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# Advances in Deposit Control for Cooling Water Systems

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*The studies and conclusions reported in this paper are the results of the author's own work.  
The paper has been presented before and reviewed by the Cooling Tower Institute,  
and approved as a valuable contribution to cooling tower literature.*

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## Introduction

This paper presents laboratory and field data which documents the evaluation and effective application of a unique copolymer. This copolymer, SA/AA, is a significant advance in deposit control chemistry for use in cooling water systems.

Many recirculating cooling systems are now being operated to further conserve water because of environmental restrictions on discharge, the cost of water and its scarcity. Companies are tightening up their systems and operating at higher cycles of concentration by reducing or even eliminating blowdown. Other companies are finding it necessary to use poor quality water as makeup due to limited availability of good quality water and the high cost of clarification, softening, or filtration.

Cooling tower makeup water contains organics, muds, silts, metal oxides, and other colloidal suspended solids which enter the recirculating water and are concentrated. This particulate matter can settle out in heat transfer equipment causing fouling and loss of cooling capacity. The problem of fouling is further compounded by the buildup of suspended matter in the cooling water due to atmospheric particles of clay, dust, pollen, insects, etc., which are scrubbed from the air. Another source of foulant particles in recirculating water is migrating iron oxide corrosion products from a corroding part of the system, such as the distribution piping, which is transported and deposited on heat transfer surfaces.

The composition of muds and silts in a given system can vary depending on geographic location, but generally they are a mixture of hydrous aluminosilicates. Kaolinite, montmorillonite, illite and chlorite are the most common types of clay. Montmorillonite is the most reactive of the clays and will swell when immersed in water due to its cation exchange properties.

The forms of iron oxides found in cooling water systems are usually ferric oxide, hematite or hydrated ferric oxide, lepidocrocite or goethite. Magnetite found in cooling water systems enters as an air or water borne suspended solid. Magnetite is rarely formed in cooling water systems because its formation requires high temperature and/or anaerobic conditions.

Problems which are caused by water borne deposits include loss of heat transfer efficiency, reduction of water flow, increased underdeposit corrosion, increased scale formation, and in most cases, higher water usage due to increased blowdown.

## Factors Influencing Water Borne Deposition

The rate and amount of deposition is influenced by the interactions, both physical and chemical, between the water, suspended particles and system design. The larger, more dense particles will settle more rapidly than smaller particles. Higher water velocity will decrease the settling rate and slow deposition of suspended particles. Bulk water and heat transfer surface temperatures affect the rate of deposition.

The higher the temperatures, the greater the poten-

tial for deposition. High heat flux usually results in higher surface temperatures.

Biofouling produces a sticky matrix which is capable of trapping suspended solids and particles. Microorganisms also contribute directly to the suspended solids in the system.

Control of suspended solids can be done either mechanically, chemically, or by a combination of the two. Mechanical control involves increasing the linear velocity by increasing flow, reducing the cross sectional area, pretreating the makeup through clarifying or filtering, side stream filtration or softening and by periodic cleaning. Increased blowdown will also reduce the suspended solids level in the cooling water by reducing the cycles of concentration.

Chemical control is best achieved by dispersion of the suspended particles. The earliest dispersants used in cooling water systems were the naturally occurring polymers — starches, lignins, tannins and cellulose derivatives. Starch and cellulose act as nutrients for microbial growths. Improved dispersants based on modifications of these natural polymers were introduced in the 1950's; sulfonated lignins fall into this group.

During the 1950's, synthetic polymers were first utilized as dispersants. Performance characteristics of the synthetic polymers greatly exceed those of the original natural organic polymers. Synthetic polymers not only provided superior dispersion, but often functioned as effective scale inhibitors for calcium carbonate, calcium sulfate and calcium phosphate. Through the 1970's, the synthetic polymers emerged as the most effective approach for chemical control of water borne deposits. The polycarboxylates which includes polyacrylate found widespread use as dispersants. Other synthetic polymers used were polymethacrylates, polymaleic acid and acrylate copolymers. Until recently, polyacrylate has been considered the most effective dispersant of metal oxides and mud and silt suspended solids.

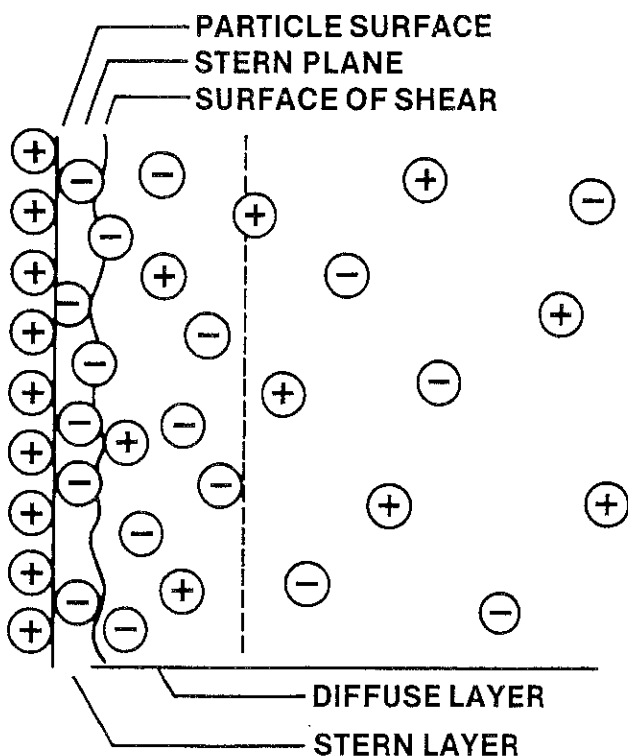
Before discussing some recent developments and improvements in dispersant chemistry, a review of the chemical/physical phenomenon of dispersion and the test methods used to identify and evaluate dispersants is in order.

## Electric Double Layer and Dispersion of Suspended Solids

The dispersion of suspended particles is a function of factors such as particle size, particle shape and the surface electrical properties, which in turn, influence particle-particle and particle-solvent interactions. Particle size and shape are determined by the specific process of formation and chemistry. Generally, iron oxide and clay particles common in cooling systems are more plate-like in shape than spherical.

Particles of iron oxide and clay acquire a surface electric charge when brought into contact with an aqueous medium. This charge occurs through the mechanism of ionization, ion adsorption and ion exchange in the lattice structure. This surface charge also influences the distribution of nearby ions in the water surrounding the particle. Ions of opposite charge are

Figure 1  
SCHEMATIC OF THE ELECTRIC DOUBLE  
LAYER ACCORDING TO STERN'S THEORY



attracted towards the particle surface and ions of like charge are repelled away from the surface. This, together with the mixing caused by thermal motion, leads to the formation of an electric double layer made up of the charged surface and surrounding counter-ions over co-ions distributed in a diffuse manner in the water. The electric double layer can be diagrammed from the model proposed by Stern, Figure 1.

The particle surface has an electric charge due to its crystal lattice or adsorption of potential determining ions. Specifically adsorbed to the particle surface are counter-ions, whose location are defined by the Stern plane. The Stern plane is the boundary between the inner part of the double layer and the outer or diffuse part, which consists of counter and co-ions. A surface of shear between the charged particles and the bulk liquid exists adjacent to the Stern plane (and is often equated with the Stern plane). The potential at this shear surface is known as the electrokinetic or zeta potential.

The stability of colloids and suspended solids is generally explained by the interaction of electrical double layer repulsive forces and van der Waals attractive forces. Random Brownian movement, thermal motion and induced mixing cause particles to come in close proximity with each other. If the repulsive forces predominate over the van der Waals forces, the particles will veer apart and remain in a dispersed state. This type of behavior is desirable in cooling systems, especially at the heat exchanger surfaces. Opposite behavior is needed in a thickener/clarifier where flocculation is desired.

Predominance of the repulsive forces can be enhanced by the addition of ionically charged chemical compounds. Since most colloids in nature have a negative charge, anionic (negatively charged) polymers in cooling waters will increase repulsive forces by adsorbing onto the particle surface and contributing their negative charge to the particle. The adsorption of polymeric material onto the particle surface also promotes stability through increased particle — solvent affinity.

### Measurement of Dispersion

The adsorption of polymers onto the surfaces of particles and the resulting dispersion phenomena can be measured in several ways. Instruments and techniques are available for determining the electrokinetic charge or zeta potential for specific particles. Measurement of the zeta potential before and after exposure to chemical treatment will reveal the change in the charge on the particle resulting from the chemical adsorption. Anionic chemicals adsorb onto the particles and increase the existing negative charge, a phenomena called charge reinforcement. If the particle charge is high, generally greater than  $-40$  millivolts, then the particles will repel one another and the colloid will be stable and dispersed.

The predominant method in use today of evaluating dispersion is by measurement of the light transmitted through a colloidal suspension. Clay and iron oxide suspensions are prepared with and without a dispersant. The suspensions are mixed and allowed to settle for a prescribed period of time. Aliquots of the suspension are then analyzed by spectrophotometric technique for transmittance. Water chemistry, pH, temperature, dispersant concentration, and agitation can all be varied to simulate cooling water conditions. Dynamic systems, primarily plants themselves, are the optimum test for determining dispersion because they contain all of the mechanical and chemical variables that impact on dispersion. The variables such as water velocity and shear stress, surface roughness and adhesiveability, degree of turbulency or the ability to shed fouling deposits, characteristics of the particles such as sticky or abrasive, and tube wall temperature variations all effect dispersion.

### Dispersion of Mud and Silt

A significant factor in keeping cooling tower systems operating free of corrosion and scale is to control deposits of mud and silts. Mud and silt will usually form hard, baked on deposits as they accumulate on heated surfaces. In addition to these deposits, mud and silt can be incorporated into water-formed scales, such as calcium carbonate, and act as nucleation sites for scale growth. They also interact with microorganisms in a cooling system by becoming entrapped in biofilms and supporting their growth.

The composition of muds in a given system can vary depending upon geographic location, but generally they will be a mixture of hydrous aluminosilicates all with phyllosilicate structure and very small grain size. Kaolinite, montmorillonite, illite and chlorite are the com-

monest clay types and were evaluated in a ratio of 50% kaolin, 30% bentonite, 10% illite and 10% chlorite in laboratory tests discussed in this section.

The primary chemical method for controlling mud and silt deposition is by dispersion. Since the clays, silts, metal oxides and other suspended solids encountered in a cooling water system are negatively charged, anionic polymers are effective in reinforcing the charge and improving dispersion. All anionic polymers vary in composition and charge density, however, and both of these factors significantly affect their dispersing properties.

The following discussion presents laboratory data which compares the performance of various traditional dispersants used in cooling water systems. Also included in the evaluations is a recently developed SA/AA (sulfonic acid/acrylic acid) copolymer.

The SA/AA copolymer has both a unique composition and a significant charge density which give it improved dispersing properties over other water treatment polymers. A high charge density allows for greater particle/particle charge interaction and modification.

In these tests, with water containing clays from all four clay groups, the performance of various polymers ranged from 0 to 100% dispersion as calculated from spectrophotometer light transmittance data. The factors of pH, temperature and settling time all impact on dispersant performance. Under the conditions of 130°F, pH 8.5, with 80 mg/L calcium and a settling time of four hours, the polymers were evaluated as a function of dosage, on an active polymer basis, Figure 2. Good dispersants generally are effective at relatively low dosages and their performance will plateau when this dosage is achieved. Of the polymers tested, only the SA/AA copolymer was capable of completely dispersing the clay in this test. One-hundred percent dispersion was achieved with 5 mg/l of the SA/AA copolymer. The other polymers of AA/HPA (acrylic acid/hydroxypropyl acrylate), PAA (polyacrylic acid), SP/MA (sulfonated polystyrene/maleic acid) and PMA (polymaleic acid) ranked below. This performance of the SA/AA copolymer was achieved at temperatures typical of those of heat exchanger surfaces.

The addition of HEDP, a common organic phosphonate scale inhibitor used in treating cooling systems does not significantly alter the dispersion by the SA/AA copolymer, even when evaluated at a 1:1 ratio, Figure 3.

Figure 4 shows the slight advantage gained in dispersion by operation at alkaline pH's. The SA/AA copolymer is an especially effective dispersant of clay at pH 8.5, giving 100% dispersion with 5 mg/l active polymer. Operation at alkaline conditions is conducive to improved dispersion because of the natural increase in particle charge, or zeta potential, that occurs as a function of increasing pH.

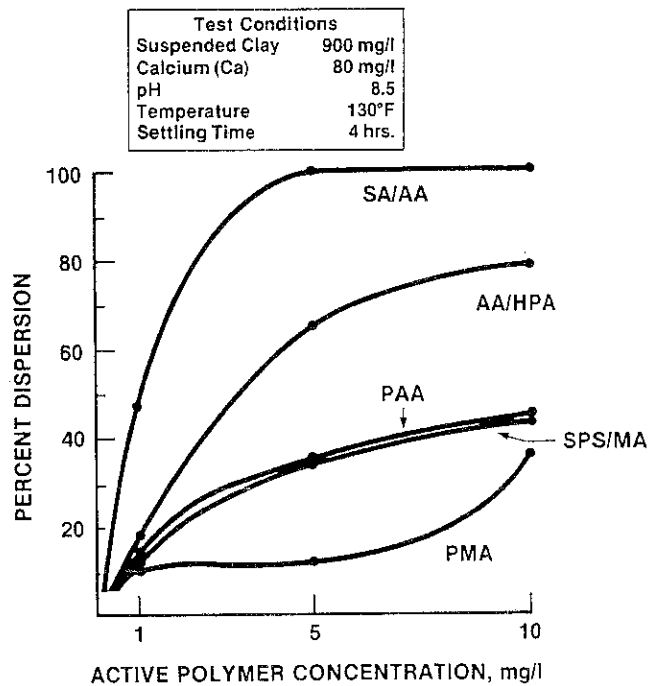
The superior performance of the SA/AA copolymer has been demonstrated in industrial cooling water systems over more traditional treatment programs. A utility station was using 5-10 ppm of a copolymer for suspended solids control. This 500 megawatt fossil fired generating unit had been derated to 460 megawatts due to backpressure limitations. Analysis confirmed that

80% of the deposits on the condenser were aluminum silicate clays. The continuous feed of the SA/AA copolymer, at 1 ppm active, was initiated to improve the system cleanliness and return it to its designed production capacity. In less than a week after start up of the new treatment, a dramatic cleanup was noted. The lost megawatt generating capacity had been recovered and the unit was now producing at 520 megawatts. This cleanup occurred in early 1985. The unit has remained clean and is continuing to operate at the 500 to 520 megawatt rating.

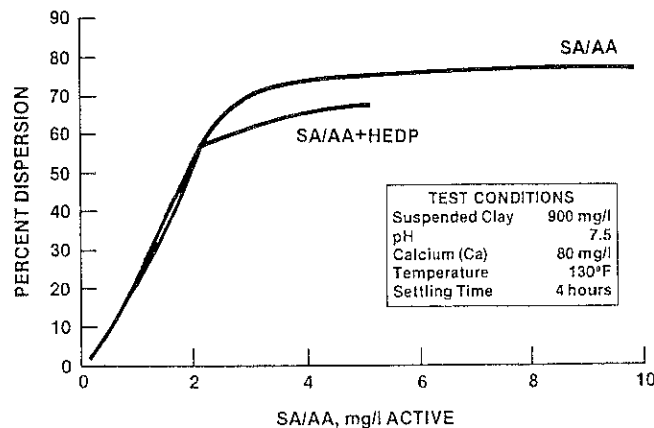
## Suspended Metal Oxide Control

The other suspended solids in cooling systems requiring stabilization and dispersion are iron oxides. Soluble iron from well waters and corrosion products rapidly

**Figure 2**  
**DISPERSION OF CLAY BY**  
**VARIOUS POLYMERS**



**Figure 3**  
**EFFECT OF ORGANIC PHOSPHONATE**  
**ON DISPERSION OF CLAY WITH SA/AA**



oxidize to ferric oxides. Several polymers were evaluated in laboratory tests for their ability to disperse iron oxide. As in mud and silt dispersion, a wide variety of performance was observed depending upon polymer composition.

Metal oxide dispersion testing was performed with 10 mg/l of freshly prepared amorphous ferric hydroxide (representative of corrosion products) added to synthetic cooling tower water having a pH of 7.9 and containing 400 mg/L HCO, 180 mg/L Ca, 20 mg/L Mg, 1000 mg/L Cl, and 1000 mg/L SO. The temperature was maintained at 70°C (158°F). The comparisons in Figure 5 demonstrate the effectiveness of polymeric building blocks as a function of time. No loss in dispersion ability with the SA/AA copolymer was observed for up to 72 hours at this high temperature.

Cooling water quality has a dramatic effect on the performance of polymers used for iron dispersion. Different concentrations of calcium were investigated in the presence of polyacrylate and the SA/AA copolymer so that the effect of calcium on iron dispersion could be determined. The test conditions examined 10 mg/l of each polymer. Figure 6 shows the continued good dispersant performance with SA/AA. Under the test conditions, calcium interferes with polyacrylic acid's performance as an iron oxide dispersant. Polyacrylic acid has a known poor tolerance to the calcium ion and will precipitate as calcium acrylate, leaving little polymer available for effective dispersion. SA/AA remains an effective iron dispersant even under high calcium ion concentrations because it is relatively insensitive to the calcium ion.

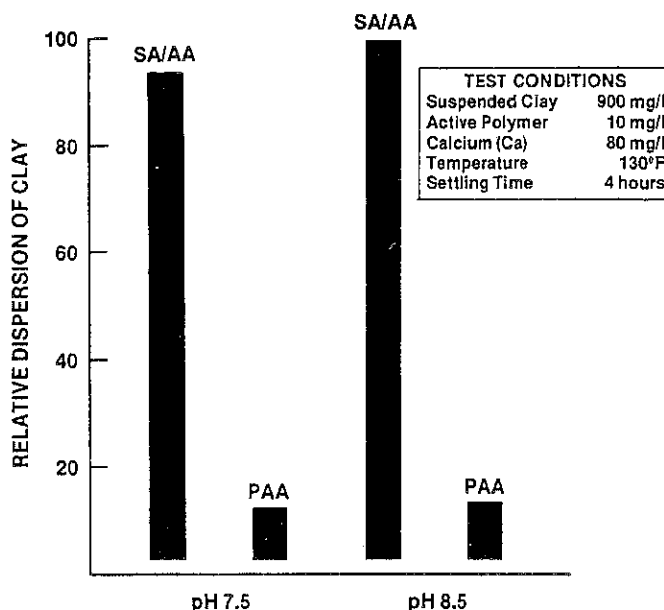
The addition of phosphonate, such as HEDP, in the iron dispersion tests did not adversely affect the dispersion of iron with the SA/AA polymer. This allows chemicals for calcium carbonate scale inhibition, and silt and metal oxide dispersion capabilities to be combined in an effective treatment program.

### Iron and Manganese Stabilization

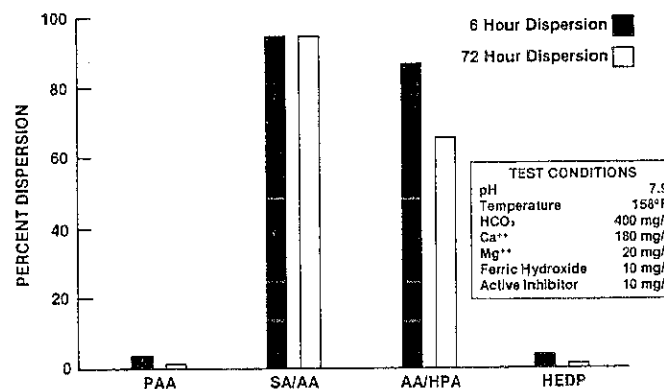
Soluble iron and manganese in makeup water sources can be stabilized by the SA/AA copolymer. The addition of HEDP to the SA/AA copolymer improves Fe & Mn stabilization. In stabilization, the oxidation of the soluble iron and manganese is not actually prevented but the SA/AA is adsorbed on tiny particles of iron oxide and manganese oxide and this keeps the individual particles separated and limits their growth to a colloidal size where settling can not occur. The particles are present as a well dispersed colloidal suspension but for practical purposes, the iron and manganese remain in solution. Both stabilization and dispersion contribute to the successful control of metal oxides in a cooling system.

Percent iron stabilization for several compounds is illustrated in Figure 7. Stabilization can be achieved by many compounds, but they require much higher dosages than the SA/AA+phosphonate combination or SA/AA alone. Results were achieved by analyzing water passed through a 2.5u filter paper after 2 hours for soluble iron content. Percent stabilization was calculated against an untreated control.

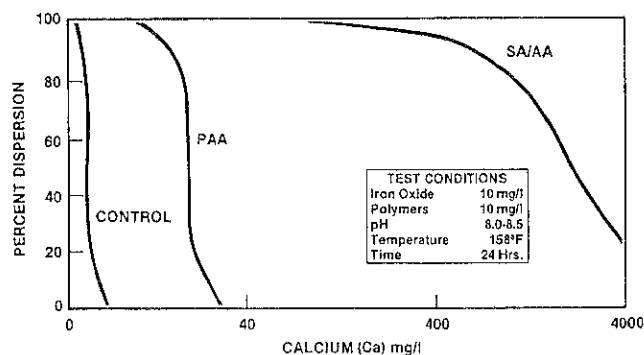
**Figure 4**  
EFFECT OF pH ON DISPERSION OF CLAY BY SA/AA COPOLYMER AND POLYACRYLIC ACID



**Figure 5**  
EFFECTIVENESS OF VARIOUS ORGANIC INHIBITORS FOR METAL OXIDE DISPERSION

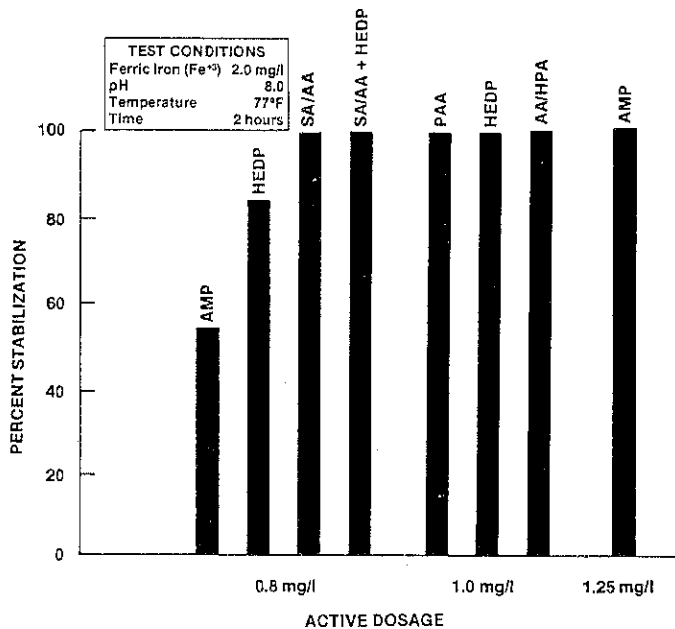


**Figure 6**  
IRON OXIDE DISPERSION VS CALCIUM CONCENTRATION FOR SA/AA COPOLYMER AND POLYACRYLIC ACID



The superiority of SA/AA+phosphonate organic treatment or SA/AA alone is also evident in the stabilization of manganese. Figure 8 compares the effectiveness of the SA/AA+phosphonate treatment versus phosphonates and polyacrylic acid in a similar test to that performed for iron stabilization.

**Figure 7**  
**SOLUBLE IRON STABILIZATION**



## Summary—Dispersion Case History

The effectiveness of the SA/AA copolymer for dispersion of suspended solids can be best summarized in the following case history of its application at an eastern U.S. chemical plant. At this plant, a mixture of water from four wells and a river supplies make up to a recirculating cooling water system. This water cools a sulfonation unit used in the manufacture of detergents for motor oil. Table I shows averaged analyses for both the composite and the individual waters. Iron levels ranged from 0.5 to 7.0 mg/l.

Tower supply water is distributed to four shell and tube heat exchangers, all with tube-side cooling. The critical exchanger is a six pass condensing unit with an admiralty tube bundle. Outlet water temperature for this exchanger approaches 160 F. Within the cooling water system, there are areas where velocity is less than 0.9 ft/sec.

Fouling of heat transfer surfaces was adversely impacting heat exchanger performance, increasing energy consumption, and reducing production. Downtime and maintenance costs for mechanical and chemical cleanings were frequent and significant. Iron oxide deposition was a serious problem.

The organic phosphonate/polyacrylate treatment being used in the system had not proven totally effective in controlling iron oxide deposition. Analyses of deposits from the critical exchanger also indicated both calcium organic phosphorus and calcium phosphate. Figure 9 illustrates the severity of the fouling problem, as

**Table 1**  
**AVERAGED WATER ANALYSES — CASE HISTORY**

	Cooling Tower Make-Up Water	Individual Make-Up Water Sources				
		Well Waters				River Water
		A	B	C	D	
pH	6.9	6.7	6.7	6.6	6.9	7.3
Total Alkalinity (CaCO <sub>3</sub> )	68	101	144	102	107	36
Conductivity; mmhos	426	470	730	375	330	195
Dissolved Solids	212	300	470	210	180	100
Suspended Solids	10	5	10	10	<5	10
Total Solids	230	315	480	225	180	115
Chloride (Cl)	19	22	47	11	11	16
Silica (SiO <sub>2</sub> )	6.6	8.9	10.0	9.3	8.4	3.4
Sulfate (SO <sub>4</sub> )	58	93	140	63	38	25
Orthophosphate (PO <sub>4</sub> )	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Fluoride (F)	0.2	0.2	0.2	0.2	0.3	0.2
Sodium (Na)	23	16	49	25	5	9
TOC	5.0	4.0	7.0	<1.0	2.0	1.0
Total Iron (Fe)	2.9	4.4	7.0	5.1	0.6	0.5
Total Copper (Cu)	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Total Manganese (Mn)	0.6	0.9	1.2	0.9	0.2	0.1
Total Aluminum (Al)	<0.1	<0.1	<0.1	0.1	<0.1	<0.2
Total Zinc (Zn)	<0.05	<0.05	<0.05	<0.05	<0.1	<0.05
Calcium (Ca)	31	58	72	35	56	18
Magnesium (Mg)	7	11	15	8	8	8
Total Hardness (CaCO <sub>3</sub> )	106	190	241	120	172	72

All species expressed in units of mg/l unless otherwise noted.

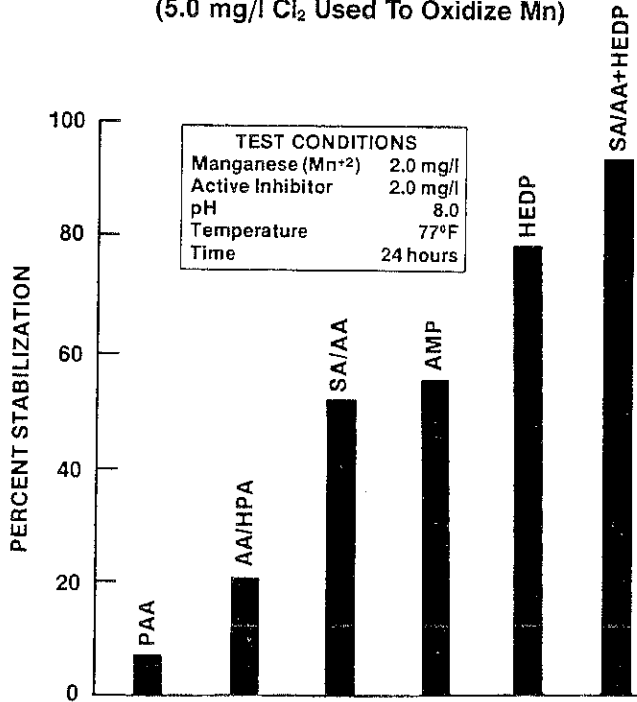
measured in a test heat exchanger connected to the tower return water line.

A change in the organic treatment was enacted to replace the acrylate in the product with the SA/AA copolymer. Also of concern was iron stabilization, corrosion, calcium tolerance, and scale control. The recirculating water was treated with 80 mg/L of a product containing SA/AA, mixed phosphonates and tolyltriazole.

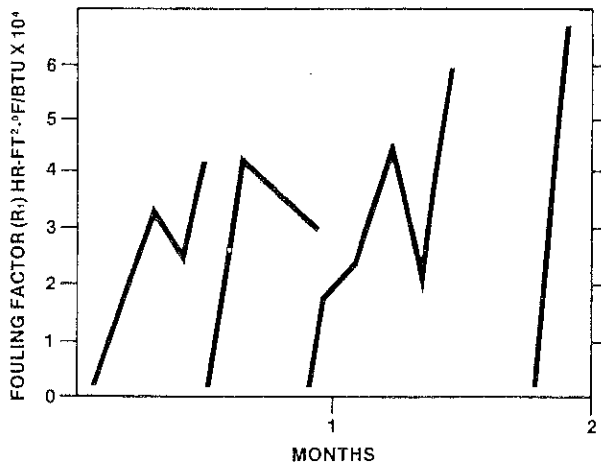
Results of the new SA/AA+phosphonate treatment were a significant improvement over the PAA+phosphonate treatment, Figure 10. On the test heat exchanger, there was no increase in fouling rates

and no buildup on the heater tubes during a month-long evaluation. The effectiveness of the SA/AA+phosphonate treatment in preventing fouling was confirmed at the critical exchanger when it was taken down for scheduled mechanical and acid cleaning. With the new treatment, daylight could be seen through the tubes and deposits that had been accumulated with the old treatment prior to the SA/AA+phosphonate usage had been conditioned so that the exchanger was simply water-washed and returned to service, without the need of the usual mechanical or acid cleaning. Analyses of some very small deposits that could be collected revealed no evidence of calcium phosphate or calcium organic phosphorus in the sample. Steel corrosion rates ranged from 1 to 4 mpy; admiralty corrosion rates were consistently less than 0.1 mpy. No mechanical cleaning has been necessary since the SA/AA treatment was initiated, over two years ago.

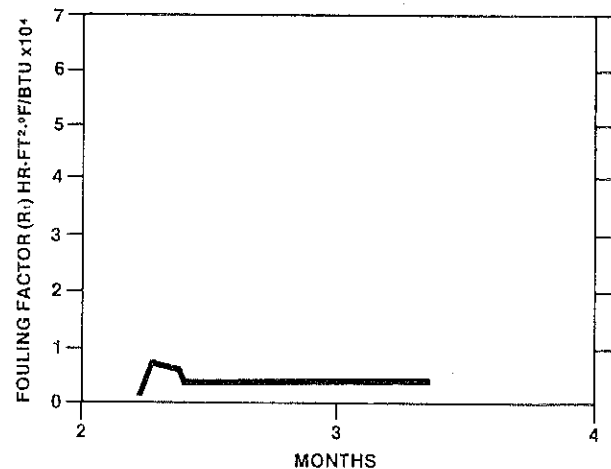
**Figure 8**  
**SOLUBLE MANGANESE STABILIZATION**  
(5.0 mg/l  $Cl_2$  Used To Oxidize Mn)



**Figure 9**  
**CASE HISTORY — TEST HEAT EXCHANGER**  
**FOULING FACTORS VS TIME WITH**  
**PREVIOUS POLYACRYLATE:**  
**PHOSPHONATE: TT TREATMENT**



**Figure 10**  
**CASE HISTORY — TEST HEAT EXCHANGER**  
**FOULING FACTORS VS TIME USING**  
**SA/AA: PHOSPHONATE: TT TREATMENT**



### Conclusion

Cooling water systems frequently experience operational problems due to fouling by muds and heavy metal precipitates. In this paper the properties of a new multifunctional copolymer, SA/AA, were discussed. Along with laboratory generated data, performance obtained on dynamic plant systems was presented.

The use of the SA/AA copolymer provides improved dispersion and stabilization of muds and metal oxides. Superior stabilization and dispersion is obtained at a neutral and alkaline pH and the performance of SA/AA does not deteriorate due to high calcium levels. Also, the SA/AA copolymer's compatibility with HEDP makes it possible to formulate a single product for silt and scale control.

### References

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- Cowan, J. C. and Weintritt, D. J., *Water Formed Scale Deposits*, 1976, Gulf Publishing Co.