



A NEW GENERATION OF COOLING WATER TREATMENT

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ABSTRACT

A newly developed inhibitor for calcium orthophosphate scale eliminates the disadvantages of existing inorganic phosphate corrosion control programs. Data show this new inhibitor to be a superior calcium orthophosphate inhibitor, an effective calcium carbonate and calcium sulfate inhibitor and a superior metal oxide deposit inhibitor. It not only has a higher calcium tolerance than other commonly employed scale and corrosion inhibitors, but also inhibits precipitation of commonly employed treatment components with calcium.

The superior calcium orthophosphate and iron oxide deposit inhibiting properties of this new inhibitor permit operation of inorganic phosphate corrosion control programs at elevated pH. The inhibitor is effective at alkalinity concentrations sufficiently high to allow reduction and, in many installations, complete elimination of acid feed for pH control. The utility industry can realize significant economic benefits from the improved performance, reliability, convenience and safety which result from application of treatment programs based on this new technology.

INTRODUCTION

Inorganic phosphates have been employed as cooling water scale and corrosion inhibitors for more than 40 years.⁽¹⁾ Their use in recirculating systems during the last 20 years has been largely precluded due to lack of an effective calcium orthophosphate inhibitor.

During the past two decades, environmental restraints created a need for cost-effective, environmentally acceptable corrosion inhibitors. Many utility industry personnel questioned the availability of such an inhibitor. As a result, during the 1970's, the electric utility industry endeavored to design the need for corrosion inhibitors out of new generating plants. With few exceptions, this effort has been unsuccessful. Many utility cooling systems are plagued with severe corrosion which results in expensive maintenance outages and costly equipment replacement. Corrosion damage is particularly severe in many auxiliary cooling systems.

Inorganic phosphates, along with an effective calcium orthophosphate inhibitor, were reintroduced as a cooling water treatment in 1979.⁽²⁾ The inhibitor, a copolymer of acrylic acid and hydroxypropylacrylate (AA/HPA), allowed maintenance of inorganic phosphate concentrations sufficiently high to provide effective carbon steel corrosion control in recirculating cooling water systems. Operation at neutral and moderately alkaline pH conditions was now achievable.

Other inhibitors for calcium orthophosphate have

been used during the past three years but, generally, they have been inferior to AA/HPA. The most commonly used inhibitors are polymaleic anhydride homopolymers, sulfonated homopolymers and carboxylate/sulfonated copolymers. As a result of this technology, inorganic phosphate based corrosion and scale control programs have received good reception and now are used widely in several industries. These programs allow maintenance of sufficient inorganic phosphate concentrations to provide excellent carbon steel corrosion inhibition, but precise pH control is still required. Alkaline pH excursions incur the risk of calcium orthophosphate precipitation. Acidic pH excursions destroy the protective oxide film, cause corrosion, and create the potential for metal oxide deposition as proper pH control is reestablished.

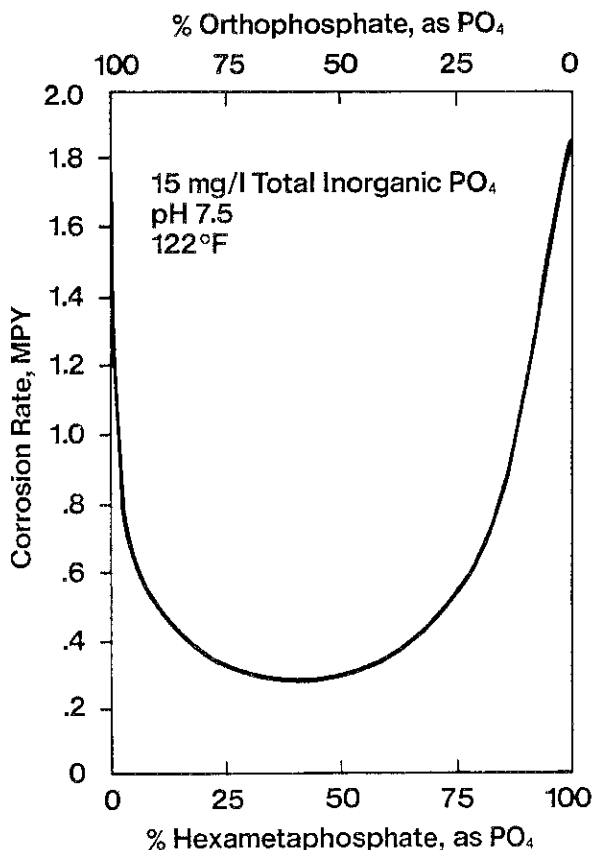
Recent research has resulted in a calcium orthophosphate inhibitor which overcomes the limitations of existing inorganic phosphate corrosion control programs. This new inhibitor is a copolymer of a sulfonic acid and an acrylic acid (SA/AA). This new, more effective calcium phosphate inhibitor allows operation of inorganic phosphate corrosion control programs at elevated pH. It is effective at sufficiently high alkalinity concentrations to minimize acid feed and, in many installations, allow complete elimination of acid feed for pH control. The significant economic benefits provided by this new generation of cooling water treatment include improved performance, reliability, convenience and safety.

CARBON STEEL CORROSION INHIBITION BY INORGANIC PHOSPHATES

Inorganic condensed phosphates are classified and named by varying and inconsistent methods and nomenclature.⁽³⁾ In order to conform to common practice, the term polyphosphate is used as encompassing all inorganic condensed phosphates. Polyphosphates most commonly employed in water treatment are hexametaphosphate (SHMP), tripolyphosphate, and pyrophosphate.⁽¹⁾ Polyphosphates, when dissolved in water, hydrolyze or revert to orthophosphate. The rate of reversion depends on many variables. Primary among these are temperature and pH. The commonly employed polyphosphates each provide similar degrees of carbon steel corrosion inhibition.

Polyphosphates provide effective inhibition of carbon steel corrosion.⁽⁴⁾ They are cathodic inhibitors, and divalent metal ions are required for them to function effectively as carbon steel corrosion inhibitors. Employed alone, polyphosphates provide most effective carbon steel corrosion inhibition near neutral pH. Their

Figure 1 — Effect of Polyphosphate/Orthophosphate Ratio on Steel Corrosion



corrosion inhibition effectiveness is relatively insensitive to electrolyte concentrations.

Orthophosphate also is an effective inhibitor for carbon steel corrosion.(4) It functions as an anodic inhibitor and promotes formation of a thin, dense protective iron oxide film. Inhibition of carbon steel corrosion with orthophosphate is a function of pH and improves with increasing pH. Increasing electrolyte concentrations, however, degrade its corrosion inhibition effectiveness.

Combinations of polyphosphate and orthophosphate are synergistic as carbon steel corrosion inhibitors (Figure 1).(4) This treatment functions in the mixed mode, that is, both anodic and cathodic inhibition are provided. Relative concentrations of ortho and polyphosphates are not critical. Concentration of either may vary between 20 and 80 percent of the total inorganic phosphate concentration. Typically, carbon steel corrosion can be controlled at less than 1 mpy with a concentration of 15 mg/l total inorganic phosphate. The orthophosphate-polyphosphate corrosion inhibitor pair is applicable above pH 6.0 and provides improved performance with increasing pH. This inhibitor system is moderately sensitive to chloride and sulfate ions. The required concentration of inhibitor increases with electrolyte concentration. While a slight increase in inhibitor concentration is required with increasing temperatures, the system is relatively insensitive to temperature.

CALCIUM PHOSPHATE INHIBITION

The degree of calcium orthophosphate supersaturation depends on the temperature, orthophosphate concentration, calcium concentration and pH of the cooling water.(5) Acceptable carbon steel corrosion inhibition typically requires an inorganic phosphate concentration in the 8–15 mg/l range. Typically 50–60% of the inorganic phosphate in a cooling water system is orthophosphate. Optimum operation of many cooling systems will result in concentrations of several hundred mg/l calcium ion and an elevated pH. These conditions represent a high degree of calcium orthophosphate supersaturation, and consequently the need for a superior calcium orthophosphate inhibitor.

Under controlled laboratory conditions, performance of SA/AA was compared with AA/HPA and polymaleic anhydride (PMA), two inhibitors widely used for calcium orthophosphate inhibition in inorganic phosphate corrosion control programs (Figure 2). Percent inhibition, as used in Figure 2, is defined by Var-sanik.(5).

The elevated pH and calcium concentrations of this performance evaluation represent a potential for calcium phosphate precipitation that very few systems treated with inorganic phosphate would exceed. Under these conditions, PMA has minimal threshold inhibition properties for calcium orthophosphate. Both SA/AA and AA/HPA provided 100% inhibition of calcium orthophosphate, but more than two times as much active AA/HPA was required as was required for SA/AA. Treatment with AA/HPA to provide 100% calcium orthophosphate inhibition under these conditions would not be cost effective.

SA/AA, AA/HPA, PMA and a commercially available maleic anhydride/ sulfonated styrene copolymer (PM/SPS) were compared at less demanding water

Figure 2 — Inhibition of Calcium Orthophosphate as a Function of Inhibitor Concentration

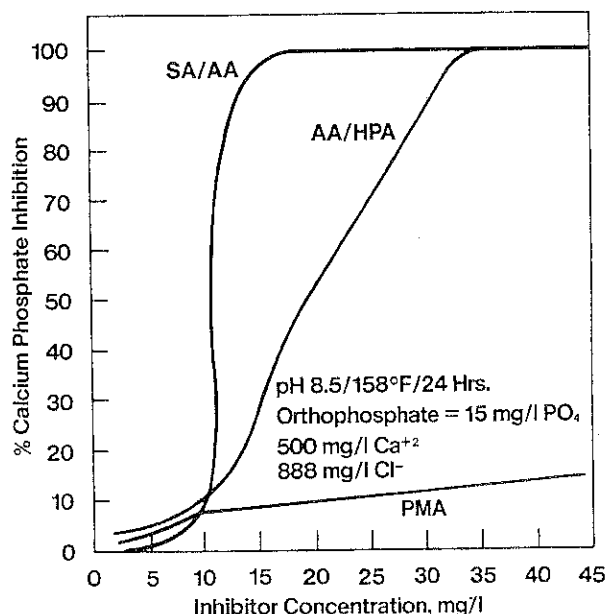
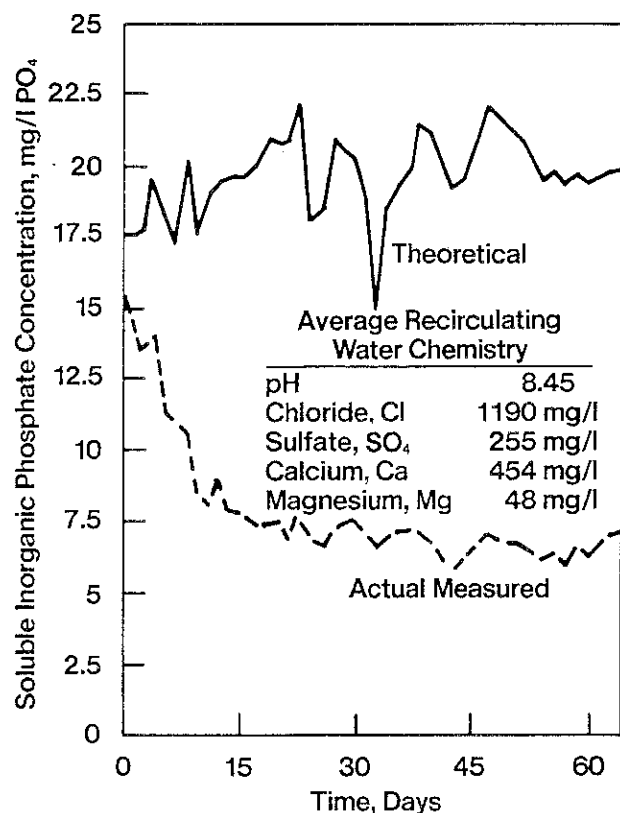


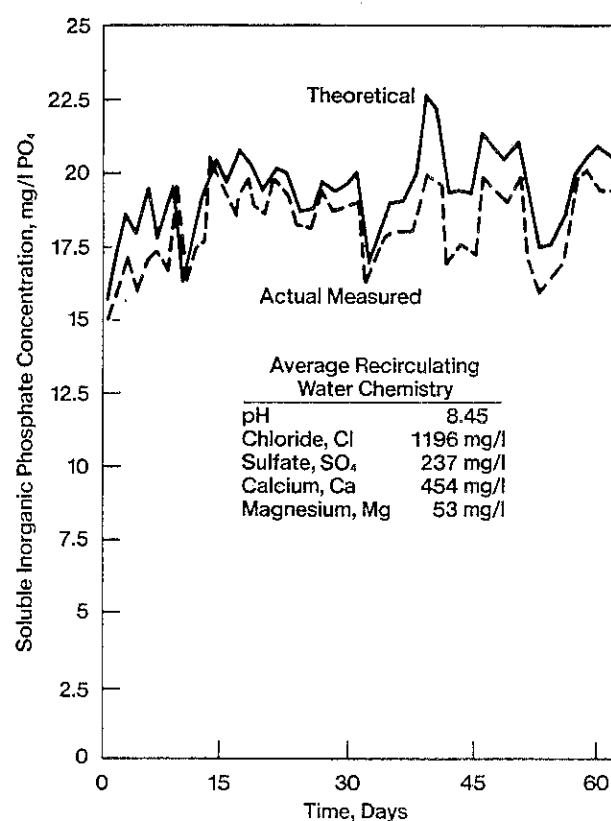
Figure 3 — Pilot-Scale Cooling System Soluble Phosphate Concentration vs. Time AA/HPA Treated System



quality conditions for 24 hours (data not shown). A PM/SPS copolymer was recently reported to have calcium phosphate inhibition properties superior to AA/HPA.⁽⁶⁾ At 140°F, pH 8.5, 200 mg/l calcium and 9 mg/l orthophosphate, 6 mg/l active SA/AA was required, compared to 18 mg/l of active AA/HPA, to achieve 100% calcium phosphate inhibition. Complete inhibition of calcium phosphate required 17 mg/l of PM/SPS. At 158°F, pH 8.5, 250 mg/l calcium and 6 mg/l orthophosphate, the difference in the SA/AA and AA/HPA required for complete inhibition was similar. More than 12 mg/l AA/HPA were required, relative to 5 mg/l active SA/AA. Under the latter conditions as much as 40 mg/l active PMA provided no more than 16% inhibition of calcium orthophosphate.

Performance of AA/HPA and SA/AA inhibited inorganic phosphate treatment programs were compared for a 63-day period in identical pilot-scale cooling systems. Water quality conditions were similar to those in the laboratory evaluation presented in Figure 2. Equal concentrations of active calcium phosphate inhibitor, an organic phosphonate, and a copper corrosion inhibitor were fed to each system. The control parameters for each of the two systems were: 124°F cooling water supply temperature, 146°F return water temperature, 8,600 BTU/hr-ft² heat flux for the series heat exchangers and 3 ft/sec tubeside linear cooling water velocity. The control point for the carbon steel corrosion inhibitor was 20 mg/l inorganic phosphate in the recirculating water. The theoretical recirculating water inorganic

Figure 4 — Pilot-Scale Cooling System Soluble Phosphate Concentration vs. Time SA/AA Treated System



phosphate concentration represents the inorganic phosphate concentration expected in the cooling water assuming no precipitation. The theoretical inorganic phosphate concentration reflected normal variations of a dynamic system. Actual analyses of cooling water inorganic phosphate concentrations were compared with the theoretical to provide an indication of the efficiency of the calcium phosphate inhibitors.

Performance data for the AA/HPA treated system are presented in Figure 3. Analyses showed the recirculating water to be grossly deficient in both soluble inorganic and organic phosphorous. Insufficient inhibitor remained in solution to prevent corrosion and scale formation. Inspection of the heat exchanger tubes showed them to be badly fouled with both calcium phosphate and calcium phosphonate.

Performance data for the SA/AA treated system are presented in Figure 4. Analyses of the recirculating water show the inorganic phosphate corrosion inhibitor and organic phosphonate inhibitors compared closely with theoretical. Inspection of the heat exchanger tubes showed they were clean and free of deposit. Excellent corrosion inhibition was provided by the treatment.

CALCIUM CARBONATE INHIBITION

The most effective threshold inhibitors for calcium carbonate are 1-hydroxyethylidene, 1-1-diphosphonic acid (HEDP), and aminotris (methylene phosphonic acid) (AMP). However, a limitation of phosphonates, espe-

Table I
Calcium Tolerance of Various Inhibitors

pH 8.3, 250 mg/l Ca ⁺² , 75°F	
Inhibitor	Tolerance Concentration, mg/l
PAA	9
HEDP	17
AMP	42
SHMP	135
PMA	530
AA/HPA	> 1300
SA/AA	> 1300

cially HEDP, is that they have a low tolerance for the calcium ion. That is, in high-pH/high-calcium water they form insoluble calcium compounds. Problems arising from precipitation of calcium phosphonate are twofold. The insoluble compounds deposit on heat exchanger surfaces, impede heat transfer and cause under-deposit corrosion. More importantly, precipitation of phosphonate results in loss of the calcium carbonate inhibitor. The relative tendency of several commonly employed inhibitors to form insoluble compounds with calcium at high pH is shown in Table 1. Calcium tolerance is the concentration of active inhibitor, under the constant water quality conditions, which resulted in precipitation. The data show SA/AA has excellent calcium tolerance.

In addition to its superior inhibition of calcium orthophosphate, SA/AA was found to be superior to all other inhibitors evaluated for inhibition of insoluble calcium/HEDP formation (Figure 5). Notice that not only did polyacrylic acid (PAA) not act as an inhibitor for calcium/HEDP formation, but it actually caused

Figure 5 — Inhibition of Calcium/HEDP Precipitation

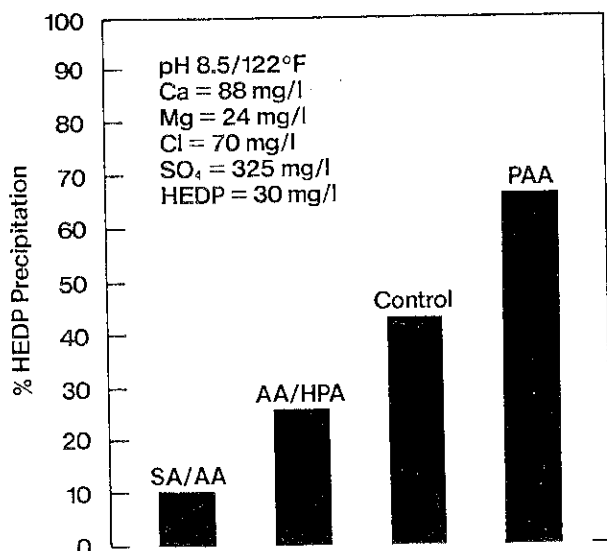


Table II
Threshold Inhibition of Calcium Sulfate

Minimum Requirement For 100% Inhibition 2000 mg/l Ca and 4800 mg/l SO ₄	
Inhibitor	Concentration, mg/l
PAA	2.7
SA/AA	3.7
AMP	3.9
AA/HPA	4.0
PMA	4.1
HEDP	7
SHMP	> 20

increased precipitation of HEDP. Even under demanding water quality conditions and an abnormally high concentration of HEDP, SA/AA provided essentially complete inhibition of calcium/HEDP precipitation. This is especially fortunate since HEDP is the most effective calcium carbonate inhibitor and is the ideal component for calcium carbonate inhibition in systems operating at high degrees of calcium carbonate supersaturation. The performance of SA/AA and HEDP are complementary in high-pH/high-cycle operation of inorganic phosphate treatment programs.

CALCIUM SULFATE INHIBITION

Many utility cooling systems operate above calcium sulfate supersaturation and an effective calcium sulfate inhibitor is required. The effectiveness of SA/AA was compared with other commonly employed calcium sulfate inhibitors and AA/HPA (Table II). Data show SA/AA to have superior calcium sulfate inhibitory properties; being surpassed only by PAA. The ability to operate cooling systems at very high pH and high cycles of concentration allows reduction, and for many systems complete elimination, of sulfuric acid feed for pH control. Reduction of sulfuric acid feed reduces the demand for calcium sulfate scale inhibition. Only in instances of very high makeup water calcium and sulfate concentrations would it be necessary to supplement treatments containing SA/AA in order to achieve complete calcium sulfate inhibition.

METAL OXIDE DEPOSIT INHIBITION

The success of any treatment program is highly dependent upon the prevention of deposition of dissolved metals and suspended metal oxides. Many cooling system makeup waters contain dissolved ferrous iron. Once the water containing ferrous iron is exposed to air, the iron is oxidized to less soluble ferric iron where it may precipitate as a hydrated oxide. SA/AA was compared with other inhibitors for precipitation inhibition of sol-

Table III
Ferrous Iron Stabilization

2 mg/l Fe ⁺⁺		
Inhibitor	Concentration, mg/l	% Inhibition
SA/AA	1	87
PAA	1	85
AA/HPA	1	46

Table IV
Ferric Iron Stabilization

2 mg/l Fe ⁺³		
Inhibitor	Conc. mg/l	% Inhibition
SA/AA	0.75	100
AA/HPA	1.0	100
PM/SPS	4.0	85
AA/AM	4.0	60
Lignosulfonate	4.0	60

Table V
Iron Phosphate Stabilization

7.9 mg/l PO ₄ , 4.6 mg/l Fe ⁺³			
Inhibitor	Conc. mg/l	% PO ₄ Stabilized	% Fe ⁺³ Stabilized
SA/AA	2	94	56
	3	98	96
AA/HPA	3	43	41
	4	100	92
	5	100	99

Table VI
Aquatic Toxicity of SA/AA

(Active Concentration < 50%)		
Species	Exposure Time, Hours	LC ₅₀
Bluegill Sunfish	96	> 10,000 mg/l
Rainbow Trout	96	4,900 mg/l
Daphnia	48	2,800 mg/l

uble ferrous iron and insoluble ferric iron. Table III shows the effect of the inhibitors on iron which was initially present as ferrous iron. Under the conditions employed, 90% of the ferrous iron was oxidized to ferric iron within 15 minutes. Data show SA/AA to be slightly better than PAA and very superior to AA/HPA for iron stabilization over a two-hour period.

Table IV shows the effectiveness of SA/AA, AA/HPA, PM/SPS, an acrylic acid/acrylamide copolymer (AA/AM) and lignosulfonate (LS) for inhibition of iron that initially existed as ferric iron. Data show SA/AA to be superior to AA/HPA for stabilization of insoluble ferric iron over a two-hour period. PM/SPS, AA/AM and lignosulfonate, which are employed in many cooling water treatment programs for control of iron deposition, have only marginal effectiveness relative to SA/AA.

Table V shows the relative inhibition effectiveness of SA/AA and AA/HPA on a mixture of ferric iron and orthophosphate over a two-hour period. Under these conditions, if not inhibited, part of the iron precipitates as the orthophosphate and part of it precipitates as the oxide. Again, the effectiveness of SA/AA was superior to AA/HPA.

Manganese often is present in cooling system makeup waters as the soluble divalent form. On aeration at elevated pH, the manganous ion will oxidize slowly to the tetravalent form and precipitate as manganese dioxide. SA/AA was found to be more effective in stabilizing oxidized manganese than AA/HPA over a 24-hour period.

AQUATIC TOXICITY

The impact of any cooling water treatment on the aquatic environment is of paramount importance. The toxicity profile in Table VI shows SA/AA to be quite innocuous.

BENEFITS OF A MORE EFFECTIVE CALCIUM ORTHOPHOSPHATE INHIBITOR

The new-generation calcium orthophosphate inhibitor presented here permits cooling system operation at higher calcium and alkalinity concentrations. This allows operation at higher cycles of concentration.

The following benefits of higher-cycle operation may be significant:

- Quantity of makeup water is reduced.
- Makeup water pumping costs are reduced.
- Quantity of required treatment chemicals is normally reduced.
- Quantity of discharge water is reduced.

The ability of many cooling systems to operate at higher cycles of concentration with existing treatment programs is limited, based on circulating water suspended solids concentrations. The superior deposit control properties of SA/AA, in combination with the deposit control properties of polyphosphate, permit higher concentrations of suspended solids to be maintained safely

in recirculating systems. Deposit control properties of an SA/AA-inorganic phosphate treatment program further contribute to the ability to operate safely at higher cycles of concentration.

For most utility cooling systems, the greatest benefit of SA/AA is the ability to operate at higher alkalinity concentrations by minimizing or eliminating acid feed. The benefits of minimizing acid feed are:

- Polycarboxylate scale and deposit inhibitors have a greater degree of ionization, and consequently improved performance with increasing pH.
- Acidic cooling water is very aggressive to many materials of construction. In addition to metallic surfaces, concrete and asbestos cement board are of special concern. Operation at higher alkalinity concentrations provides a greater acid neutralization capacity during periods of accidental acid overfeed that result from acid feed system and/or controller malfunction.
- Addition of sulfuric acid increases the cooling water sulfate ion concentration, which may impede corrosion inhibitor performance. Reduction in acid feed lowers the concentration of the sulfate ion.
- Concrete construction is employed for parts of many utility cooling systems. High concentrations of sulfate ion are aggressive to concrete. Reduction of sulfuric acid feed reduces the concentration of this aggressive ion.
- Reduced sulfuric acid addition lowers calcium sulfate scale potential and, consequently, the demand for calcium sulfate inhibition.
- Reduced acid consumption usually results in significant cost savings.

Two additional benefits are achievable by total elimination of acid feed:

- Maintenance costs of acid storage, feed, and control equipment can be eliminated. For most systems, cost savings are very significant.
- Concerns for the safety aspects of feeding acid and maintaining acid feed equipment are eliminated.

SUMMARY

Data have been presented which document the superiority of SA/AA over other calcium orthophosphate inhibitors. The degree of superiority over the next most effective and most widely used inhibitor is dramatic. This characteristic of SA/AA alone constitutes a significant advancement in cooling water treatment technology.

Many utility systems are provided with makeup water which contains orthophosphate. Ability to optimize operation of many of these systems has been limited due to the potential deposition of calcium orthophosphate. Application of SA/AA to these systems allows elimination of acid feed and operation at higher cycles of concentration. In most cases, this provides greatly improved system performance and a significant overall reduction in treatment costs.

Operation at high degrees of calcium sulfate super-

saturation is required by many utilities in the western United States. The superior calcium sulfate inhibiting properties of SA/AA provide complete calcium sulfate inhibition under these conditions. This performance characteristic may be beneficial to either systems operating on inorganic phosphate based programs or other programs requiring only scale and deposit control.

The weak element in many cooling water treatment programs is the control of metal oxide deposits. If metal oxide deposition is not controlled, microbial growth, corrosion, and often scale formation, cannot be controlled cost-effectively. Data presented demonstrate that the performance of SA/AA as a metal oxide inhibitor is superior to AA/HPA and PM/SPS. Superior performance can be realized in either inorganic phosphate-based treatment programs or in programs designed to inhibit only scale and deposits.

Inorganic phosphate programs dependent on other inhibitors not only have inferior calcium orthophosphate inhibition, but do not adequately complement the calcium carbonate inhibitors required at elevated pH. It was demonstrated that SA/AA not only has unequalled calcium tolerance, but is effective for the inhibition of insoluble calcium/inhibitor compounds that plague many treatment programs. Calcium tolerance and the superior calcium orthophosphate inhibition properties are key factors in the newly attained ability to advance to high-cycle/high-pH operation of cooling water systems. Recirculating cooling water alkalinity concentrations can now be permitted to rise to the point where only discharge regulations establish the upper pH limit.

The performance data presented here are laboratory and pilot system data, obtained under controlled conditions. These conditions represent cooling water needs of today. Each cooling system has specific water quality, design parameters and treatment objectives. Each treatment component has varying abilities to meet the varying needs of each specific system. The choice of optimum components and proportions for any specific system requires an extensive data base and many calculations. These calculations can be performed efficiently only by computer modeling. While the relative performance characteristics of the treatment components presented here will vary with changing conditions, they have been demonstrated to be valid over a wide range of cooling system conditions. The superior performance of treatment programs based on SA/AA has been verified in pilot-scale cooling systems using very demanding water quality and operating conditions. Treatment programs based on this technology are successfully operating in more than 25 cooling systems, in all parts of the country.

Development of a single compound that provides so many superior performance characteristics represents a significant achievement. Improved performance, reliability, convenience and safety features which result from these performance characteristics provide the utility industry with more economical options for treatment of cooling water. Inorganic phosphate corrosion control programs are the most cost-effective, environmentally acceptable corrosion control programs available to the utility industry today.

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