

New Non-Phosphorous Calcium Carbonate Inhibitor Reduces Phosphorus Levels and Overcomes Limitations of Phosphonates

Author: G. E. Geiger

Introduction

Modern cooling water treatments can be broadly classified according to the pH range over which they operate. Treatment programs can be divided into those that operate at near-neutral pH (6.8 to 8.0) or alkaline pH (>8.0).

Near-Neutral pH Technology

The near-neutral pH programs require the addition of acid for pH control and, because of the low alkalinity of the cooling water, tend to be corrosion inhibitor intensive. These treatments generally employ high levels of inorganic phosphate (10 to 25 ppm as PO_4) to control the corrosion of steel.^{1,2} The phosphate can be orthophosphate, polyphosphate, or a combination of the two. Since polyphosphates revert (hydrolyze) to orthophosphate, the rate of reversion is an important consideration when designing a treatment program. Zinc, molybdate and organic phosphate may be incorporated in the treatment to minimize the amount of inorganic phosphate required for steel corrosion protection. Azoles, e.g., tolyltriazole, benzotriazole and butybenzotriazole, are used for the protection of yellow metals.

The performance of the inorganic phosphate-based programs is most dependent on the use of a calcium phosphate inhibitor to prevent scaling of heat transfer surfaces and precipitation of phosphate in the cooling water. If calcium phosphate cannot be adequately controlled, corrosion and deposition will occur. When zinc is included, the inhibitor must also be capable of preventing zinc phosphate precipitation and scaling.

Alkaline pH Technology

Alkaline programs operate with or without acid addition under conditions where the cooling water is supersaturated with calcium carbonate. The degree of calcium carbonate supersaturation is commonly expressed as the Langelier Saturation Index (LSI). Because of their higher pH, alkalinity and calcium carbonate supersaturation, alkaline waters (pH >8.0) have a greater potential for scaling and a lower potential for corrosion than near-neutral pH waters. In most cases, the LSI of the circulating water dictates the relative ratio and the amount of deposit control agent and corrosion inhibitor. High LSI (> +2.0) water requires more scale inhibitor but less corrosion inhibitor than low LSI (+1 to +2) water.

The composition of alkaline programs is similar to that of near-neutral treatments, except that less corrosion inhibitor is needed and a calcium carbonate deposit control agent is required. Steel corrosion inhibition is achieved with low levels of inorganic phosphate (3 to 8 ppm as PO_4), zinc (0.5 to 3 ppm, molybdate (5 to 15 ppm), and/or phosphonate (3 to 8 ppm). Phosphonates and polymers are used for deposition control. The polymers disperse particulate matter and, depending on the corrosion inhibitor package, inhibit precipitation of zinc salts and calcium phosphate.

Virtually all programs utilize a phosphonate for calcium carbonate control. Since their development over 25 years ago, phosphonates have remained the benchmark for preventing calcium carbonate precipitation and deposition. In addition to scale control, phosphonates contribute to steel corrosion inhibition.^{3,4,5} The most common



Find a contact near you by
visiting gewater.com or
e-mailing custhelp@ge.com.

Global Headquarters
Trevose, PA
+1-215-355-3300

Americas
Watertown, MA
+1-617-926-2500

Europe/Middle East/Africa
Heverlee, Belgium
+32-16-40-20-00

Asia/Pacific
Shanghai, China
+86-21-5298-4573

©2006, General Electric Company. All rights reserved.

*Trademark of General Electric Company; may be registered in one or more countries.

TP404en Jun-06

phosphonates used today are hydroxyethylidenediphosphonic acid (HEDPI) and phosphonobutanetricarboxylic acid (PBTC). Other phosphonates include hydroxyphosphonoacetic acid (HPA) and complex aminophosphonates (CAP). HPA is primarily a steel corrosion inhibitor, but exhibits scale control properties when used at sufficiently high dosages.

Phosphonates are the cornerstone of alkaline technology and have served industry well, but they are known to have limitations. Phosphonates are susceptible to both degradation by oxidizing biocides and precipitation with calcium. Oxidation by halogens, e.g., hypochlorite and hypobromite, degrades or destroys the phosphonates' scale inhibiting properties, and produces orthophosphate. Operating at low halogen residuals can minimize Phosphonate degradation or using a stabilizing agent.⁶ The calcium tolerance (solubility) of the phosphonate generally limits the maximum dosage that can be maintained in the cooling water. Under standard conditions of operation, i.e., in the absence of high pH excursions or over-cycling, calcium solubility limitations can be overcome by using a highly calcium-tolerant phosphonate or an inhibitor that prevents calcium phosphonate precipitation.^{7,8}

Alkaline treatments have gained in popularity over the past few years because of their low environmental impact (low phosphorus and zinc discharge) and their ability to eliminate or reduce acid addition for pH control. Restrictions on phosphorus discharge are under continuous review by state environmental agencies, and limits have been imposed to prevent overloading receiving waters. For example, phosphorous effluent discharge is restricted to less than 3 ppm PO₄ (1 ppm as P) in the Lake Michigan Basin. Operating without acid for pH control eliminates the possibility of acid overfeeds and the associated accelerated corrosion. For systems feeding acid, the high buffering capacity of alkaline water minimizes the adverse effects of acid overfeeds.

Non-Phosphorous Alternative to Phosphonate

Alkylepoxycarboxylates (AEC) has been recently developed as replacements for the phosphonate scale inhibitors used in alkaline programs. The AEC

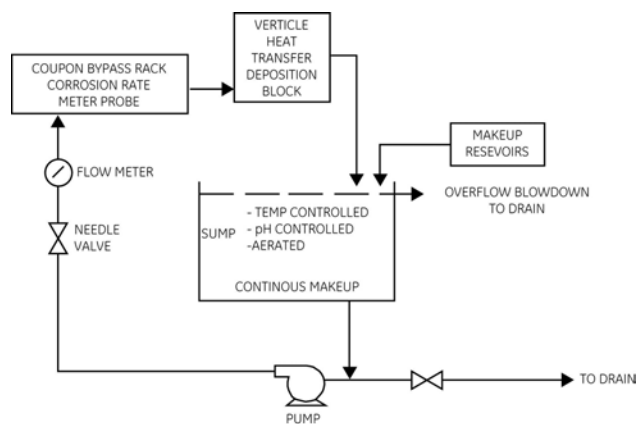


Figure 1: Recirculator unit

compounds are equivalent or superior to phosphonates as calcium carbonate inhibitors, but do not have the halogen instability and calcium tolerance problems.⁸ These properties provide a greater degree of safety during upset conditions that can lead to rapid calcium carbonate scaling. Because of their high calcium tolerance, the AEC dosage can be increased during upset conditions to prevent scale formation without encountering treatment-induced fouling of heat transfer surfaces.

In addition to its ability to inhibit calcium carbonate deposition, AEC is an effective precipitation inhibitor for zinc hydroxide.

Laboratory Evaluations

Experimental

Laboratory studies were performed under recirculating, heat transfer conditions. The unit used for testing simulates conditions encountered with industrial heat exchangers, albeit in most cases, test conditions are chosen to be more severe.

Figure 1 is a diagram of the unit. In this unit, water is continually circulated via a constant displacement pump from an 11-liter sump through a bypass rack composed of a series of pipe tees. From the bypass rack, flow is channeled past a heat exchange surface and returned to the sump. Corrosion testing is accomplished in one of two ways. The first method allows for corrosion coupons to be inserted into the bypass rack. Corrosion rates are measured by differential weight loss. The second method allows for the installation of electrochemical test probes that permit instantaneous corrosion rates to be measured.

Table 1: Test conditions

Water Chemistry	Operating Parameters
400 ppm Ca, as CaCO ₃	Water Temperature 120°F (49°C)
150 ppm Mg, as CaCO ₃	Skin Temperature 135°F (57°C)
210 ppm M Alk., as CaCO ₃	Heat Flux 8000 Btu/ft ² -h 21700 kcal/m ² -h
50 ppm SiO ₂ , as SiO ₂	Water Velocity 2.8 ft/sec (0.85 m/sec)
2400 µmhos (µS cm ⁻¹) Conductivity	System half-life 0.9 days "Retention time" : 1.3 days
8.6 pH	Test Duration 7 days

The process side of the heat transfer surface is filled with a heat transfer medium and fitted with an electric heater. The heat load (flux) or surface temperature is adjusted by controlling the power to the heater. The unit is designed so that the water velocity past the coupons and heat transfer surface is equivalent, and controllable up to 5 ft/sec (1.5 m/sec). pH control is automatic and accurate to within 0.2 pH units. Circulating water temperature is controlled automatically to the desired range by heating and cooling elements in the sump.

The waters used for testing are prepared by chemical addition to deionized water. Provisions for continuous makeup and blowdown are made by pumping from supply tanks to the sump. Overflow from the sump serves as blowdown. The system retention time (half-life) is defined by the makeup water rate. Two separate feed solutions are used as makeup. The chemical composition of the feed solutions are such that when they mix in the sump the resulting water has the desired chemical composition.

Low carbon steel (AISI-1010) and admiralty brass (CDA-443) coupons are used to determine corrosion rates. Low carbon steel (AISI-1010) heat exchanger tubing is used for the heat transfer surface. With the exception of degreasing and scrubbing with a mild abrasive, metal surfaces are not pretreated or conditioned prior to exposure.

Water chemistry and test conditions are shown in Table 1.

Results

Laboratory testing compared the performance of AEC to phosphonate in alkaline-phosphate and Alkaline-zinc programs. A scale-prone water (LSI=2) was chosen for testing purposes, but inhibitor concentrations were adjusted to ensure that fouling would not occur. During short duration testing, scale deposits can act as a barrier film and suppress corrosion. Eliminating deposition provides a fair assessment of the scale inhibitor's contribution to corrosion inhibition. This is particularly important when eliminating phosphonate in a treatment, since it can play a significant role in steel corrosion protection.

Chlorine was not used in the testing in order to avoid phosphonate destruction. Two of the phosphonates (CAP and HPA) included in the evaluations are known to be very susceptible to oxidation.

The alkaline-phosphate treatment program used for comparative purposes contained orthophosphate, tolyltriazole, copolymer and phosphonate or AEC. The copolymer served as the calcium phosphate inhibitor, and its concentration was adjusted to prevent calcium phosphate precipitation in the bulk circulating water and deposition at the heat transfer surface. All studies contained equivalent amounts of tolyltriazole. Studies performed with phosphonate contained 4 ppm orthophosphate, while the AEC program was run with 3 ppm orthophosphate. The phosphonates were evaluated at equivalent dosages, based on the active component in the acid form.

As can be seen in Table 2, excellent corrosion rates were obtained with all of the treatments. Localized corrosion was not significant with any of the programs, indicating that preventing phosphate precipitation did not impair its action as a cathodic inhibitor. The results of these tests clearly demonstrate that AEC can be substituted for phosphonate without a loss in steel corrosion protection. Environmentally, the AEC program offers the advantage of lower total phosphate levels, which may be an important consideration for the direct discharge of cooling tower blowdown.

Table 2: Alkaline-Phosphate test results

CaCO ₃ Inhibitor	Total Phosphate (ppm as PO ₄)	Coupon Corrosion Rate mpy (mm/y)	
		Steel	Brass
AEC	3.0	0.51 (0.013)	0.08 (0.002)
HEDP	9.5	1.30 (0.033)	0.08 (0.002)
HPA	8.0	0.51 (0.013)	0.08 (0.002)
CAP	9.5	1.79 (0.020)	0.08 (0.002)
Total Phosphate = Orthophosphate + Organic Phosphate			

Table 3: Alkaline-Zinc test results

CaCO ₃ Inhibitor	Total Phosphate (ppm as PO ₄)	Coupon Corrosion Rate mpy (mm/y)	
		Steel	Brass
AEC	0.0	0.08 (0.002)	0
HEDP	5.5	0.39 (0.010)	0

Alkaline-zinc treatment evaluations compared AEC to HEDP in a program that included zinc, tolyl-triazole, and copolymer. The two programs contained equal levels of zinc and TTA, but differed in the copolymer concentration. A higher copolymer dosage (3x) was needed for the HEDP program to prevent zinc hydroxide and calcium HEDP formation. The results of this testing (Table 3) were similar to that of the alkaline-phosphate evaluations. Both programs provided excellent corrosion rates.

Field Performance

Case History – 1

Background

A United States PVC manufacturer was operating with an alkaline-phosphate cooling water treatment and experiencing control problems that led

to scaling of some hot process equipment. The treatment utilized a state-of-the-art approach employing: phosphonate, orthophosphate, azole, and a copolymer dispersant/inhibitor.

Table 4: Cooling tower makeup water

Calcium, ppm CaCO ₃	96
Magnesium, ppm CaCO ₃	16
M Alkalinity, ppm CaCO ₃	91
Chloride, ppm Cl	22
Silica, ppm SiO ₂	9
pH	7.8
Phosphate, ppm PO ₄	0.4 to 0.7
Conductivity, μS cm ⁻¹ (μmhos)	350

Orthophosphate was not added as part of the treatment. Orthophosphate concentrations of 5 to 9 ppm developed in the cooling water from cycling the makeup water and from the degradation of the phosphonate by chlorine. Makeup water to the cooling tower is clarified river water (Table 4) treated with low levels of inorganic phosphate, nominally 0.5 ppm as PO₄, to prevent corrosion of transfer piping.

Control parameters for the treatment were: pH 8.2– 8.5 (HCl, automatic control), 0.2 to 0.5 ppm free Cl₂ (Cl₂ gas, continuous feed), 5 to 9 ppm PO₄ and 5 to 6 cycles of concentration (manual control). A non-oxidizing biocide (dodecylguanidine-hydrochloride/methylenebisthiocyanate blend) was shot-fed as needed to control sulfate-reducing bacteria.

The alkaline-phosphate program provided acceptable corrosion and scale control. Scale deposits formed in hot process equipment, but did not cause sufficient loss of heat transfer to limit production between the yearly system shutdowns. A deposit removed from the system indicated that the scale was mostly calcium carbonate (>60%), with a minor amount of calcium phosphate present (6%). High steel corrosion rates 7.0 to 11.1 mpy (0.178 to 0.279 mm/y) were occasionally observed during upset conditions, but for the most part were <2.0 mpy (<0.051 mm/y).

Constant manipulation of the copolymer and phosphonate feedrates was required to compensate for fluctuations of the phosphate concentration in the makeup water and normal variations in

cycles of concentration. Adjustments in treatment feedrates were also required to prevent calcium carbonate and calcium phosphate scaling during periods of high chlorine feed, when significant degradation of the phosphonate occurred. Maintaining tight control of system operating parameters (pH, Cl₂, cycles, treatment residuals) to ensure good results was a constant, time-consuming, challenge.

Table 5: Corrosion rate data

Corrosion Rate mpy (mm/y)			
LCS	Pt-LCS	ADM	o-PO ₄ Level ppm
0.71 (0.018)	0.31 (0.008)	0.20 (0.005)	4.8 to 7.8 (a)
0.98 (0.025)	0.39 (0.010)		3.8 to 4.1
0.39 (0.010)	0.20 (0.005)	0.08 (0.002)	2.8 to 3.1
1.18 (0.030)	0.51 (0.013)	0.72 (0.018)(b)	2.8 to 3.3
(a) Period after treatment conversion (b) Period of high chlorination; spikes of 0.8 ppm free Cl ₂ LCS – Low Carbon Steel Pt-LCS – Pretreated low carbon steel ADM – Admiralty brass			

Treatment Program Modification

The alkaline-phosphate program was replaced with a combination of AEC, copolymer, and TTA. The AEC concentration was adjusted so that the orthophosphate developed from the cycled makeup would be sufficient for steel corrosion protection. The control parameters for the AEC-based treatment remained the same as the previous program.

Results

Table 6: Case 1 – Cooling Water Composition

Calcium, ppm CaCO ₃	510 to 648
M Alkalinity, ppm CaCO ₃	180 to 300
Chloride, ppm Cl	400 to 500
Silica, ppm SiO ₂	45 to 60
pH	8.0 to 8.8
Conductivity, μS cm ⁻¹ (μmhos)	1,800 to 2,100

Corrosion data collected during the trial period (52 weeks) demonstrate that the AEC-based program provides excellent corrosion protection, even at low phosphate concentrations.

Table 5 summarizes the coupon corrosion rates as a function of the cooling water's phosphate concentration. The total iron level of the cooling water was also monitored as an indication of steel corrosion. Steel corrosion was not judged to be significant, since the iron concentration of the cooling water closely tracked its theoretical value, based on the iron level of the makeup water and the cycles of concentration.

During the trial period, the system experienced high pH (8.9) and high LSI (+2.8) due to loss of acid feed, low pH (< 5), and high chlorine residuals (>0.8 ppm free). The response to high pH excursions included increasing the AEC and the copolymer concentrations. Low pH upsets were also treated by increasing the AEC and polymer dosages, concurrent with increasing the blowdown. Instituting the appropriate recovery procedures minimized the effects of these upsets and ensured continued good results.

The system was not pretreated (prefilmed) with high dosages of phosphate after conversion to the AEC program. Phosphate levels ranged from 4.8 to 7.8 ppm for the thirty-day period following conversion, due to dissolution of calcium phosphate deposits. The orthophosphate level in the cooling water depends on the phosphate concentration in the makeup water and cycles. Typically, the orthophosphate level of the cooling water ranged from 3 to 4.5 ppm.

The range of cooling water chemistries encountered during the trial period is presented in Table 6.

Table 7: Case 2 – Cooling water composition

Calcium, ppm CaCO ₃	480 to 590
M Alkalinity, ppm CaCO ₃	110 to 180
Silica, ppm SiO ₂	33 to 44
pH	8.0 to 8.4
Conductivity, μS cm ⁻¹ (μmhos)	1,800 to 2,500

Case History – 2

Background

A United States MTBE chemical manufacturer was using an alkaline-phosphate cooling water program with acid feed for pH control and chlorine gas for microbiological protection. The treatment was a combination of phosphonate, molybdate (4 to 6 ppm MoO_4 at use-dosage), azole, and a copolymer. Boiler blowdown was used as the source of inorganic phosphate. Boiler blowdown contains 20 to 40 ppm inorganic phosphate and has a pH of 9.5 to 10.7 and a conductivity of 400 to 600 $\mu\text{S cm}^{-1}$ (micromhos). It contributes 7 to 10 ppm o-PO_4 to the cycled cooling water. Control parameters for the program were: pH 7.8 to 8.2 (H_2SO_4 , automatic control), 0.2 to 0.6 ppm free Cl_2 (gas Cl_2 , continuous feed), and 5 to 6 cycles of concentration. Cooling tower makeup water is a combination of clarified river water and boiler blowdown.

Corrosion results were excellent, averaging 0.51 mpy (0.013 mm/y) for non-pretreated, low carbon steel and 0.20 mpy (0.005 mm/y) or less for admiralty brass. Loss of heat transfer efficiency was experienced with hot process equipment as a result of scaling. The major components of the deposits were calcium phosphonate (primary) and calcium orthophosphate (secondary). Fouling resulted from upset conditions that exceeded the scale control capabilities of the treatment program. Control of the chlorine gas feedrate was poor and high free chlorine residuals (>1 ppm) caused degradation of the phosphonate to orthophosphate. High pH excursions, along with phosphonate degradation, necessitated increasing the phosphonate feedrate to avoid calcium carbonate scaling. This often caused overfeeds of phosphonate, which led to calcium phosphonate deposition in hot bundles.

Treatment Program Modification

The program was modified by substituting AEC for the phosphonate and eliminating the molybdate. The only change in operating control parameters was increasing the pH control range to 8.0 to 8.4. Typical cooling water chemistry is summarized in Table 7.

Results

Corrosion rates are unchanged, 0.51 mpy (0.013 mm/y) for LCS, <0.20 mpy (<0.005 mm/y) for ADM, since conversion to the AEC-based program and fouling has been almost totally eliminated. After 16 months of operation, equipment inspections revealed a significant reduction in scaling compared to previous openings. Only very minor, paper-thin calcium orthophosphate deposits are observed in some hot process equipment. Corrosion is general and not considered significant. The process surface condenser remains free of deposits and no loss in vacuum has occurred since the new treatment program was implemented.

On a number of occasions, the system experienced upsets that could have resulted in rapid and severe scaling. Prolonged periods (up to 10 days) without acid feed caused the pH to increase to 8.8 to 9.0. On two other occasions, electric power was lost to the cooling tower fans and acid feed pumps. The cooling tower supply water increased to over 110°F (43°C), exchanger exit water temperatures exceeded 150°F (66°C), and the pH increased to 8.9. Calcium phosphate and calcium carbonate (LSI +2.8 to +3.1) supersaturations were high at these conditions. In both cases, the copolymer and AEC concentrations were increased to very high dosages, which successfully avoided scaling.

Conclusions

- AEC provides steel corrosion protection comparable to phosphonate when used in an alkaline-phosphate or alkaline-zinc treatment. Excellent corrosion protection can be obtained at orthophosphate concentrations as low as 3 ppm (1 ppm as P).
- Substituting AEC for phosphonate can significantly reduce the phosphorus content of alkaline-phosphate and alkaline-zinc treatments.
- Excellent calcium scale control can be obtained with AEC. Calcium carbonate scaling can be avoided during high pH (high LSI) excursions by increasing the AEC dosage, without experiencing treatment-related fouling.
- High free chlorine residuals do not affect AEC's calcium carbonate control properties.

References

1. May, R. C., Geiger, G. E., Bauer, D. A., "A New Non-Chromate Cooling Water Treatment Utilizes High Orthophosphate Levels Without Calcium Phosphate Fouling," Corrosion/80, Paper No. 196, 1980.
2. Beer, W. F., Ertel, J. F., "Experience With High-Phosphate Cooling Water Treatment Programs," Corrosion/85, Paper No. 125, 1985.
3. Geiger, G. E., Ertel, J. F., "Advances In Alkaline Cooling Water Treatment Technology," Corrosion/84, Paper No. 320, 1994.
4. Neagle, W., "Hydroxy Phosphono Acetic Acid (HPA) – A Mechanistic Investigation Of Corrosion Inhibition Under Cooling Water Conditions," Corrosion/91, Paper No. 568, 1991.
5. Ashcraft, R., Bohnsack, G., Holm, R., Kleinstueck, R., Storp, S., "The Mechanism Of Corrosion Inhibition And Transition To Under-Deposit Corrosion," Corrosion/87, Paper No. 328, 1987.
6. Sullivan, P. J., "A Mechanistic Study Of Corrosion Inhibition By Phosphonates," CTI Journal, Volume 16, No. 1, pp 62–67, 1995.
7. Thevissen, P., Cleuren, W., DeCrom, A., "Development Of An All-Organic Program For Open Evaporative Cooling Water Systems Based On A New Copolymer," Proceedings Of The 7th European Symposium, Ann. Unv. Ferrara, 1990.
8. U. S. Patent 4, 759, 851. Brown, J. M., Carey, W. S., McDowell, J. F., "Development Of An Environmentally Acceptable Cooling Water Treatment Program: Non-Phosphorus Scale Inhibitor," Corrosion/93, Paper No. 463, 1993.