



High-Performance Additive for Scale and Deposit Control in Industrial Water Treatment

Introduction

AkzoNobel Chemistry has Surface introduced a new generation of highperformance additive for scale and deposit control in industrial water treatment. Versaflex ONE is designed for superior functionality in stressed cooling water conditions where high pH and/or high calcite saturation exists. In addition, Versaflex ONE effectively stabilizes calcium phosphate, iron and zinc while tolerating high levels of contaminants, such as elevated total dissolved solids (TDS), suspended solids and soluble iron. It is also stable in the presence of halogens, even the high concentrations present during hyper-halogenation.

Versaflex ONE delivers:

- superior inhibition of calcium carbonate in extreme conditions
- outstanding stabilization of calcium phosphate, iron and zinc
- unequaled prevention of adherent deposits
- extended stability in harsh environments

Versaflex ONE

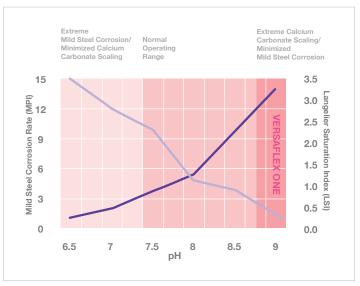
Use Patterns

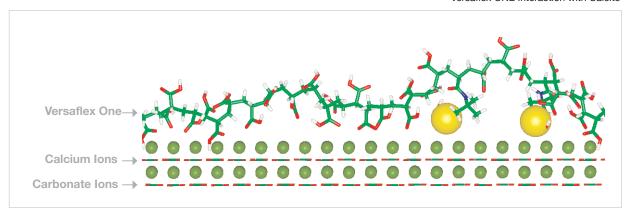
Over the past 30 to 40 years, the treatment of cooling water systems has changed dramatically. The early use of chromate provided effective mild steel corrosion control at pH levels below 7.0, where precipitation of mineral scale is minimized. Elimination of chromate in today's water treatment procedures has resulted in systems being operated under alkaline conditions, where the potential for mild steel corrosion is minimized. However, these more alkaline operating conditions significantly increase the potential for mineral scale precipitation and deposition.

Today, cooling water systems are treated almost exclusively at operating pH levels of 7.5 to 8.8. Increased potential for corrosion and the absence of effective corrosion inhibitors preclude operation of systems at pH levels below 7.5. In contrast, the substantially increased potential for mineral scale formation and the absence of effective scale inhibitors preclude the operation of many systems at pH levels much above 8.8. Until now...

Versaflex ONE effectively increases the upper limits at which cooling water can be treated without risking scale depositon. As depicted in Figure 1, Versaflex ONE is designed to be used in applications where the driving force for calcium carbonate precipitation is extremely high. Generally, this would include high pH waters where calcite saturation exceeds 250X and Langelier Saturation Index (LSI) approaches or exceeds 3.0.

Figure 1: Advancement of Cooling Water Treatment





Advanced Polymer Design

Until recently, it has not been possible to effectively control both calcium carbonate and calcium phosphate with the same polymer. Materials such as polymaleic acid (PMA) homopolymer effectively control calcium carbonate but are poor inhibitors for calcium phosphate and readily fail in the presence of contaminants such as iron. Acrylic Acid:AMPS® copolymers (AA:AMPS) effectively control calcium phosphate but are poor calcium carbonate inhibitors.

AkzoNobel Surface Chemistry has developed a polymer that is superior to PMA in calcium carbonate control yet incorporates functionality to allow control of calcium phosphate, iron and zinc. AkzoNobel's research group has used a combined approach of molecular modeling, polymer architecture and pilot evaluation and commercial results to ensure the product meets the industry's needs.

In designing Versaflex ONE, AkzoNobel Surface Chemistry used molecular modeling to study polymer-surface interactions with calcium carbonate (calcite) and calcium phosphate. Figure 2 shows the modeled surface of calcite and the resulting surface interaction with Versaflex ONE. The model shows that the design of Versaflex ONE maximizes polymer interaction with the calcite surface, resulting in improved calcium carbonate control.

Figure 3 shows a comparison of molecular interaction energies between calcite and Versaflex ONE, AA:AMPS and PMA. Interaction energies are measured in kcal/mole. Increasingly negative values indicate stronger polymer interface with the calcite surface. Figure 4 shows a comparison of interaction energies for calcium phosphate.

Using this design technology, AkzoNobel Surface Chemistry has optimized the architecture of Versaflex ONE to maximize polymer binding to calcite while also incorporating effective calcium phosphate binding properties.

Figure 3: Calcite Binding Energies

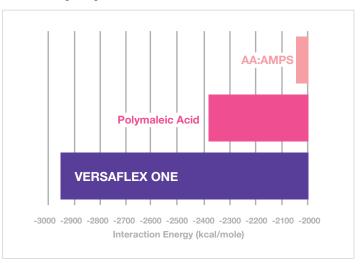
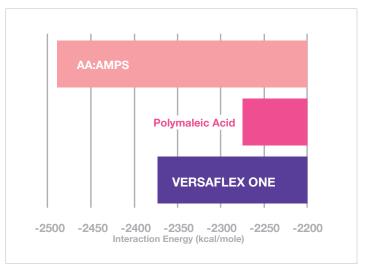


Figure 4: Calcium Phosphate Binding Energies



Control of Calcium Carbonate In Extreme Conditions

Operation of cooling towers using increasingly severe water mandates the use of new chemistries to address the greater challenges of deposit and corrosion control. While presenting many challenges, the demand to operate such systems at increased cycles of concentration also provides benefits such as decreased water consumption, reduced potential for mild steel corrosion and lower chemical usage. Versaflex ONE was specifically designed to control calcium carbonate, the primary foulant found in severe conditions. This functionality allows the user of Versaflex ONE to:

- operate systems at increased cycles
- reduce mild steel corrosion rates
- reduce water consumption
- eliminate acids
- use poorer-quality feed water
- reduce corrosion inhibitor demand

Versaflex ONE has been shown to provide superior calcium carbonate control across a wide range of water conditions. Pilot evaluations were conducted to examine the effects of temperature, pH and contaminants such as iron. In these pilot tests, Versaflex ONE was evaluated versus polymaleic acid (PMA), 2-Phosphonobutane 1,2,4-TriCarboxylic acid (PBTC) and AA:AMPS copolymer. The conditions of testing are described in Tables 1 and 2.

Figure 5 shows the Langelier Saturation Index (LSI) and Calcite Saturation Index for the cycled water (pH 8.8) at 104°F, 110°F and 132°F.

Optimizing Dosage

Pilot evaluations were conducted to determine the optimum dosage necessary to achieve the highest stabilization of calcium carbonate. Figure 6 shows percent calcium carbonate inhibition versus increasing cycles of concentration using 5, 10 and 20 mg/L of Versaflex ONE. The experiments demonstrate that under these conditions, a concentration of 10 mg/L maximizes performance and use costs.

Operating Conditions

Concentration
16,000 BTU/hr/ft ²
104°, 110°, 132°F
8.7-8.9
3.25 ft/sec

Table 2:

Versaflex ONE Dosage Determination

100 90 80 70 80 90 90 90 90 90 90 90 90 90 90 90 90 90		10	omg/L	VERSAF VERSA VERSA	FLEX	ONE				, o o ^{m a}		4.0 Langelier Saturation Index (LSI) 3.5 3.0 2.5 2.0	
0	1	1.5	2	2.5	3	3.5	4	4.5	5	5.5	 6	1.5	
	Cycles of Concentration												

Performance Feature

Figure 5: Langelier Saturation Index (LSI) and Calcite Saturation Index

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	4.0						132 9		300x	
S-	3.5						110 ° F		250x	ς,
l) xək	3.0					104 °F			 00X	alcite
Langelier Saturation Index (LSI)	2.5								200x	Calcite Saturation Index
ıratio	2.0								150x	ıratio
Satu	1.5								130%	on In
elier	1.0								100x	dex
Lang	0.5									
	0.0	1	2	3	4	5	6	7	50x	
		-	_		f Concent		9			

Make-up Water Conditions

Table 1:

Concentration
150 mg/L as CaCO ₃
162 mg/L as CaCO ₃
750 micro-mhos
As indicated

Performance versus Competitive Materials

The potential for calcium carbonate precipitation in stressed conditions requires the additive to maintain its stability and functionality in this environment. For this reason, polymers such as polyacrylic acid (PAA) and phosphonates such as hydroxyethylidine diphosphonic acid (HEDP) are not effective inhibitors in stressed conditions.

For many years, the standard procedure for treating cooling towers with severe calcium carbonate scaling involved the use of PMA. While it is an effective additive for controlling calcium carbonate inhibition, PMA lacks effective functionality for the control of other deposit-forming materials such as phosphate, iron and zinc. In addition, PMA is a poor dispersant of particulates, and its performance is diminished in the presence of iron. AA:AMPS copolymers, on the other hand, effectively control phosphate, iron and zinc and are good dispersants. However, AA:AMPS copolymers have not been found to be effective inhibitors of calcium carbonate.

Pilot tests conducted at 104°F, 110°F and 132°F at a pH of 8.8 confirm that Versaflex® ONE is more effective than PMA and far more effective than AA:AMPS in controlling calcium carbonate.

Figures 7, 8 and 9 demonstrate the superiority of Versaflex ONE over both PMA and AA:AMPS in controlling calcium carbonate. In fact, the advantages of Versaflex One become even more pronounced at higher temperatures when calcium carbonate becomes even less soluble.

Figure 7: Calcium Carbonate Inhibition Bulk Water Temperature = 104°F

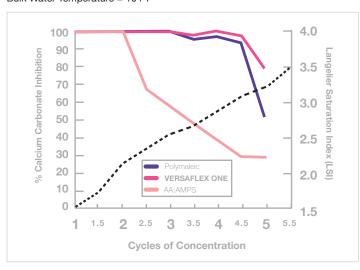


Figure 8: Calcium Carbonate Inhibition Bulk Water Temperature = 110°F

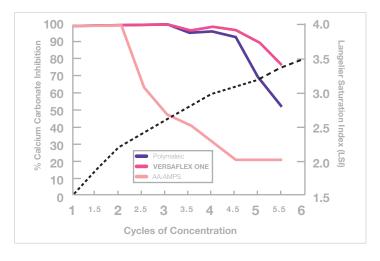
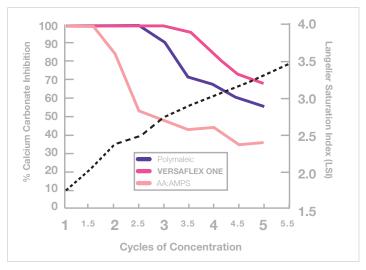


Figure 9:Calcium Carbonate Inhibition
Bulk Water Temperature = 132°F

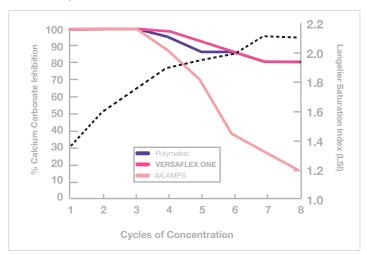


Performance At Lower pH Levels

Versaflex® ONE has also been tested against PMA and AA:AMPS under conditions of lower stress, at a pH of 8.3 and a bulk water temperature of 104°F.

Figure 10 shows that under these conditions, the performance of Versaflex ONE matched PMA and far exceeded AA:AMPS.

Figure 10: Calcium Carbonate Inhibition Bulk Water = pH 8.3

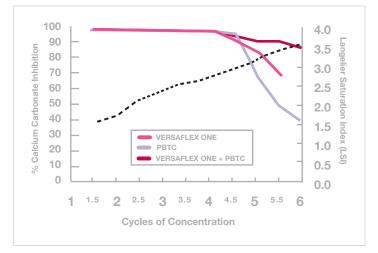


In Combination with PBTC

In most systems, a polymer is not the sole calcium carbonate inhibitor but is added in combination with a phosphonate. In high stress waters with LSI indices above 2.5, the most commonly used phosphonate is PBTC.

Versaflex ONE was tested at a concentration of 10 ppm in combination with 3 ppm PBTC. Figure 11 shows that the combination of Versaflex ONE and PBTC is superior to either Versaflex ONE or PBTC alone. In fact, the tests indicated that the combination treatment could allow operation at levels as high as 5.5 to 6.0 cycles of concentration, equivalent to waters with an LSI as high as 3.25 to 3.50.

Figure 11: Calcium Carbonate Control Polymer/PBTC Combination



Ortho-Phosphate Stabilization

Ortho-phosphate is commonly added to cooling water as a corrosion inhibitor. A test was conducted over a period of 33 days comparing Versaflex ONE with PMA and AA:AMPS. The test was performed with water conditions much like those used in previous testing, except that 400 mg/L NaCl was added to the make-up water to help increase initial corrosion rates. The bulk water was maintained at a pH of 8.7 to 8.8 and a temperature of 110°F. The cycles of concentration were carried up to 3.75 cycles and maintained for the duration of the test. All polymer dosage rates were maintained at 20.0 mg/L active polymer. No other calcium carbonate inhibitor was added.

Figures 12 through 16 indicate the cycles of concentration, pH, bulk water temperature, TDS and conductivity over time throughout the test. The results demonstrate that Versaflex ONE is a strong inhibitor for calcium phosphate. This benefit allows the user to:

- simplify formulations
- prevent deposition of phosphonate oxidation products
- provide effective corrosion control

Figure 12: Cycles of Concentration

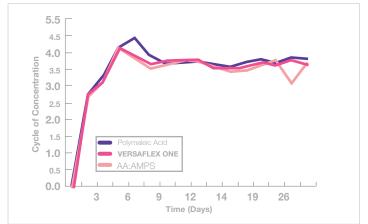


Figure 13: System pH

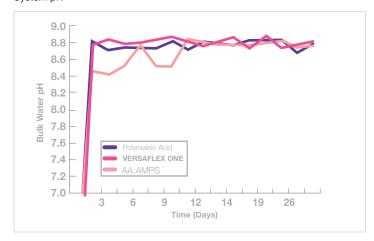


Figure 14: Bulk Water Temperature

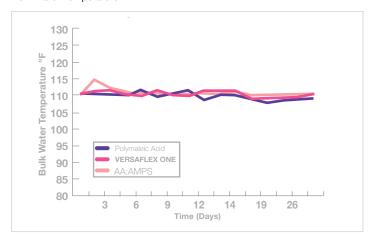


Figure 15: Total Dissolved Solids

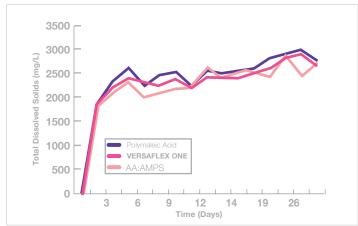
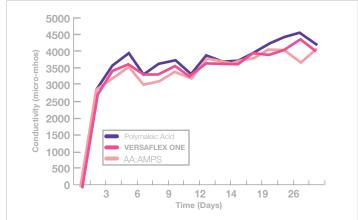


Figure 16: Conductivity



At the beginning of the test, no ortho-phosphate was added to any of the systems in order to obtain an untreated corrosion rate baseline of the water. This was accomplished after 9 days, and the test was then allowed to continue for 24 additional days with a dose of 3.0 mg/L ortho-phosphate. During this time, both ortho-phosphate concentration and corrosion rates were carefully monitored.

Figure 17 shows that both Versaflex® ONE and AA:AMPS were able to achieve and maintain the intended 3.0 mg/L ortho-phosphate in the system, while the PMA was not. In fact, the PMA was able to achieve only 1.75 mg/L, which gradually dropped to 1.25 mg/L by the end of the test. The remaining ortho-phosphate precipitated as calcium phosphate.

Figure 18 shows how the addition of ortho-phosphate was able to lower corrosion rates for all treated systems. However, only Versaflex ONE was able to achieve corrosion rates of less than 2.0 mpy (mils per year). The AA:AMPS was able to drop corrosion rates to only about 4.0 mpy, even though it was able to stabilize all the ortho-phosphate added to control corrosion. PMA performed better than AA:AMPS, dropping corrosion rates to around 2.50 mpy. Generally, corrosion rates above 2.0 mpy are considered unacceptable in field applications. Therefore, Versaflex ONE was the only truly acceptable treatment of the three tested at these conditions.

After the introduction of ortho-phosphate above, carbon steel C1010 coupons were added to the system's corrosion rack as a visual means of monitoring corrosion at test's end. Coupons were installed, each at the same corresponding location on each corrosion rack. The coupons were removed after the completion of the test and photographed to show the presence or absence of corrosion and/or scale deposits on the metal surface.

The photograph (Photo 2) shows the dramatic difference in the coupons exposed to the different treatments. The coupon from the system containing Versaflex ONE contains only a minor amount of general corrosion. The coupon from the PMA treated system also shows minor general corrosion but is coated with mineral scale. The coupon from the system treated with AA:AMPS copolymer shows severe corrosion.

Figure 17: Ortho-Phosphate Stabilization

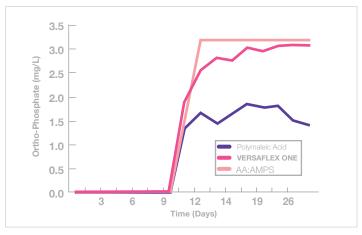


Figure 18: Mild Steel Corrosion

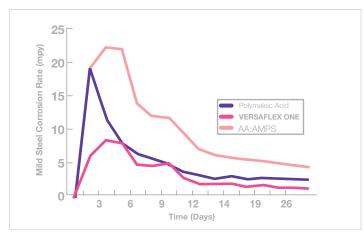
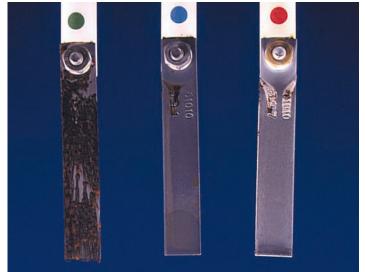


Photo 2:
Carbon Steel C1010 Coupons

■ AA:AMPS ■ Versaflex ONE ■ Polymaleic Acid



Zinc Stabilization

Zinc is a cathodic corrosion inhibitor that is typically used in combination with other inhibitors for cooling water. It is very rarely used alone and is usually dosed at a lower concentration than ortho-phosphate, with concentrations generally not exceeding 1.0–2.0 mg/L. Its solubility is severely reduced at pH values above 7.5, but can be improved significantly by polymers used for calcium phosphate control, such as AA:AMPS. The ability of Versaflex ONE to stabilize zinc further enhances its multifunctional properties. This provides the user with the following benefits:

- cathodic corrosion protection at high pH
- reduced general corrosion rates
- control of "white rust" in galvanized systems

Versaflex ONE, AA:AMPS and PMA were tested at 20 mg/L for their ability to stabilize various concentrations of zinc. These static tests were conducted at water conditions like those used for all dynamic testing. The cycles of concentration were maintained at 3.2 cycles, with a pH of 8.0 and a temperature of 122°F. These conditions produced an LSI index of around 2.7. The results can be found in the bar graph to the right.

Figure 19 shows that Versaflex ONE was able to stabilize zinc as well as AA:AMPS at concentrations commonly used in the field for corrosion control.

Since the actual result desired from zinc stabilization is lower corrosion rates, it is important that additives do not over-stabilize zinc. Tests that monitored corrosion rates as they related to the presence and stabilization of zinc were conducted. Two solutions were prepared, each at 2.5 cycles of concentration and treated with 20 mg/L Versaflex ONE. The initial pH of each solution was 8.7. The bulk water temperature was kept constant at 104°F. All these conditions produced an LSI of about 2.5, but no additional calcium carbonate inhibitor was added. The Versaflex ONE acted alone as the calcium carbonate inhibitor. To one of the solutions, two doses of 0.5 mg/L zinc were added once the corrosion rate climbed above 2.5 mpy. No zinc was added to the other solution, so that a corrosion baseline could be obtained for an untreated system. The results can be found on the graph to the right.

Figure 20 demonstrates that the treated system maintained a corrosion rate of around 1.5 mpy, while the corrosion rate of the untreated system climbed to above 6.5 mpy. This is due to the ability of Versaflex ONE to stabilize zinc, allowing it to provide its desired cathodic protection.

Figure 19: Zinc Stabilization

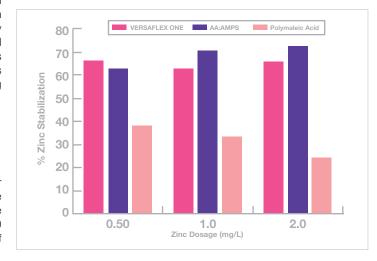
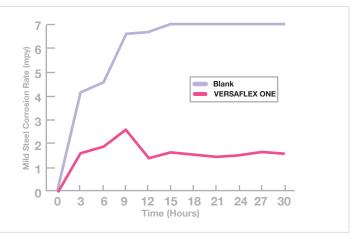


Figure 20: Versaflex ONE Mild Steel Corrosion Control



Deposit Control

Perhaps the greatest benefit of Versaflex ONE is its ability to prevent surface deposition. An example of this property was documented during the ortho-phosphate stabilization test described earlier. During this test, the degree of scale deposition was photographed and quantified for each polymer treatment. This unmatched property provides the user with the following benefits:

- · maximization of heat transfer
- elimination of under-deposit corrosion
- continued operation during upset conditions

Photos 3 and 4 clearly show the dramatic difference between the cleanliness of the rod from the Versaflex ONE treated system versus the rods from the other two treated systems. After photographing, each rod was cleaned in a known volume of 2.5% nitric acid until all the scale and deposits were dissolved. This solution was then analyzed for calcium carbonate and calcium phosphate. The analysis results were then converted from concentrations in mg/L to the actual weight of each component deposited on the rod in mg. These converted results can be found in Figures 21 and 22.

Photo 3:
Heat Exchanger Rods (Glass)

■ AA:AMPS ■ Versaflex ONE ■ Polymaleic Acid







In addition to the rods themselves, the glass surrounding the rods also accumulated a large amount of scale deposits on the inner surface. Photographs were then taken of the rods and glass, side by side. Photo 3 clearly documents the extraordinary ability of Versaflex® ONE to prevent adherent deposition under extreme conditions.

These photographs document a single example of the performance of Versaflex ONE. In every dynamic testing condition in which treatments were taken beyond calcium carbonate threshold inhibition failure, Versaflex ONE maintained amazingly clean heat exchangers to a degree that has never been seen with other treatments.

Figure 21 shows the relative effectiveness of Versaflex ONE in preventing deposition of calcium carbonate versus AA:AMPS and PMA.

Figure 22 shows the relative effectiveness of Versaflex ONE in preventing deposition of calcium phosphate versus AA:AMPS and PMA. Note that Versaflex ONE is as effective as AA:AMPS, which is specifically intended for use as a phosphate inhibitor.

Figure 21: Calcium Deposit Weights on Heat Exchangers

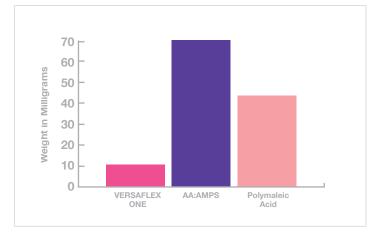
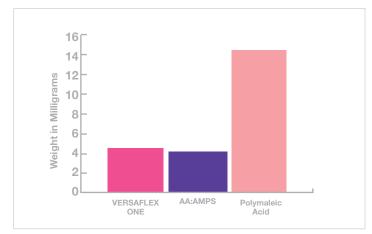


Figure 22: Phosphate Deposit Weights on Heat Exchangers



Stability in Harsh Environments

In many systems where the potential for severe calcium carbonate fouling exists, extreme levels of other contaminants such as iron, suspended or dissolved solids and high levels of halogens may be present. It is essential that additives maintain their stability and performance in the presence of such contaminants. The unique composition and manufacturing method of Versaflex ONE provide polymer stability in harsh conditions. This stability benefits the user by:

- providing continued control where phosphates fail
- allowing the use of hyper-halogenation
- continuing effective control where there are high levels of suspended and dissolved solids

Resistance to Iron "Poisoning"

Maleic polymers such as PMA are typically regarded as good calcium carbonate inhibitors. However, they can be susceptible to losses in performance due to the presence of high concentrations of iron. This can result in premature failure of the maleic polymer for calcium carbonate control in situations where corrosion is high or there is iron present in the make-up water. Versaflex ONE, however, is not negatively affected by iron and is able to effectively control calcium carbonate in the presence of relatively high concentrations.

Figure 23 shows the ability of as little as 5 ppm of Versaflex ONE to stabilize ferrous iron at cycles of concentration up to 3.5, and the ability of higher concentrations to be effective at even higher cycles.

Figure 24 demonstrates the ability of Versaflex ONE to stabilize soluble iron, allowing it to remain effective as a calcium carbonate inhibitor.

Versaflex ONE, AA:AMPS and PMA were evaluated in static tests for their calcium carbonate inhibition performances in the presence of various concentrations of ferrous iron. This test was conducted at 4.0 cycles of concentration, with a pH of 8.80 and a bulk water temperature of 122°F. These conditions correspond to an LSI index of around 2.8. The results can be found in Figure 25.

Although there is a slight decrease in the performance of Versaflex ONE from 68% inhibition to 62% inhibition, there is a much more significant decrease in the performance of PMA, from 58% inhibition to 38% inhibition.

There is also a decrease in the performance of AA:AMPS. However, since its performance was very poor to begin with, it is difficult to compare it to the other two treatments.

Figure 23: Ferrous Iron Stabilization

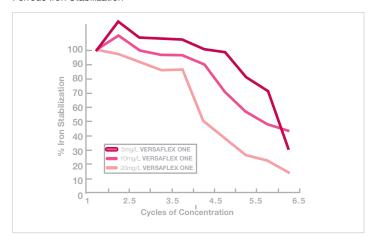


Figure 24: Ferrous Iron Stabilization

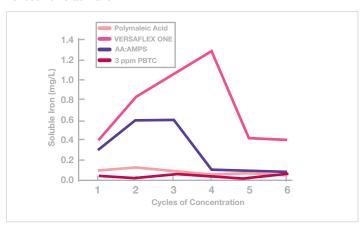
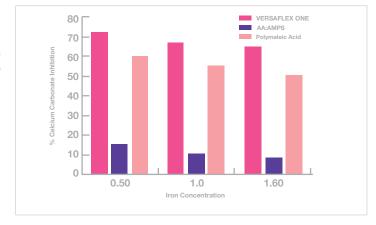


Figure 25: Calcium Carbonate Inhibition in the Presence of Iron

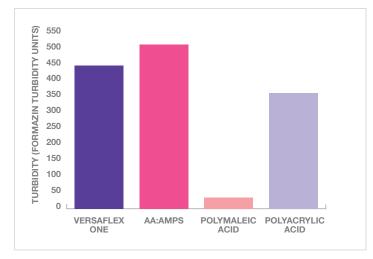


Suspended Solids Dispersion

One of the key advantages of Versaflex® ONE is its ability to disperse and suspend particulates, preventing their deposition in low flow areas. To document this, Versaflex ONE was evaluated for its dispersancy capabilities against several competitive products. The results indicate that the performance of Versaflex ONE compares favorably to that of standard polyacrylates and AA:AMPS copolymers, while the maleic homopolymer does not perform nearly as well after 24 hours.

The results, expressed in Formazin Turbidity Units, can be seen in Figure 26.

Figure 26: 24-Hour Kaolin Clay Dispersion

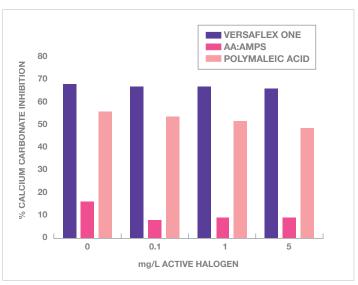


Exposure to Halogens

Versaflex ONE was also evaluated in static tests for its calcium carbonate inhibition performance in the presence of high concentrations of halogens. Stability of additives in the presence of halogens is important in conditions encountered during hyper-halogenation, which is sometimes required for control of problematic bacteria such as *Legionella*. Additionally, it is well documented that many phosphonates are readily degraded in the presence of halogens. Degradation of phosphonates results in loss of performance and generation of orthophosphate. The performance of Versaflex ONE as a strong inhibitor for calcium carbonate and calcium phosphate make it an excellent choice in systems where phosphonate degradation may occur.

Figure 27 shows that there was very little to no change in the performance of Versaflex ONE. There was a small decrease in the performance of the PMA, from 55% inhibition to 48% inhibition. This test was conducted at 4.0 cycles of concentration. The oxidizer chosen was a blend of 1-bromo-3-chloro-5,5-dimethylhydantoin, 1,3-dichloro-5,5-dimethylhydantoin, and 1,3-dichloro-5-ethyl-5-methylhydantoin. This blend results in a product that contains 39.2% available bromine and 44.4% available chlorine.

Figure 27: Calcium Carbonate Inhibition in the Presence of Halogen at 4.0 Cycles



Versaflex® ONE Outperforms the Competition

Based on the extensive testing described in this brochure, Versaflex ONE is best positioned versus PMA and AA:AMPS as illustrated by the icon below.

Figure 28: Versaflex ONE Competitive Performance

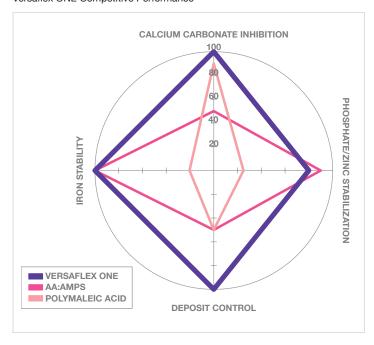


Figure 28 demonstrates that while PMA provides adequate calcium carbonate inhibition, it is not effective in stabilizing iron, zinc or phosphates and it does not prevent scale deposition. AA:AMPS, on the other hand, provides adequate stabilization of iron, zinc and phosphates but is not effective in stabilizing calcium carbonate or in preventing scale deposition.

Versaflex ONE, however, not only stabilizes calcium carbonate, iron, zinc and phosphates but also offers unprecedented protection against scale deposition.

Physical Properties

Versaflex ONE is supplied as a 40% aqueous solution at pH 4.5.

Storage and Handling

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

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

Versaflex ONE 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 ONE.

Feature	Benefits
Calcium carbonate control to LSI of 3.0+, 250X calcite saturation	 operates at increased cycles of concentration reduces concentration of additives for mild steel corrosion control reduces water consumption permits use of poorer-quality feed water eliminates use of acids
Stabilizes phosphate, zinc and iron	 simplifies formulations by requiring only one polymer prevents precipitation and deposition of phosphonate oxidation products prevents precipitation and deposition of heavy metals
Stable and effective in the presence of halogens	 provides continued control of deposit-forming scales where phosphonates fail allows use of hyper-halogenation for control of problematic bacteria such as Legionella
Effectively disperses and suspends particulates	 prevents accumulation of solids in low flow areas allows effective operation of systems with high levels of total suspended solids
Prevents deposition of mineral scales on heat exchanger surfaces	 maximizes heat transfer eliminates under-deposit corrosion avoids shutdown during upset conditions

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/

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