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A Non-Phosphorous Chemical Treatment Program for Cooling Water Systems

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Abstract

The scope of this work is demonstrate the results of a non-phosphorous corrosion inhibitor (alkyl epoxy carboxylate, AEC) in replacement of phosphate based chemicals, which are the most widely used corrosion inhibitors for carbon steel in open cooling water system under conditions of alkaline water. Cooling systems in most industries, are major contributors in the generation of liquid discharge into the environment. The principle this of study was to select an open cooling system where environmental regulations implied the restriction of phosphorus in the plant effluent and to use this corrosion and scale inhibitor technology that doesn't use any phosphorus in their chemical composition having the challenge to maintain a great performance in protecting the cooling system. The performance of this AEC/Zinc application is reviewed. Excellent corrosion and scale control was achieved with AEC/Zinc chemistry. This case history discusses the performance with a low hardness water (60 mg/L calcium, as CaCO3) operating at 3-4 cycles of concentration. The highly corrosive nature of the water and the long retention time of the system stressed both the corrosion and scale control capabilities of the program.

ASTM D2688 methodology was used to measure the overall corrosion performance measuring corrosion rate (weight loss of the material exposed during a specified period of time) on carbon steel and admiralty brass. Deposition control was achieved following up critical heat exchangers thermal transfer coefficient under alkaline conditions (LSI values up to 2,80). Microbiology control was accompanied by daily measurements of biomass (ATP), and cross-check with conventional total heterotrophic bacteria counts. Results of this paper demonstrate the successful application of a chemical treatment program in an open system cooling tower, which contains no phosphorus in its composition, but promotes an effective and excellent control of corrosion and deposition, under continuous oxidant conditions, meeting with more strict environmental regulations and protection proves carbon steel anode type together with low concentration of zinc in alkaline water conditions

Keywords: **corrosion rate, deposition, zinc, phosphate, cooling tower effluent, concentration cycle**

Introduction

The development of cooling water treatment technologies, since the introduction of phosphonates in the late 1960's has become increasingly more driven by environmental considerations. Phosphonate-based programs are still the most prevalent cooling water treatment programs now. Phosphonates serve the dual function of calcium carbonate scale control and

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steel corrosion protection. Although the commonly used phosphonates are applied as calcium carbonate scale inhibitor, they can contribute to steel corrosion protection when used with inorganic phosphate and/or zinc. When applied alone, they are weak corrosion inhibitors.
Recently, environmental concerns have been raised about the discharge of phosphorous-containing compounds in the effluent streams resulting in eutrophication of receiving waters. As a result, the use of phosphorous-based water treatment chemicals is being viewed as less environmentally acceptable.

Removal of total phosphorus contribution by phosphonate-based programs could be achieved by using non-phosphorous scale inhibitors in combination with low zinc dosages. However, this would require that the scale inhibitor have the same or superior scale control capabilities as phosphonate materials and contribute to steel corrosion protection in a comparable manner.

The replacement of phosphonate-based programs by non-phosphorous or low-phosphorous containing corrosion inhibitors would require the use of more effective polymeric scale inhibitors to control both corrosion and scale deposition[1].

A non-phosphorous scale inhibitor has been developed that provides calcium carbonate control superior to phosphonate inhibitors and that provides enhanced steel corrosion protection. The patent protected material, an Alkyl Epoxy Carboxylate (AEC), is the most significant advance in calcium carbonate inhibitors in the past 30+ years, and is an effective non-phosphorous calcium carbonate inhibitor for highly saturated waters.

In combination with zinc, AEC enhances the corrosion inhibition of a cooling water treatment program. Improved or equivalent corrosion control can be achieved with lower concentrations of zinc compared to conventional alkaline pH programs[2].

AEC is not susceptible to hydrolysis or breakdown by chlorine used in microbiological control programs. Therefore, unlike most organic phosphates commonly used, no loss of scale control or corrosion inhibition is experienced during periods of chlorination of the system. AEC also has a high calcium tolerance and therefore, compared to certain organic phosphates, doesn't form insoluble calcium salts within the system[2]. AEC low-phosphorous programs have been successfully applied in many open recirculating cooling systems.

Development

Over the past years, the changes in the water treatment technologies have been extremely rapid in most industrial areas, driven by the new or proposed Government regulations. The scope of the changes is best exemplified by some of the major trends driving the cooling water treatment technology today, including minimizing waste discharge, reducing water consumption and minimizing or eliminating use of phosphorous containing compounds.

With the increased consciousness of environmental protection, many countries in Latin America have already restricted the discharge of phosphorous. Low-phosphorous and non-phosphorous water treatment chemicals have become desirable.

For the petrochemical industry, the open recirculating cooling water system is the largest water user in the plant. The discharge standard for the petrochemical industry is regulated under "Resolution 336/2003 – Annex II" established in Buenos Aires Province, Argentina. Most waste water effluents are required to meet discharge standard listed in table 1[3]".

Parameter	Unit	Discharge limits to:			
		Domestic Sewage	**Rain Collector or Surface Water Body**	**Absorption in Soil**	**Open Sea**
pH	-	7,0 – 10,0	6,5 – 10,0	6,5 – 10,0	6,5 – 10,0
Total Phosphate	mg/L as P	≤ 10,0	≤ 1,0	≤ 10,0	≤ 10,0
Zinc	mg/L as Zn	≤ 5,0	≤ 2,0	≤ 1,0	≤ 5,0

Table 1: Quality Parameters Allowable Discharge Limits

Notes:
1. Issued on November, 25th 2003 by The Directory of the water authority of the Province of Buenos Aires.
2. The petrochemical site wastewaters at where the AEC/Zn program was applied is regulated by column #4, "Rain Collector or Surface Water Body" standard.

For low phosphate programs, AEC is used primarily for scale control and inorganic phosphate is used for steel corrosion protection. Substituting AEC for phosphonate inhibitors lowers the overall phosphorus level without sacrificing corrosion protection. Although these formulas have good performance, they lose the green advantage of AEC. There is a need for a more environmentally friendly corrosion inhibitor package for ferrous-based metals in contact with aqueous systems. In particular, there is a need for a non-phosphorous containing treatment program.

In addition to its good deposit control properties, AEC has good corrosion inhibition for carbon steel when applied at concentrations higher than those needed for scale control. It is not only a kind of green scale inhibitor, but also a green corrosion inhibitor[4]. The corrosion inhibition properties of AEC, unlike conventional phosphonates, are characterized by a strong anodic inhibition with moderate cathodic inhibition component. The existence of oxygen atom in AEC molecular structure makes it easy to form stable chelated pentacyclic structures[1].

Zinc is an extremely powerful cathodic corrosion inhibitor for steel. In many respects, zinc based program offers some performance advantages over inorganic phosphate treatments. This is especially noticeable when the effluent goes to waste treatment plants. In contrast to phosphate which may be difficult to remove, most treatment plants can readily remove zinc to a very low concentration with no additional treatment step. In low hardness conditions, zinc containing cooling water programs are generally acknowledged as being the preferred treatment, since they do not depend on calcium hardness (calcium phosphate) to provide cathodic inhibition.

Combinations of AEC and zinc have been shown to be synergistic in their ability to inhibit steel corrosion[2]. Programs based on AEC and zinc have a long history in industrial cooling water applications and are the mainstay of non-phosphorous programs provided by GE Water &

Process Technologies. In order to eliminate the impact of phosphorous on wastewater and meet the Rain Collector or Surface Water Body discharge standard, a non-phosphorous, AEC-based program was proposed for this petrochemical open recirculating cooling water systems.

1 Plant Evaluations

1.1. Corrosion Monitoring

The corrosion inhibition test activity of the AEC/Zn non-phosphorous program was evaluated using conventional Corrosion Coupons holders installed in racks mounted in each of both returns of cooling water from plants. Corrosion rates were evaluated on both metallurgies present in the cooling system, low carbon steel (AISI-1010) and admiralty brass (CDA-433), following ASTM D-2688-11 and ASTM G1-03 procedures.

1.2 Make-Up Water to Cooling System

The water supplied to the open recirculating cooling system is filtered clarified River Plate water. The make-up water profile is showed in Table 2. The relatively low calcium hardness makes it more difficult for corrosion inhibitors which depend on calcium to function effectively. The relatively high chloride levels make the water to show high pitting corrosion tendency.

Parameter	Unit	Average	Maximum	Minimum
pH	-	7,5	7,9	7,2
Conductivity	*uS/cm*	677	970	510
Total Alkalinity	mg/L as $CaCO_3$	106	140	80
Total Hardness	mg/L as $CaCO_3$	112	170	70
Calcium Hardness	mg/L as $CaCO_3$	60	90	40
Magnesium Hardness	mg/L as $CaCO_3$	52	80	30
Chlorides	mg/L as *Cl*	144	214	94
Sulfates	mg/L as SO_4	39	55	29
Silica	mg/L as SiO_2	14,3	19,9	11,0
Total Iron	mg/L as *Fe*	0,28	0,35	0,14
Turbidity	*NTU*	0,5	1,2	0,4
COD	mg/L	18	24	11

Table 2: Make-Up Water Profile

Note:

1. Information gathered within the nine months evaluation period (December 2011 – August 2012).

1.3. Cooling System Information

The petrochemical plant is located in Buenos Aires Province, Argentina, and has a natural draft hyperbolic tower with a 66,000 gpm recirculation rate. The system supplies cooling water to the whole industrial complex and has two independent main returns. Makeup water is filtered, clarified river water, which has low calcium, and moderate pH, alkalinity and conductivity (See

Table 2). In order to eliminate the impact of phosphorus on the discharge, the cooling water program was strictly limited to < 1 mg/L of total phosphorous and < 2 mg/L of zinc.

1.4. Chemical Treatment Program

AEC/Zinc non-phosphorous program has been applied in this unit. The program provides for both corrosion and deposition control by utilizing: AEC to control calcium carbonate scaling and inhibit steel corrosion, a sulfonated terpolymer (STP) to prevent zinc precipitation and disperse particulate solids (clays, silt, iron oxides, etc.), zinc to inhibit steel corrosion and a proprietary azol named HRA, to prevent copper alloy corrosion. Sodium hypochlorite solution is used in combination with sodium bromide to generate hypobromous acid as oxidizing biocides, supplemented with a bio-dispersant and weekly shocks of a non-oxidizing biocide for microbial control.

1.5. Treatment Results

After a three months transition period, when a conventional alkaline pH phosphate-based treatment program was implemented as the beginning of a new contract period with the plant. During this time, the concentration cycles were maintained in the 2-3 range without using zinc as carbon steel cathodic inhibitor.

At the same time the non-phosphorous treatment program was implemented at the site, improvements in concentration cycles were achieved. The average cooling water information in the evaluation period is in Table 3. As can be seen, the cooling water total phosphorous was well below 1mg/L, and zinc residuals were lower than 2 mg/L, which meets the demand of the “Rain Collector or Surface Water Body” standard.

Items	Unit	Average	Maximum	Minimum
pH	-	8,8	9,1	8,2
Conductivity	µS/cm	2081	2740	1040
Total Alkalinity	mg/L as $CaCO_3$	275	370	150
Total Hardness	mg/L as $CaCO_3$	320	440	181
Calcium Hardness	mg/L as $CaCO_3$	181	270	90
Magnesium Hardness	mg/L as $CaCO_3$	139	170	91
Chlorides	mg/L as Cl	451	589	224
Sulfates	mg/L as SO_4	100	145	73
Silica	mg/L as SiO_2	38,2	52,1	7,2
Total Iron	mg/L as Fe	0,51	0,62	0,37
Copper	mg/L as Cu	0,06	0,10	0,03
Ortho-PO_4	mg/L as PO_4	0,46	0,78	0,07
Zinc	mg/L as Zn	1,73	2,20	0,50
Turbidity	NTU	8	20	0,4
Free Chlorine Residual	mg/L as Cl_2	0,34	2,20	0,03
COD	mg/L	58	118	29
Concentration cycles	-	3,20	4,90	1,15

Table 3: Cooling Tower Water Information

The low calcium hardness and relatively low concentration cycles make it very corrosive for ferrous metal. The low iron level of the cooling water indicated that the system was being protected. For about nine months of normal operation, coupon corrosion results demonstrated excellent performance (see the carbon steel coupon corrosion rate information). Corrosion rates measured by coupons were consistently below 1.0 mils per year (0.025 mm/year) for carbon steel and below 0.2 mils per year (0.005 mm/year) for admiralty brass. The equipment inspections also showed excellent scale, corrosion and biological control.

Coupon corrosion rates results during the evaluated period are showed in Table 4.

Period	**Carbon Steel**		**Admiralty Brass**	
	1	**2**	**1**	**2**
December 2011	2,61 (0,066)	2,42 (0,061)	0,05 (0,0012)	-
January 2012	0,39 (0,010)	1,49 (0,038)	0,02 (0,0005)	0,03 (0,0012)
February 2012	0,53 (0,013)	0,51 (0,013)	0,03 (0,0007)	0,03 (0,0007)
March 2012	0,71 (0,018)	0,70 (0,018)	0,04 (0,0010)	0,05 (0,0012)
April 2012	-	0,84 (0,021)	-	0,05 (0,0012)
May 2012	0,20 (0,005)	0,37 (0,009)	0,02 (0,0005)	0,02 (0,0005)
June 2012	0,18 (0,004)	0,42 (0,010)	0,02 (0,0005)	0,02 (0,0005)
July 2012	0,44 (0,011)	0,72 (0,018)	-	-
Specification	**≤ 2,0 (0,05)**	**≤ 2,0 (0,05)**	**≤ 0,2**	**≤ 0,2**

Table 4: Corrosion rates on Carbon Steel and Admiralty

Note: units in mils per year (mm/year)

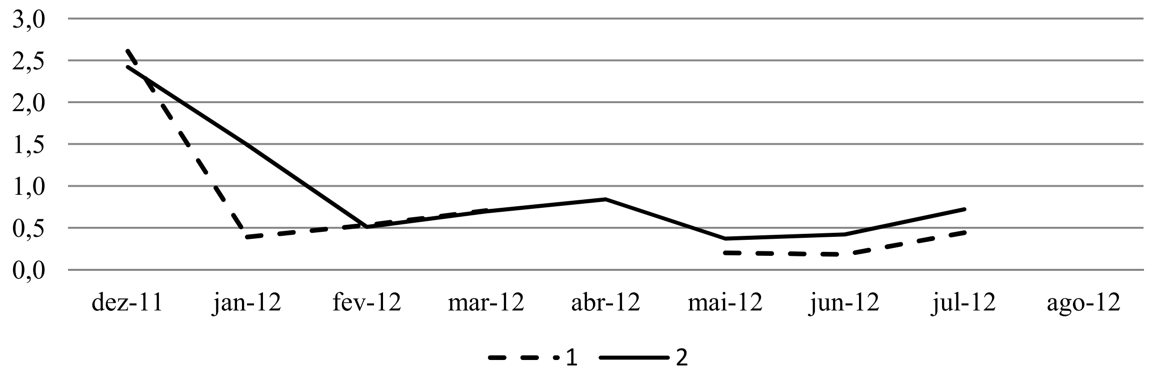

Figure 1 - Carbon steel corrosion rates on both returns to CT (mpy)

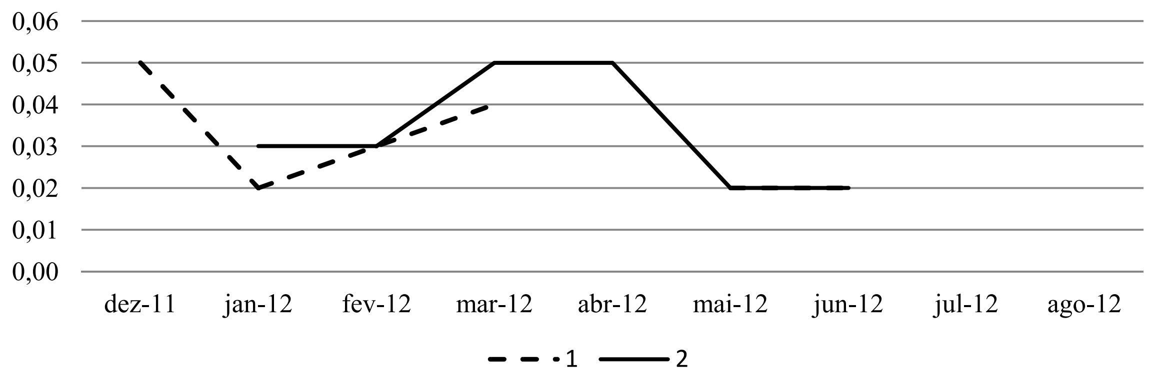

Figure 2 - Admiralty corrosion rates on both returns to CT (mpy)

From Table 4, it can be observed that AEC non-phosphorous program can provide excellent control of corrosion on carbon steel in low calcium hardness water and high chloride water. Increasing the concentration of AEC and/or zinc can increase the corrosion inhibiting ability of the program on carbon steel. AEC and zinc demonstrate a complementary effect in corrosion inhibition.

MB Results – The microbiological treatment program was composed by the use of bleach, together with a sodium bromide component in order to generate hypobromous acid in-situ, plus the continuous application of a biodispersant and eventually an isothiazolin based non-oxidant biocide during process leaks events.

Biomass (ATP) results are showed in Figure 3 below from the two returns. Note the high value excursion due to a hydrocarbon leak that was immediately detected and the equipment isolated.

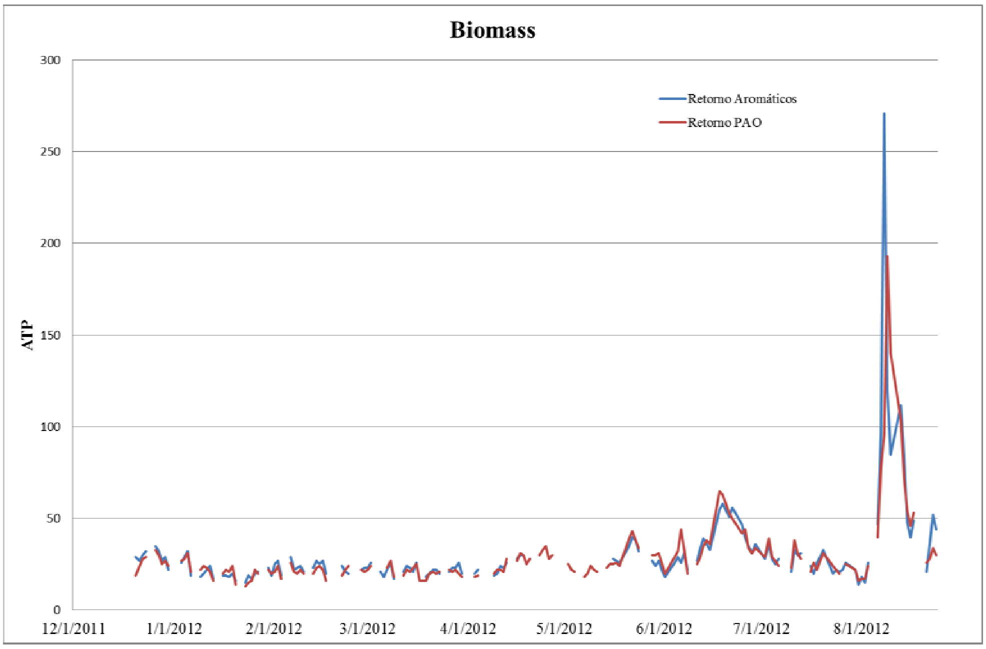

Figure 3: Biomass – ATP values

Figure 4 shows free halogen residuals maintained during the period of the study. A great control was achieved for the 0,2 – 0,5 mg/L specified range.

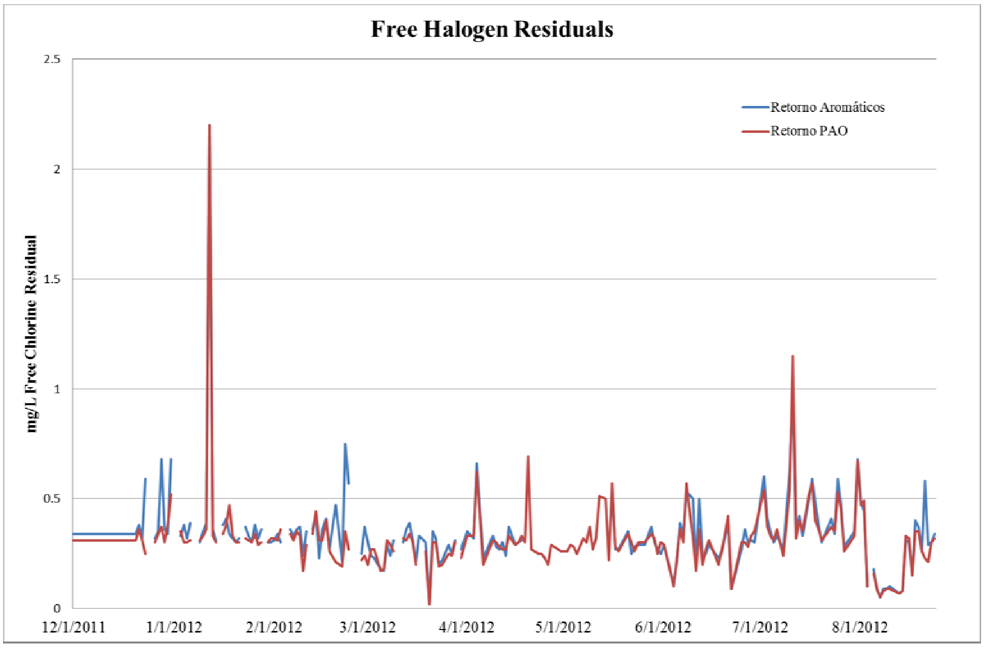

Figure 4: Free Halogen Residuals (mg/L)

Deposit Control – No deposition events were reported along the evaluation study. Good calcium carbonate control was achieved by the application of AEC, maintaining relatively high values of Langelier Saturation Indexes, as shown in the following graph. This treatment program with AEC allows LSI values up to 2,85, and skin temperatures up to 90°C.

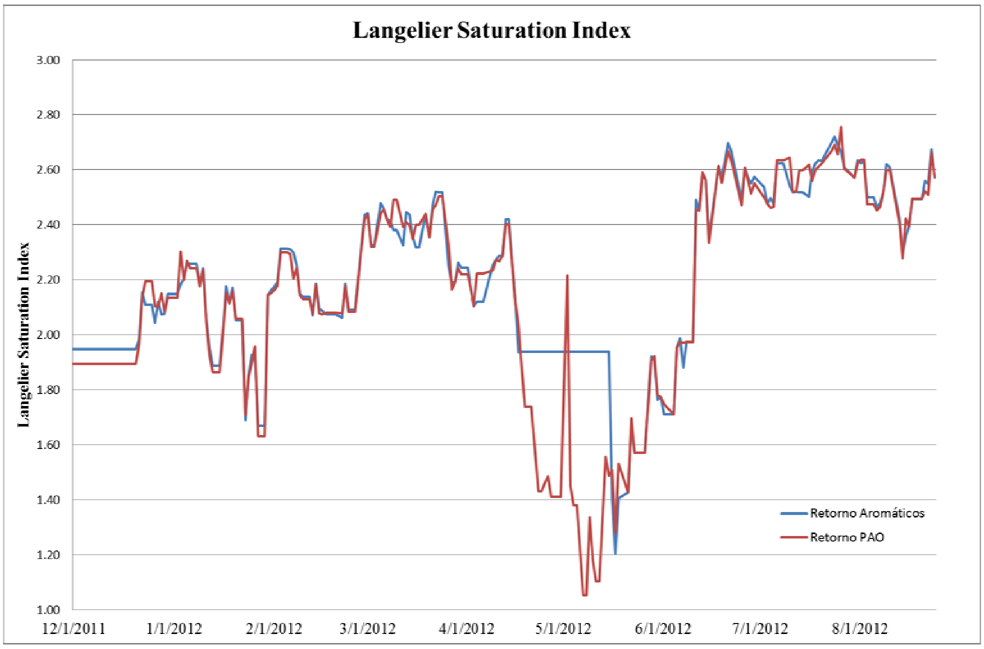

Figure 5: Langelier Saturation Index

Conclusions

From the above test results, AEC/Zinc program without phosphorus showed great control of corrosion on ferrous metal in cooling water systems. AEC/Zinc program was effective in the presence of relatively high chlorides and low hardness waters in an alkaline pH environment. Eliminating inorganic phosphate for corrosion protection provides an environmentally friendly program and eliminates the associated wastewater concerns.

In summary,

- AEC, a patented non-phosphorous calcium carbonate scale inhibitor, has demonstrated better scale inhibition abilities than traditional organic phosphonates. In addition to its scale inhibition properties, AEC inhibits carbon steel corrosion when used at high dosages.
- AEC can be combined with zinc to develop a non-phosphorous program to provide an environmentally friendly treatment program, which complies with the demanding standards of wastewater discharge limitations.
- AEC/Zinc combinations have been found to be highly effective in controlling the corrosion of ferrous metals. AEC provides corrosion inhibition, through chemisorption, while zinc is known to be an excellent cathodic inhibitor. The combination of the two inhibitors is a synergistic blend that is effective over a wide range of operating conditions and water chemistries.

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