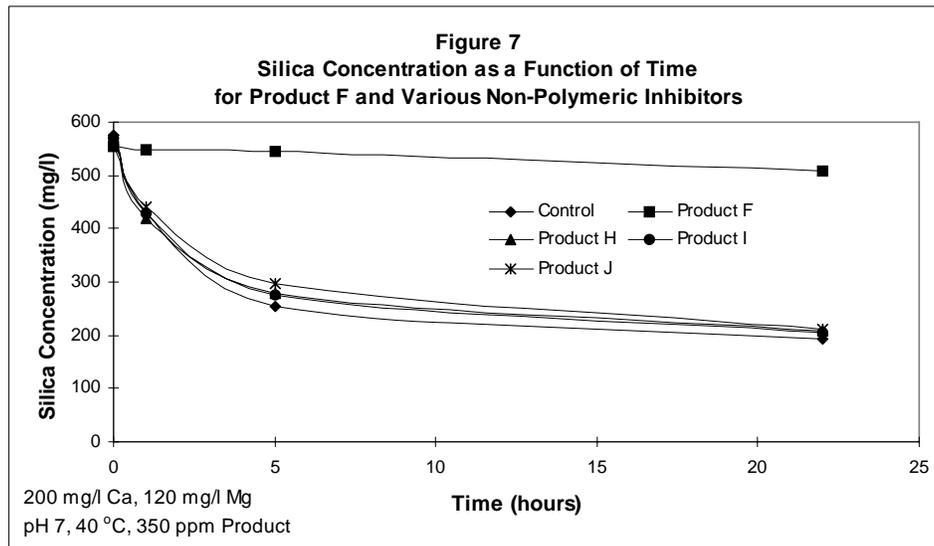
The use of polymeric inhibitors in RO system pretreatment programs has increased significantly during the last two decades. Most of the polymers that have demonstrated any efficacy in controlling foulants are either homopolymers (i.e., polyacrylic acid, polymaleic acid), acrylic copolymers, or maleic copolymers. In the present investigation, we evaluated several polymeric inhibitors commonly used in RO system pretreatment programs for their ability to inhibit silica polymerization. Figure 6 shows the profiles of soluble silica as a function of time for various polymeric-based inhibitors (Products A, C, F, and G noted in Table 1).



The data presented in Figure 6 clearly show that none of the known polymeric inhibitors tested and currently used for RO system pretreatment exhibited any efficacy for silica polymerization inhibition under the experimental test conditions (i.e., 600 mg/L silica, 200 mg/l Ca, 120 mg/L Mg, pH 7.0, 40°C, 350 ppm polymer). As illustrated in Figure 6, homo- and copolymers containing -COOH, -SO₃H, and non-ionic groups (Table 1), which are known to exhibit good inhibitory activity for CaCO₃, CaSO₄, and Ca(PO₄)₂, performed poorly in preventing silica polymerization. It is particularly interesting that a commercially available product (Product G) promoted for silica control exhibited poor silica polymerization inhibition. However, even at low concentrations (e.g., 25 ppm), Product F has a marked inhibitory effect on silica polymerization.

Non-Polymeric Inhibitors

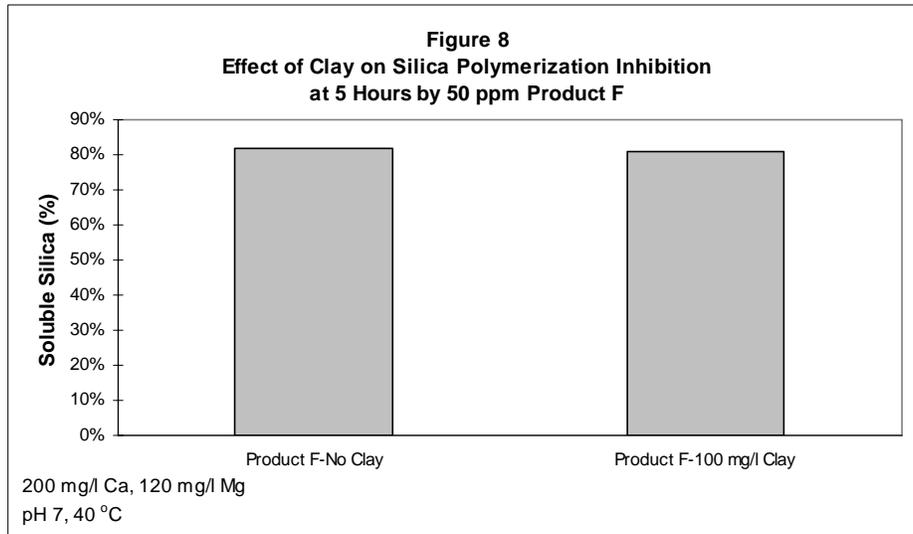
The use of non-polymeric inhibitors, such as polyphosphates and phosphonates, to control scaling especially calcium carbonate is well known.[15] However, these inhibitors suffer from the disadvantage that under stress conditions (i.e., high pH, high temperature, high hardness, etc.), they can react stoichiometrically with calcium ions leading to calcium phosphonate precipitation.[16] The application of boric acid and/or its water soluble salts to prevent silica polymerization has been reported.[3] It has been suggested that silica inhibition by borate is perhaps due to the formation of more soluble borate-silicate complexes. In the present investigation we studied the performance of several non-polymeric inhibitors. Figure 7 presents the soluble silica data as a function of time for Product F and several non-polymeric inhibitors shown in Table 1 (i.e., Product H, Product I, and Product J). The data presented in Figure 7 clearly show the superior performance of Product F compared to the non-polymeric inhibitors.



Effect of Suspended Matter on Silica Polymerization

The fouling of RO membrane by suspended matter is a critical concern for the RO industry and perhaps the major constraint in the efficient use of RO systems. Colloidal material generally consist of clay, aluminum silicates, iron silicates, organics, and other suspended matter which is usually present in natural water supplies in the submicron size. Colloidal fouling is caused by the coagulation of colloids during the RO process. Suspended matter, apart from fouling the membrane may also induce precipitation of scale forming salts and may accelerate the overall fouling process.

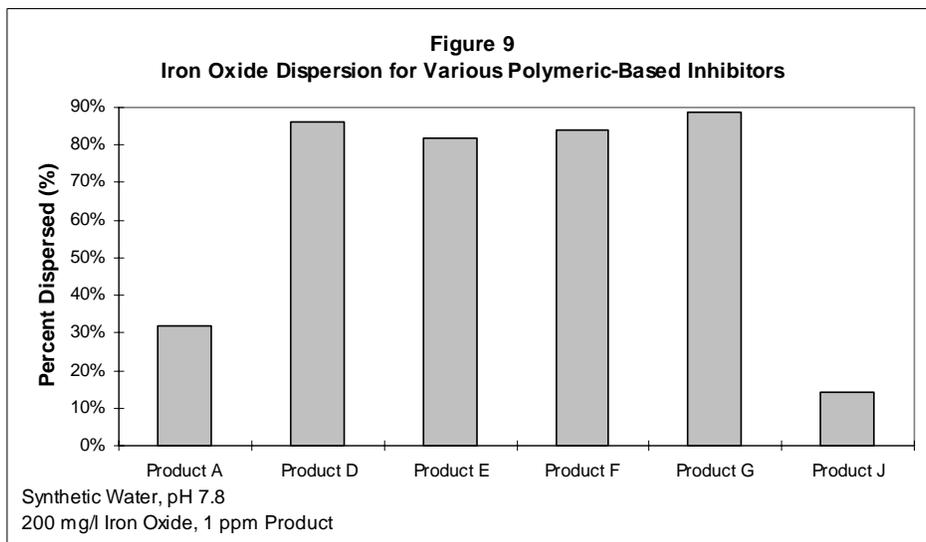
In order to understand the role of suspended matter on the silica polymerization inhibition activity of Product F, several experiments were conducted under BFG's standard test conditions. Figure 8 shows the effect of clay (Dixie) on the silica polymerization efficacy of Product F at 5 hours. The data clearly indicate that the addition of clay to the silica-supersaturated solutions has a negligible impact on the silica polymerization inhibition performance of Product F. The ability of Product F to retain performance in the presence of suspended matter (e.g., clay) helps to ensure that a process upset or a change in process variables will not adversely affect performance.



Suspended Matter Dispersion

Suspended matter, especially iron oxide and hydroxides, present in the feedwater, if not properly treated, can cause membrane fouling problems. For this reason, the use of a product exhibiting excellent dispersancy activity is necessary to disperse iron oxide particles in the concentrate and facilitate rejection by RO membranes.

Figure 9 shows the iron oxide dispersancy activity of several products as evaluated using a standard test method.[17] Figure 9 indicates that Products A and J provide relatively poor dispersion of iron oxide, whereas Products D, E, F and G exhibit comparable good (> 80% dispersed) performance.



PILOT RO SYSTEM TESTING

A short-term efficacy study was undertaken on a silica laden water that was concentrated using an RO system so as to achieve a significant silica supersaturation ($> 550 \text{ mg/L SiO}_2$). Natural waters were used so that the tests would approximate and could be translated to actual use conditions. The pilot RO unit was fitted with Dow FILMTEC® FT30 membranes and was designed to operate in a manner comparable to full size units. The pilot RO was operated such that the concentrate stream water chemistry had a significant driving force to silica polymerization ($> 550 \text{ mg/L SiO}_2$, $\approx 4,000 \text{ mg/L}$ total hardness, pH 6.5 to 7.0, and $\approx 32^\circ\text{C}$). The pilot unit was first operated without any inhibitor until the onset of fouling. The membrane began to foul in less than 24 hours under these accelerated conditions. The system was shut down and a representative membrane was removed for autopsy and foulant analysis. New membranes were installed and the unit was restarted with Product F. The test was terminated after 24 hours in order to compare the membranes directly to the control.

The membranes from the efficacy study were autopsied and the foulants were characterized. The control membrane (no inhibitor) was completely coated with a light powdery foulant that could be removed by touch. Representative swatches of the membrane were cut for elemental analysis. The electron micrographs and corresponding Energy Dispersive X-Ray (EDX) spectra of the control membrane and test membrane are shown in Figures 10 through 13. The deposit on the control membrane is predominantly silicon but there is a mixture of polyvalent ions present (as determined by EDX, see Figure 11). The membrane for the Product F test run showed no visible signs of fouling (i.e., appearance was as a virgin membrane). Scraping the membrane did not remove any material. The EDX of the test membrane (Figure 13) shows low levels of silicon based foulant. A comparison of the elemental analysis of the foulants in Figures 11 and 13 shows that the silicon peak in the control membrane (see Figure 11) dominates the field. The silicon found on the Product F test run membrane (see Figure 13) is insignificant compared to the sulfur peak. In contrast, the sulfur peak for the control membrane (see Figure 11) could not be seen due to the large quantity of silicon present. Thus, it can be concluded that the Product F had a significant impact on minimizing silica fouling.

Figure 10
Electron Micrograph of RO Membrane Operated on Silica Laden Feedwater
in the Absence of Product F

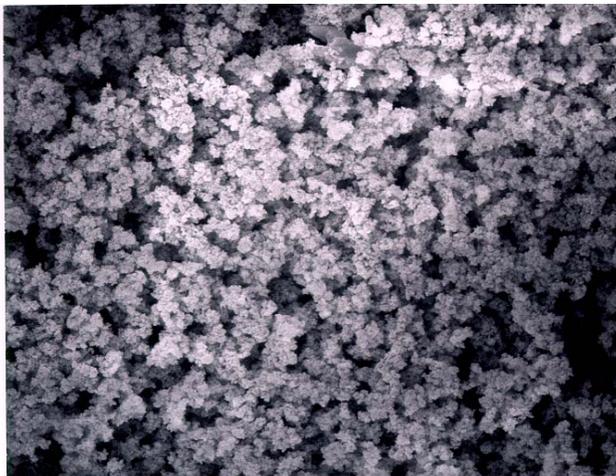


Figure 11
Energy Dispersive X-Ray Spectrograph of Fouled Membrane

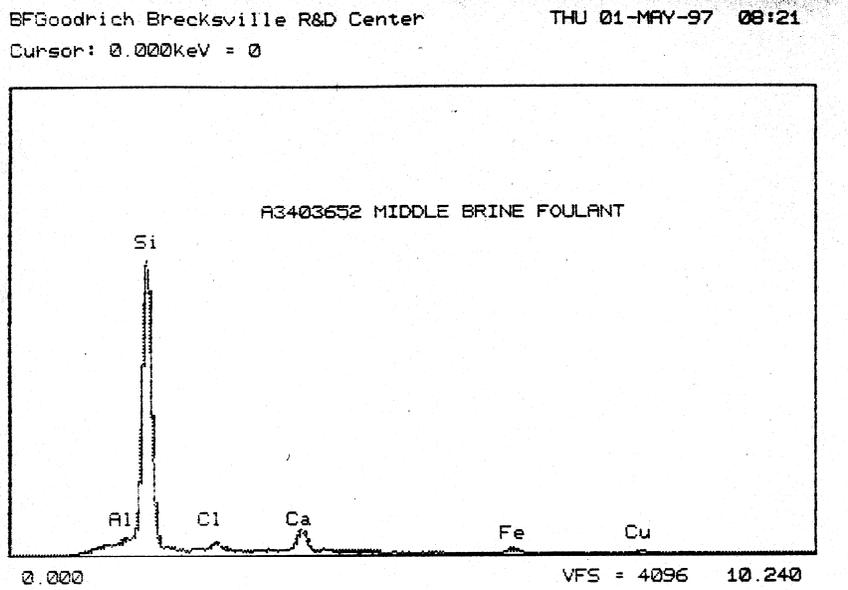


Figure 12
Electron Micrograph of RO Membrane Operated on Silica Laden Feedwater
in the Presence of Product F

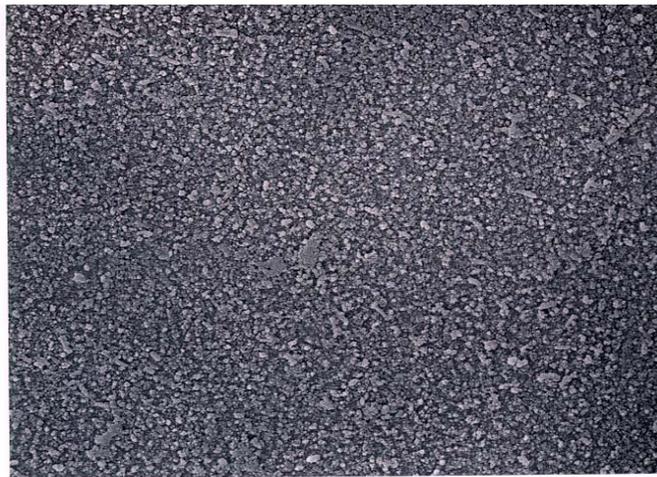
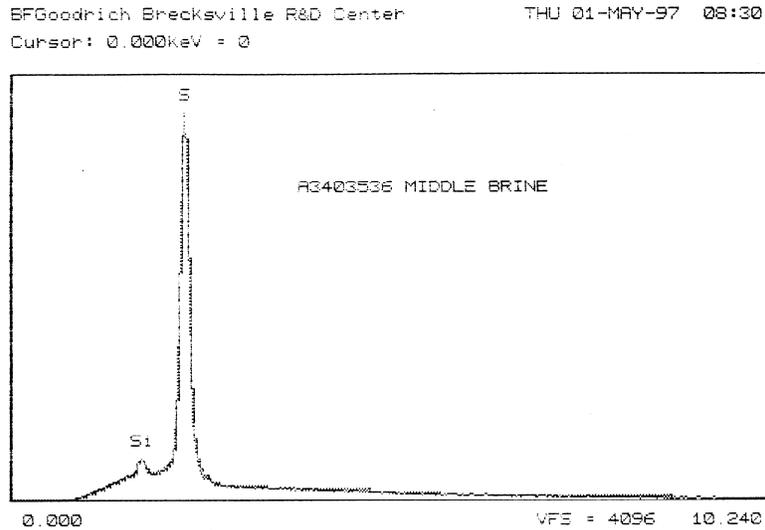


Figure 13
Energy Dispersive X-Ray Spectrograph of RO Membrane (Treated with Product F)



The results of the RO system efficacy testing discussed above confirms Noveon's laboratory testing and suggest that Product F inhibits silica polymerization and fouling. However, additional field evaluations are necessary and imminent.

Laboratory efficacy tests simulating cooling tower operations with silica fouling prone waters were conducted using a product related to Product F. These tests have shown promising results in control silica fouling (Note: Residence times for cooling tower systems are substantially longer than for RO systems). Field evaluations are underway to confirm laboratory results.

SUMMARY

The poor solubility of silica has limited the efficient use of water in RO, cooling, boiler, and geothermal applications in many parts of the world. Until recently, the conventional rule of thumb has been that silica concentrations in RO system concentrate streams should be limited to 150 mg/l SiO₂. Within the last 5 years, the use of high performance dispersant polymer technology has extended the operating rates for RO systems. However, to date, none of the approaches applied to water treatment systems have effectively controlled silica polymerization at high supersaturation (> 550 mg/l SiO₂) as well as disperse colloidal matter. The results of laboratory and pilot testing discussed herein regarding the performance of a new silica control polymer (Product F) suggest the following relative to silica control for RO systems:

1. A 1:12 ratio of inhibitor-to-silica (inhibitor = Product F) controlled silica polymerization for up to 5 hours in laboratory test conditions (e.g., 600 mg/l SiO₂, 200 mg/l Ca, 120 mg/l Mg, pH 7.0, and 40°C). Thus, given that RO system residence times are much shorter than the 5 hour laboratory test conditions, Product F should prevent silica polymerization in RO systems.
2. Product F has a marked inhibitory effect on silica polymerization and is superior to other commercially available products including those promoted for RO pretreatment and silica control in particular.

3. The presence of suspended matter (e.g., clay) does not significantly adversely influence the silica inhibiting properties of Product F.
4. Product F displays iron oxide dispersancy properties that are comparable to commercially available copolymer-based antiscalants / antifoulants for RO systems.
5. A short-term pilot study indicates that Product F minimizes silica fouling in an RO system operating with > 550 to 600 mg/l SiO₂ in the concentrate stream.

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For additional technical information pertaining to Lubrizol's TEC-RO[®] Chemicals, please contact us as follows:

Lubrizol Advanced Materials, Inc.
9911 Brecksville Road
Cleveland, OH 44141-3247, U.S.A.

Phone: 1-800-380-5397 or 216-447-5000

FAX: 216-447-6315 (USA Customer Service)
216-447-6144 (International Customer Service)
216-447-5238 (Marketing & Technical Service)

E-mail: coatings.csr@Lubrizol.com

Web Site: www.carbospense.com



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Lubrizol Advanced Materials, Inc.

9911 Brecksville Road, Cleveland, OH 44141, P/216-447-5000, F/216-447-5238

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