Versaflex® Si

AkzoNobel
Tomorrow's Answers Today

Versaflex® Si

New Water Treatment Chemical Prevents Formation of Hard-To-Remove Silica and Silicate Scales

Designed For Use With Today's Cooling Water Systems

Chemical treatment of cooling water systems has undergone significant changes over the past 30 to 40 years. Driven by higher population densities and the need to conserve limited fresh water supplies, process water users strive constantly to maximize water reuse and minimize generation of waste streams. One way to achieve these objectives, of course, is to increase cooling water cycles.

One problem with this approach, however, is that naturally occurring salts normally dissolved in fresh water—especially salts with relatively low solubilities, such as calcium carbonate, calcium phosphate, calcium sulfate and silica/silicates, for example—become increasingly concentrated as water evaporates during each recirculation cycle. When this occurs, these soon reach their maximum levels of solubility and can begin to settle out as scale on equipment surfaces, fouling the cooling systems and decreasing their efficiency. To prevent this, suppliers of water treatment chemicals have developed ways to keep such salts in solution at concentrations well beyond their normal solubility levels, allowing process water to be recirculated at higher cycles than could normally be achieved without fouling.

Technologies for control of calcium carbonate, calcium phosphate and calcium sulfate have, in fact, become well established. These technologies include:

Mineral Salt	Chemical Treatment
$CaCO_3$	Phosphonates, Acrylic or Maleic Polymers
$Ca(PO_4)_2$	Sulfonated Copolymers
$CaSO_4$	Acrylic or Maleic Copolymers

AkzoNobel, a leader in advanced water treatment technology, in fact offers a polymer called Versaflex® ONE that makes possible simultaneous control of both calcium carbonate and calcium phosphate at the higher pH levels at which modern cooling systems are normally operated to prevent corrosion.

To date, technologies for effective, economical control of silica/silicate scale have not been available, even though such scale, once formed, is unquestionably the most difficult to remove for the following reasons:

- Silica/silicate forms the hardest of all scales and is therefore the most damaging to the cooling system.
- Silica/silicate scale can occur throughout the entire system, even in difficult-to-reach places.
- Silica/silicate scale, because it is relatively inert, cannot be removed by traditional acid cleaning methods.

The only effective cleaner for silica/silicate scale is hydrofluoric acid (HF), an especially aggressive and hazardous chemical to handle.
Mechanical cleaning is labor intensive, time consuming and physically damaging to the cooling system.

Silica/silicate scaling is especially problematic in the regions of the Pacific Rim, where volcanoes are currently active or where volcanic activity has occurred in the past. The ground or surface water in these regions can easily contain SiO_2 in concentrations up to its normal solubility limit (120ppm at 25°C and pH 8.5). At this level, some of the systems that can be affected by silica/silicate scaling include:

- Open recirculating cooling water systems
- Steam generating systems
- Reverse osmosis systems
- Geothermal systems

Adding to the complexity of the problem, it is well known that naturally occurring silica can polymerize to form amorphous or colloidal silica under super saturation conditions. It can also precipitate with metal ions to form silicates of magnesium, calcium, iron or aluminum. It can even be present in different chemical and physical forms, depending on water chemistry, pH, temperature and the presence or absence of suspended solids.

Because of this, silica fouling is very complex and difficult to predict. In fact, there are currently no standard or generally accepted laboratory test methods to study silica fouling problems or to evaluate potential additives that may help to alleviate the problem. Using a combination of molecular modeling and exhaustive field trials, however, AkzoNobel has developed a polymer that is very effective at high cycles of concentration.

Molecular Modeling

AkzoNobel is a worldwide supplier of custom-designed specialty polymers for all types of water treatment applications. The company is a subsidiary of National Starch and Chemical Corporation, a leading supplier of specialty polymers for applications from adhesives to foods to microelectronics, and itself a subsidiary of Imperial Chemical Industries (ICI), one of the world's largest chemical companies.

AkzoNobel has sophisticated research instrumentation and techniques, including those necessary for molecular modeling. As a result, we are uniquely equipped us access to sophisticated research instrumentation and techniques, including those necessary for molecular modeling. As a result, we are uniquely equipped to not only develop new specialty polymers for specific applications, but also to study the interactions of different polymers with the metallic ions and other chemical structures they are designed to control.

Applying this capabilities expertise, we were able to synthesize three different polymers containing functional groups theoretically capable of interacting with polymeric silica and metallic silicate salts to keep them in solution at concentrations far exceeding their normal solubilities. We designated these Polymers A, B and C and proceeded to conduct tests that would indicate which one would be most effective with the most commonly encountered forms of silica. Schematic diagrams of these three polymers, including their different functional groups, are shown in Figure 1.

Because silica can exist in cooling water both as polymeric silica and as silicate salts, it was necessary to explore the interactions of each of the three experimental polymers with both forms of silica. Schematic diagrams of both forms are shown in Figure 2.

Figure 1:
Polymers Studied

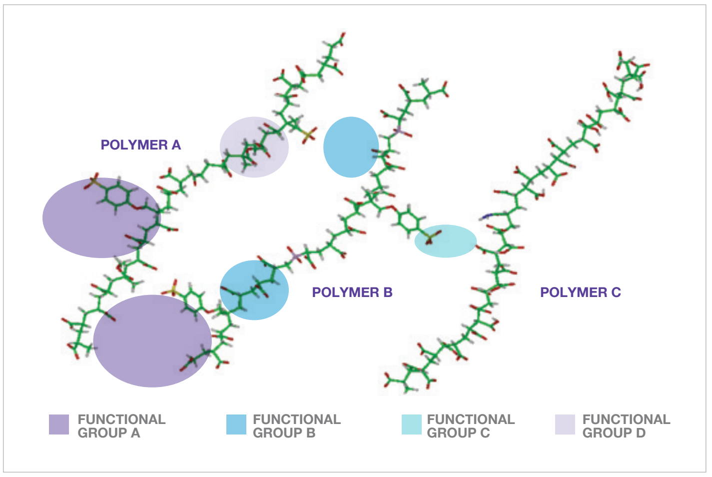


Figure 2:
Inorganic Substrates

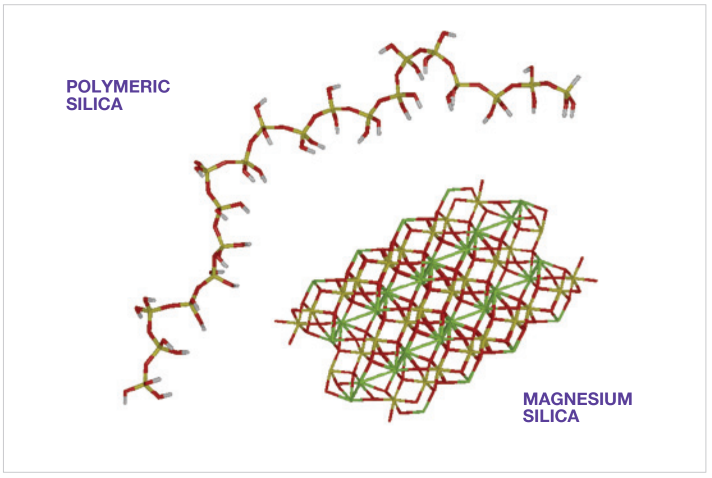


Figure 3:
Molecular Interactions between Polymer A & Polymeric Silica

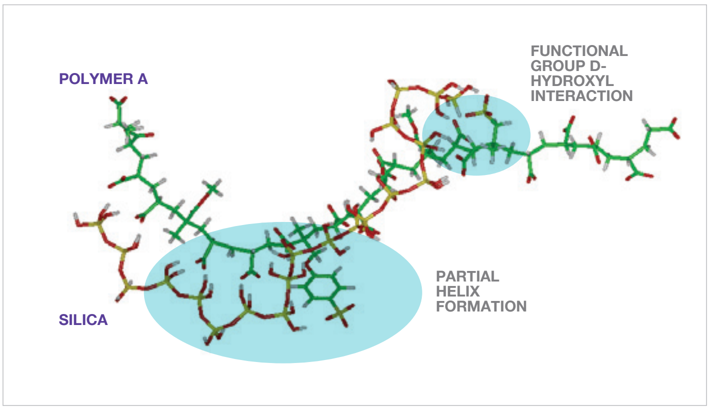


Figure 4:
Molecular Interactions between Polymer B & Polymeric Silica

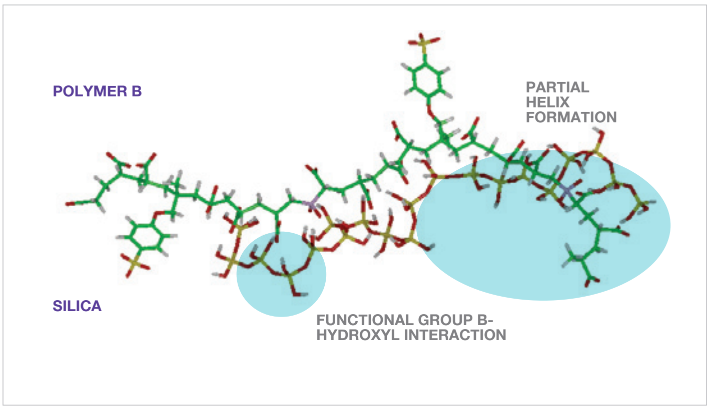
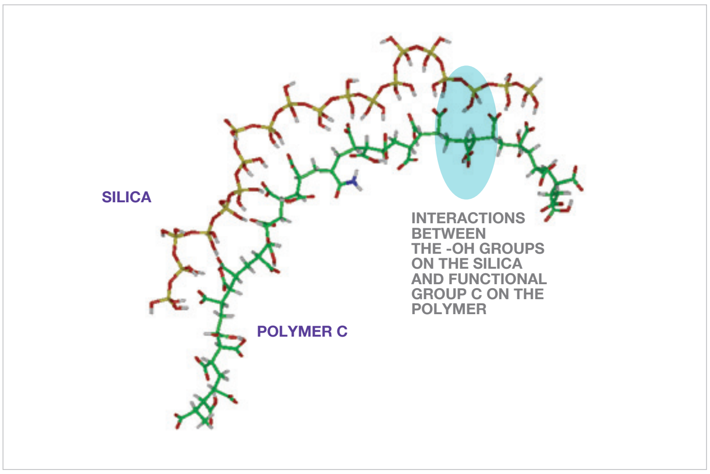


Figure 5:
Molecular Interactions between Polymer C & Polymeric Silica



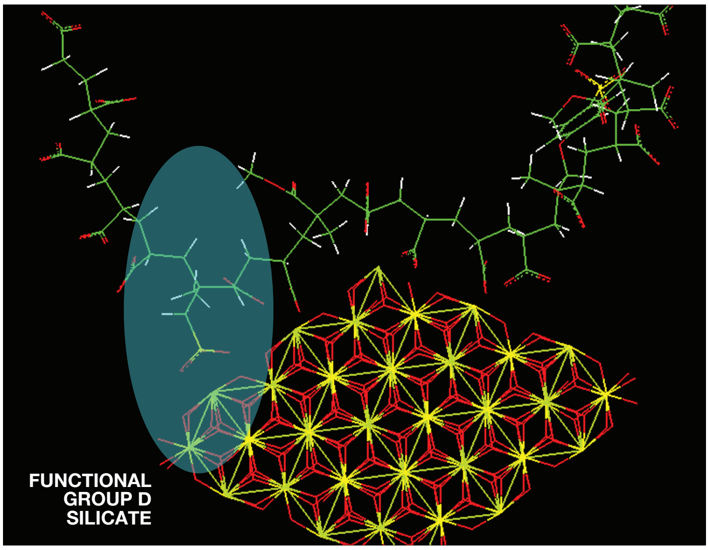
A schematic diagram of the interaction between experimental Polymer A and polymeric silica is shown in Figure 3 to the left.

A schematic diagram of the interaction between experimental Polymer B and C and polymeric silica is shown in Figures 4 and 5 to the left.

The lower the interaction energy between the experimental polymer and the polymeric silica or magnesium silicate crystals, the stronger the interaction between the polymer and the scale surface, leading to better dispersion behavior. Because of this, the schematic diagrams to the left illustrate the lowest-energy interactions between the different experimental polymers and magnesium silicate crystals.

A schematic diagram of the interaction between experimental Polymer A and magnesium silicate crystals is shown in Figure 6 below.

Figure 6:
Low-Energy Polymer A—Magnesium Silicate Pair Configuration



A schematic diagram of the interaction between experimental Polymer B and magnesium silicate crystals is shown in Figure 7 to the right.

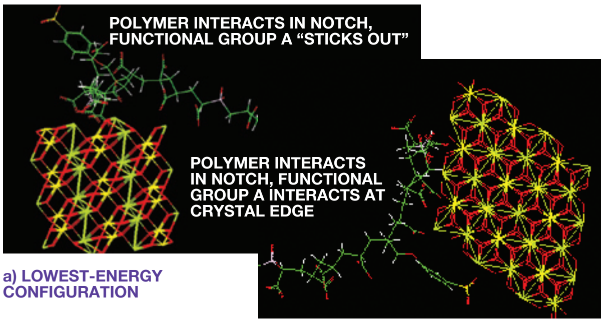
A schematic diagram of the interaction between experimental Polymer C and magnesium silicate crystals is shown in Figure 8 to the right.

The quantum mechanical calculation of the interaction energies between each of the experimental polymers and the silica/silicate surfaces shown in Figures 3 through 8 yielded the following energy values:

Polymer	Surface	Interaction Energy Kj/mole
C	$-\{OSI(OH)_2\}-$	-530.7
C	$MgSiO_3$	-615.5
A	$-\{OSI(OH)_2\}-$	-552.6
A	$MgSiO_3$	-692.9
B	$-\{OSI(OH)_2\}-$	-618.7
B	$MgSiO_3$	-858.7

As noted above, the more negative the calculated energy, the stronger is the interaction between the polymer and the scale surface, leading to better dispersion behavior. Therefore, Polymer B represents the best silica and silicate dispersant of the three polymers evaluated and was thus selected for further evaluation in pilot plant cooling tower tests and field trials.

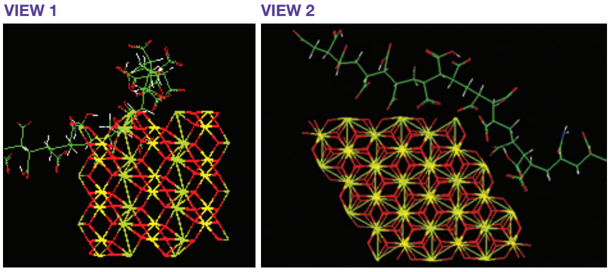
Figure 7:
Molecular Interactions between Polymer B and Magnesium Silicate



a) LOWEST-ENERGY CONFIGURATION

b) ALTERNATE CONFIGURATION

Figure 8:
Low-Energy Polymer C—Magnesium Silicate Pair Configuration


VIEW 1

VIEW 2

Pilot Plant Testing

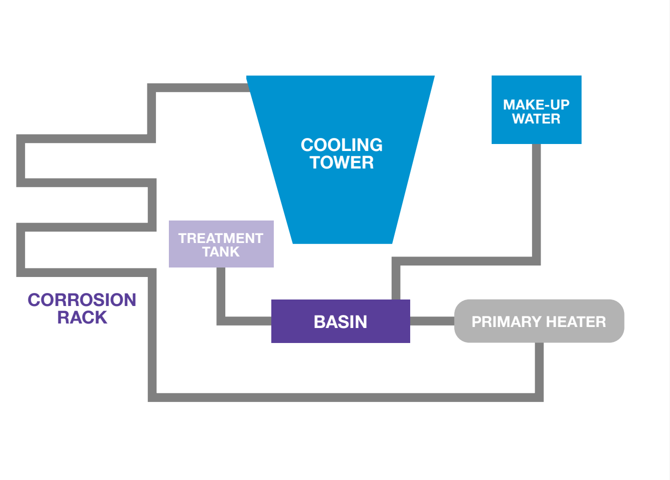
In order to compare the actual performance of the new experimental polymer, Versaflex® Si, with its theoretical performance as determined by quantum mechanical calculations, it was evaluated in a laboratory scale pilot plant cooling tower. The apparatus itself is constructed of PVC, and the fill is the standard honeycomb normally used in commercial cooling towers. A schematic diagram of the pilot plant cooling tower is shown in Figure 9.

Conducting laboratory tests using synthetic water dosed with sodium silicate to evaluate silica dispersants is generally regarded as difficult because silica exists in more than eleven different forms and thus cannot be accurately represented by laboratory-spiked sodium silicate. Because of this, naturally occurring water from the city of Madera in Southern California, an area where silica/silicate scaling is generally regarded as a problem, was used as make-up to gradually concentrate silica in the evaporative cooling system under simulated conditions.

During preliminary pilot cooling tower testing using hard water as make-up, it was observed that calcium hardness levels reached the break point and calcite precipitation began to occur, causing apparent co-precipitation of silica, after reaching a level of 250 ppm SiO_2 in the tower water. When using partially softened water as make-up to avoid potential calcite interference, however, no calcite or silica scale formation was observed throughout the test period. The chemical composition of the partially softened make-up water was as follows.

Calcium Hardness	28 ppm as $CaCO_3$
Magnesium Hardness	12 ppm as $CaCO_3$
Silica	56.5 ppm as SiO_2
Total Alkalinity	88 ppm as $CaCO_3$
Chloride	36 ppm as Cl^-
Phosphate	0.57 ppm as PO_4
Iron	0.001 ppm as Fe
Specific Conductance	240 mmhos
pH	7.9

Figure 9:
Pilot Plant Cooling Tower Schematic

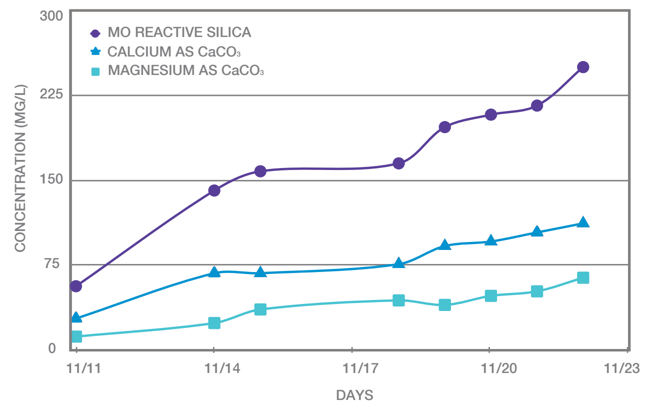


The treatment and test conditions were as follows:

PBTC	3.3 ppm active
HEDP	4.8 ppm active
TTA	2.0 ppm active
Versaflex® Si	18.0 ppm active
Biocide	150 ppm 1.5% Isothiazoline slug dosed every 2 days
Temperature	82°–92°F
Flow Rate	3.0 gpm

During the pilot cooling tower test, samples were taken every two days and tested for molybdate-reactive silica levels as well as calcium and magnesium hardness. The results, shown in Figure 10 below, demonstrate the ability of Versaflex Si to significantly increase the solubility of silica in cooling water systems.

Figure 10:
Results of Pilot Cooling Tower Test



By comparison, the same test was conducted using no silica dispersant at all and again using a competitive product at a level of 22-44 ppm active. The results were as follows:

Silica Dispersant Dosage	Maximum SiO_2 Achieved
Blank (no dispersant)	150 ppm
Competitive product as 22-44 ppm active	180 ppm
Versaflex Si at 11-20ppm active	>250 ppm

Since pilot cooling tower tests indicated the superior effectiveness of Versaflex Si under simulated conditions, field trials were run to demonstrate its performance under real-world conditions.

Field Trial Testing

A comfort cooling system in the Northwest (Spokane, WA) and a process cooling system in the Southwest (Southern Arizona) were chosen as locations in which to conduct field trials of Versaflex® Si under real-world conditions.

For the first field trial, the chemical composition of the make-up water was as follows:

Calcium Hardness	12 ppm as $CaCO_3$
Magnesium Hardness	8 ppm as $CaCO_3$
Silica	48.5 ppm as SiO_2
Total Alkalinity	128 ppm as $CaCO_3$
Chloride	34 ppm as Cl^-
Iron	0.16 ppm as Fe
Specific Conductance	240 mmhos
pH	7.8

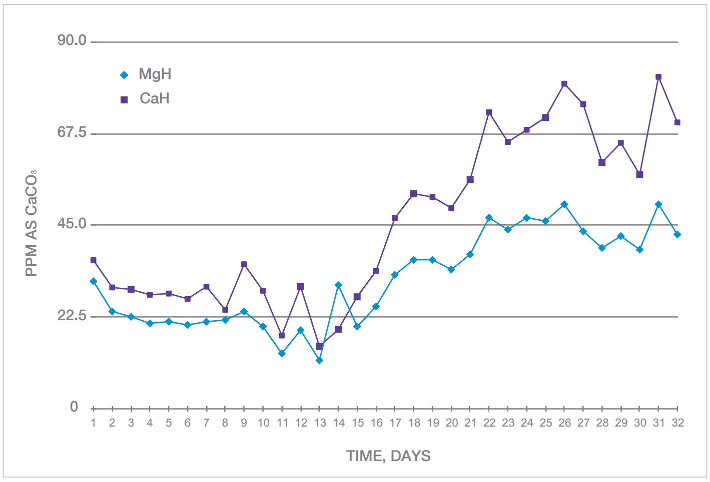
The treatment and test conditions were as follows:

HEDP	6.0 ppm active
TTA	2.0 ppm active
PAA	5.0 ppm active
Versaflex Si	20 ppm active
Biocide	150 ppm 1.5% Isothiazoline slug dosed every 2 days
Temperature	80° F
- T	10° F
Circulation Rate	720 gpm
Evaporation Rate	1008 gpd

The trial schedule was set at seven weeks, with recirculation cycles increasing from 3.0 to 6.0 cycles at the rate of 0.5 cycles per week throughout the trial period.

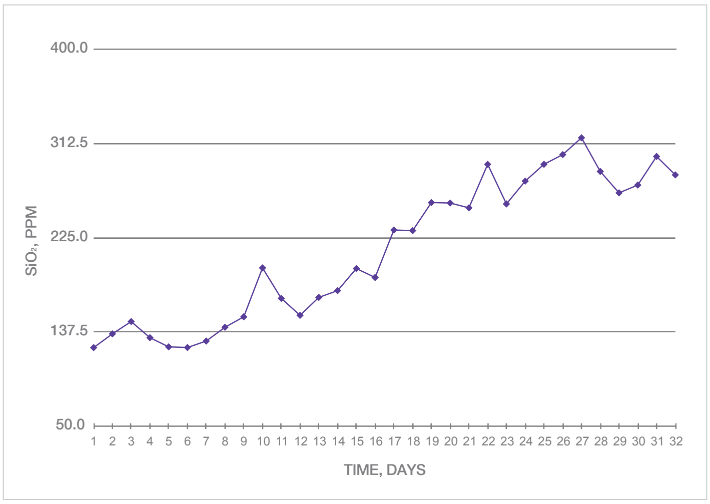
As expected, the hardness of the tower water increased with each recirculation cycle as magnesium and calcium salts (calculated as $CaCO_3$) became more concentrated as shown in Figure 11 below.

Figure 11:
Field Trial #1 — Hardness



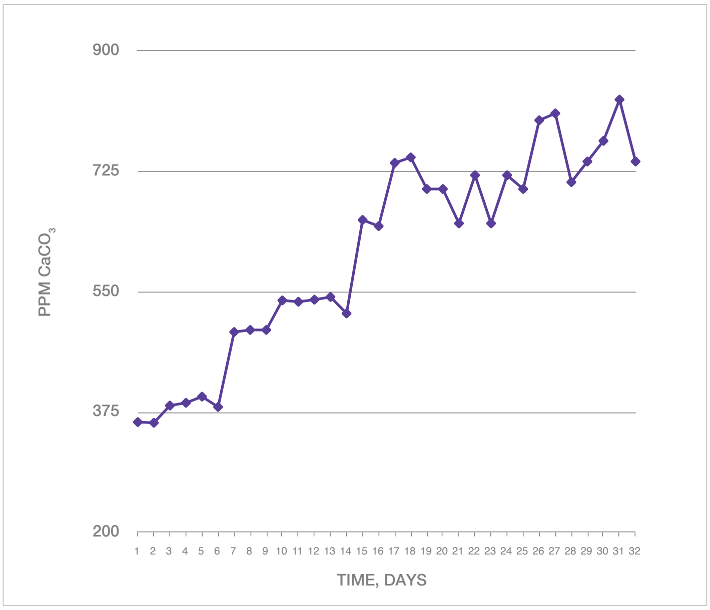
As also expected, the conductivity of the tower water increased as soluble salts became more concentrated with each recirculation cycle, as shown in Figure 12 below.

Figure 12:
Field Trial #1 — Conductivity



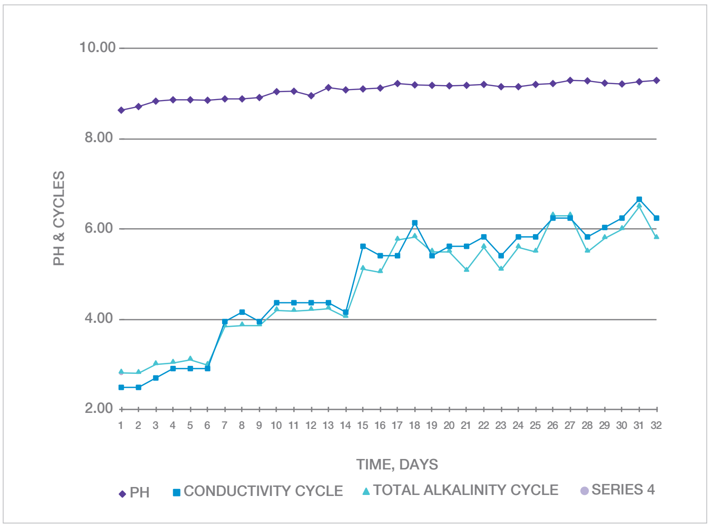
During the field trial, the total alkalinity of the tower water also increased with each recirculation cycle, as shown in Figure 13 below.

Figure 13:
Field Trial #1—Total Alkalinity



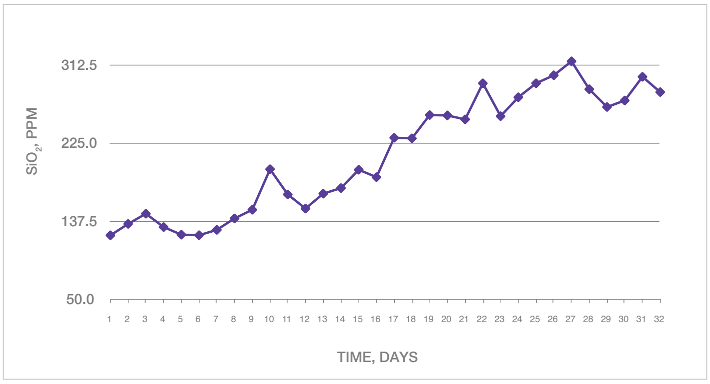
As both conductivity and total alkalinity increased significantly, however, the pH of the tower water increased only slightly as shown in Figure 14 below.

Figure 14:
Field Trial #1—-pH vs Conductivity/Alkalinity Cycles



At the same time, the presence of Versaflex® Si Silica Dispersant allowed an increase in silica levels in the cooling tower water from 132 ppm to >300 ppm SiO_2 without scale formation as shown in Figure 15 below.

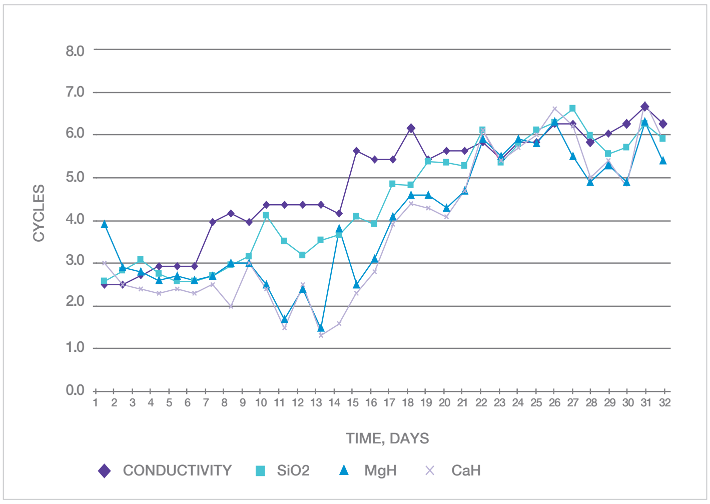
Figure 15:
Field Trial #1—Silica



This represents an increase in cycles of concentration from 2.8 to 6.5 with 100% silica retention, far exceeding the target performance the project was designed to demonstrate.

In fact, it was observed during the course of the field trial that because of the presence of Versaflex Si Silica Dispersant, the limiting factor of the cooling water began to shift from silica to calcium hardness during severe water conditions as shown in Figure 16 below.

Figure 16:
Field Trial #1—Cycles of Concentration



Overall, at the end of this field trial, the direct cost savings for the system were calculated as follows:

- Make-up water demand reduced by 24%.
- Blowdown water (waste water) reduced by 68%.
- Treatment usage reduced by 58%.

Field trial #2 was conducted at a power plant cooling tower plagued with silica fouling problems even though the make-up water contained only 22 ppm SiO_2 and the cooling water was running at 4 cycles of concentration.

For the second field trial, the chemical composition of the make-up water was as follows:

Calcium Hardness	160 ppm as $CaCO_3$
Magnesium Hardness	80 ppm as $CaCO_3$
Silica	22 ppm as SiO_2
Total Alkalinity	192 ppm as $CaCO_3$
Chloride	112 ppm as Cl^-
Iron	0.01 ppm as Fe
Specific Conductance	520 mmhos
pH	6.8

The test conditions were as follows:

Equipment	On-site evaporative deposition test rig with automatic acid feed, inhibitor feed and blowdown
Heat Exchanger	Copper nickel tube, 145° F skin temperature
Treatment Program	Proprietary formula + Versaflex® Si silica dispersant
pH Control	7.3–7.8
Test Duration	30–90 days

Before the primary test was conducted, an evaporative deposition test was conducted on a side stream using competitive silica dispersant at 25 ppm active, which still produced silica fouling at 4 recirculation cycles. X-ray analysis of the deposit showed its identity and composition to be similar to that of the main plant heat exchanger deposit—i.e., Al, Si, Ca and Fe. This suggested that the deposit was, in fact, aluminum silicate, consistent with airborne dust/dirt/silt caused by frequent dust storms in the desert.

During the primary test, when the system was switched to new Versaflex Si Silica Dispersant at only 9 ppm active, no apparent deposits occurred either during or after the dust storms. The heat exchanger remained clean even when recirculation was increased from 4 to >6 cycles with half the water velocity over the heated tube. Dispersion of silt at high-dust loadings was seen as a surprising benefit of the new silica dispersant.

An Effective Dispersant

Molecular modeling studies, pilot plant cooling tower tests and exhaustive field trials have all demonstrated that new Versaflex® Si Silica Dispersant is able to increase silica solubility by more than 2.5 times, allowing cooling systems to run at higher cycles of concentration without experiencing troublesome silica fouling.

Because silica exists in so many different forms, however, it is highly recommended that a program of actual field trials be implemented in order to determine the optimum concentrations and system conditions for use of new Versaflex Si.

Safety and Handling

Versaflex Si products are available in bulk, intermediate bulk and 55-gallon drums. The standard drum is fiber with 525 pounds net. Plastic drums are also available.

Versaflex Si polymers have very low toxicity. Consult product MSDS for further information.

Contact with the skin or eyes should be avoided. If a Versaflex Si product contacts the eyes, flush with water. If redness or sensitivity occurs and persists, consult a physician.

Versaflex Si polymers should be shipped and stored in 304 stainless steel or better, fiberglass or plastic tanks. Certain phenolic linings are acceptable for use in drums and storage tanks. Mild steel, copper, brass and aluminum should not be used.

The above materials of construction also apply to all pipes, valves and pumps used in the application or transport of Versaflex Si.

For more information on our portfolio of technologies for industrial water treatment applications, visit our website at http://www.akzonobel.com/surface/markets/water_treatment/

Brazil and South America
Akzo Nobel Ltda Divisão Química
Rodovia AkzoNobel 707
Bairro São Roque da Chave
Zip Code: 13.295-000
Itupeva, São Paulo
Brazil
Tel: +55 11 4591 8939
Fax: +55 11 4591 1744
Email: sc-southamerica@sc.akzonobel.com

Europe, Africa and Middle East
Akzo Nobel Surface Chemistry AB
Stenunge Allé 3
SE-444 85 Stenungsund
Sweden
Tel: +46 303 85000
Fax: +46 303 84659
Email: Surfactants.Europe@sc.AkzoNobel.com

Asia-Pacific
Akzo Nobel Surface Chemistry Pte Ltd
41 Science Park Road
Singapore Science Park II
#03-03 The Gemini
117610
Singapore
Tel: +65 6773 8488
Fax: +65 6773 8484
Email: surfacechemistry@ansc.com.sg

US, Canada and Mexico
Akzo Nobel Surface Chemistry LLC
525 West Van Buren Street
Chicago, IL 60607-3823
United States of America
Tel: 312 544 7000
Fax: 312 544 7410
Email: csrusa@akzonobel.com

AkzoNobel
Tomorrow's Answers Today

5301-04-0082-2M