CORROSION SCIENCE AND TECHNOLOGY, Vol.7, No.1(2008), pp.16~21

The Application of Non-phosphorous AEC Program in Cooling Water Systems of Petrochemical Industry

Li Dagang†, Mike Hong, and He Gaorong

Suite 4208, United Plaza 1468 Nanjing Road West, Shanghai 200040, China
GE Water & Process Technologies

A non-phosphorous program employing an alkyl epoxy carboxylate (AEC) has been successfully applied to petrochemical and other large industrial open recirculating cooling water systems. AEC is a patented non-phosphorous calcium carbonate scale inhibitor that has demonstrated better scale inhibition abilities than traditional organic phosphonates. In addition to its antiscalant properties, AEC inhibits carbon steel corrosion when used at high dosages.

AEC can be combined with zinc to form a non-phosphorous program with very low levels of phosphate to provide an environmentally acceptable program. In actual applications, the total phosphate developed in the cooling system from cycling the makeup is below 1 ppm as PO_4. This level has complied with the highest standards of wastewater discharge limitations.

The performance of two AEC/Zinc applications is reviewed. In both cases excellent corrosion and scale control were achieved with AEC/Zinc programs. One case history details the performance with a low hardness water (100 ppm calcium, as $CaCO_3$) operating at 8-10 cycles of concentration. The corrosive nature of the water and the long retention time of the system stressed both the corrosion and scale control capabilities of the program. The second case history demonstrates the performance of the program with a moderate hardness water (400-600 ppm calcium, as $CaCO_3$), but under harsh conditions of high temperature and low flow.

The AEC/zinc combination has been found to be highly effective in controlling the corrosion of ferrous metals. AEC can provide good corrosion inhibition at high concentrations, while zinc is known to be an excellent cathodic inhibitor. The combination of the two inhibitors not only provides a synergistic blend that is effective over a wide range of operating conditions, but also is environmentally friendly.

Keywords *: alkyl epoxy carboxylate, non-phosphorous, cooling water, corrosion inhibitor*

1. 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 “From the report”[1]. Phosphonates serve the dual function of calcium carbonate scale control and steel corrosion protection. Although the commonly used phosphonates as calcium carbonate scale inhibitor can contribute to steel corrosion protection when used with inorganic phosphate and/or zinc, 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 environmental acceptable.

Reductions in total phosphorus contributed by phosphonate-based programs could be achieved by using non-phosphorus scale inhibitors in combination with low dosage of phosphate and/or zinc. 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 “From the report”[1].

† Corresponding author: Dagang.Li@ge.com

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

In combination with orthophosphate and/or zinc, AEC enhances the corrosion inhibition of cooling water treatment programs. Improved or equivalent corrosion control can be achieved with lower concentrations of orthophosphate or zinc compared to conventional alkaline pH programs "From the reports"[2),3),4)].

AEC is not susceptible to hydrolysis or breakdown by normal concentrations of chlorine used in microbiological control programs. Therefore, unlike some conventional phosphonates, no loss of scale control or corrosion inhibition is experienced during periods of chlorination of cooling systems. AEC also has a high calcium tolerance and therefore, compared to certain phosphonates, doesn't form insoluble calcium salts within the system "From the report"[2)]. Low-phosphorous AEC programs have been successfully applied in many open recirculating cooling systems "From the reports"[2),3),5),6)].

2. Evolvement of Non-phosphorous program

Over the past decade years, the changes in water treatment technologies have been extremely rapid in every industrial sector, driven by the new or proposed government regulations. The scope of 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 the use of phosphorous containing compounds.

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

For petrochemical industry, the open recirculating cooling water system is the largest water user in the plant. The discharge standard for petrochemical industry is regulated under "Integrated wastewater standard" (GB 8978-1996) in China, and most waste water effluents are required to meet the discharge standard listed in table 1 "From the report"[7)].

For low phosphate programs, AEC is used primarily for scale control and inorganic phosphates 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 demand, for a more environmentally acceptable corrosion inhibitor package for ferrous-based metals in contact with aqueous systems. In particular, there is a demand for a non-phosphorous contained 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 "From the reports"[8),9)]. The corrosion inhibition properties of AEC, unlike conventional phosphonates, are characterized by a strong anodic inhibition with moderate cathodic inhibition component "From the report"[1)]. The existence of oxygen atom in AEC molecular structure makes it easy to form stable chelated pentacyclic structures "From the report"[8)].

Zinc is an extremely powerful cathodic corrosion inhibitor for steel. In many respects, zinc-based programs 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 very low concentrations with no additional treatment step. In low hardness con-

Table 1. National integrated wastewater discharge standard

Item	Applicable Range	First Grade Standard	Second Grade Standard	Third Grade Standard
pH	All Discharge Unit	6~9	6~9	6~9
Phosphorus [mg/L as P]	All Discharge Unit	0.5	1.0	-
Total Zinc [mg/L]	All Discharge Unit	2.0	5.0	5.0

Note: 1. The wastewater drained to the Ⅲ type water areas in GB3838 (Except for state protected and swimming areas) and to the second type sea areas in GB3097, should meet the first grade standard.
2. The water drained to the Ⅳ and Ⅴ type water areas in GB3838 and to the third type sea areas in GB3097 should meet the second grade standard.
3. The wastewater drained to the municipal drainage systems including two stage wastewater treatment factory, should meet the third grade standard.

ditions, 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 "From the reports"[3),9)]. Programs based on AEC and zinc have a long history in industrial cooling water applications and are the mainstay of non-phosphorus programs provided by GE Water & Process Technologies. In order to eliminate the impact of phosphorous on wastewater and meet the first grade discharge standard, a non-phosphorous, AEC-based program was proposed for petrochemical and other large industrial open recirculating cooling water systems.

3. Laboratory evaluations

3.1 Test methods and conditions

The corrosion inhibition test for non-phosphorous AEC programs was evaluated using the Beaker Corrosion Test Apparatus (BCTA). The BCTA consists of a 2 liter beaker equipped with air sparge, two A3 low carbon steel coupons(Size: 50×25×2 mm, area: 28 cm^2) and a magnetic stir bar. The test solution was 2 liters. Air sparging was done continuously during the test. The magnetic stirrer can control the solution temperature. All tests were conducted at 40℃, stirred at 300 RPM. The test duration was 24 hours. In all tests the coupons immersed in the beaker during the test were photographed. The corrosion rate was measured by the coupon weight loss. Please see the test photo in Fig. 1.

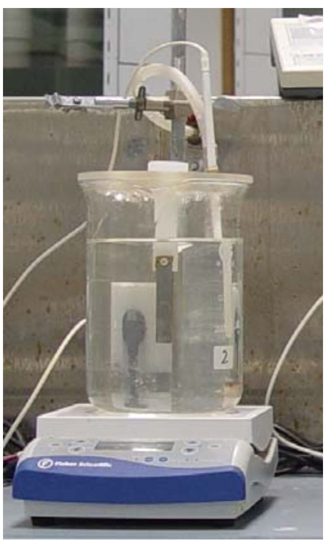

Fig. 1. BCTA photo

Table 2. low hardness water condition

Items	Unit	Data
pH		8.7
Total Hardness	mg/L as $CaCO_3$	50
Calcium Hardness	mg/L as $CaCO_3$	40
Magnesium Hardness	mg/L as $CaCO_3$	10
Conductivity	μS/cm	332
Total Dissolved Solids	mg/L	217
Chloride	mg/L	28
Sulfate	mg/L	22
Silica	mg/L as SiO_2	26

Table 3. Corrosion rate of test 1

Chemicals Name	Dosage [mg/L]	Coupon Corrosion Rate [mpy] (mm/y)
AEC3174	70	1.82 (0.046)
AZ8104	10	
AEC3174	70	1.27 (0.032)
AZ8104	10	
MS6207	10	
AEC3174	110	0.48 (0.012)
AZ8104	10	

3.2 Test 1- Low hardness water

The water used for testing is prepared by chemical addition to the deionized water. The test water condition is in table 2. The relatively low calcium hardness makes it difficult for inhibitors which depend on calcium to function effectively. The relatively low chloride and sulfate levels make the water with low pitting corrosion tendency.

The BCTA test results are shown in table 3. AEC3174 is the mixture of AEC, sulfonated polymeric dispersant and zinc. AZ8104 incorporates a halogen resistant azole (HRA) for copper corrosion protection. MS6207 contains zinc. From table 3, we know non phosphorus AEC program can well control the corrosion of carbon steel in low hardness water.

3.3 Test 2- Moderate hardness and high chloride water

The water used for testing is prepared by chemical addition to deionized water. The test 2 water condition is in table 4. The water with moderate calcium hardness and alkaline pH made the water with LSI about 1.7 at 40℃. The relatively high chloride and sulfate levels (for the given calcium level) make the water aggressive to ferrous metals, particularly with respect to pitting corrosion.

Table 4. Moderate hardness water condition

Items	Unit	Data
pH		8.5
Total Hardness	mg/L as $CaCO_3$	750
Calcium Hardness	mg/L as $CaCO_3$	500
Magnesium Hardness	mg/L as $CaCO_3$	250
Total Alkalinity	mg/L as $CaCO_3$	150
Conductivity	μS/cm	2650
Total Dissolved Solids	mg/L	1930
Chloride	mg/L	500
Sulfate	mg/L	500
Silica	mg/L as SiO_2	15

Table 5. Corrosion rate of test 2

Chemicals Name	Dosage [mg/L]	Coupon Corrosion Rate [mpy] (mm/y)
AEC3175	70	4.4 (0.112)
MS6207	13	
PY5200	15	
AEC3175	100	3.5 (0.089)
MS6207	10	
AEC3175	100	0.71 (0.018)
MS6207	20	
PY5200	10	
AEC3175	120	2.9 (0.074)
MS6207	10	
AEC3175	120	0.63 (0.016)
MS6207	20	

The BCTA test results are shown in table 5. AEC3175 is a mixture of AEC, a sulfonated copolymer and HRA. PY5200 is a single component product containing a sulfonated copolymer.

From table 5, we know non-phosphorus AEC program can well control the corrosion of carbon steel in moderate hardness and high chloride water. Increasing the concentration of AEC or zinc can both enhance the corrosion inhibiting ability for carbon steel. AEC and zinc demonstrate a synergistic effect in corrosion inhibition.

3.4 Test summary

From the above test results, AEC/Zinc program without phosphorus can well control the corrosion of ferrous metal in cooling water systems. AEC/Zinc program are effective in the presence of high chloride and is applicable to both high and low hardness waters. Eliminating inorganic phosphate for corrosion protection provides an environmentally friendly program and eliminates the associated wastewater discharge concerns.

Table 6. Cooling system make up and tower water data

Items	Unit	Make up	Cooling tower
pH		7.0	8.8
Total Hardness	mg/L as $CaCO_3$	15	168
Calcium Hardness	mg/L as $CaCO_3$	10	112
Magnesium Hardness	mg/L as $CaCO_3$	5	56
Total Alkalinity	mg/L as $CaCO_3$	15	180
Conductivity	μS/cm	60	925
Turbidity	NTU	2	6
Chloride	mg/L	9	144
Sulfate	mg/L	8	82
Silica	mg/L as SiO_2	9.6	92
Phosphate	mg/L PO_4	<0.05	0.45
Iron	mg/L	0.1	0.37
Zinc	mg/L		0.25

4. Field performance

4.1 Case history-1

4.1.1 Background

A new large Ethylene plant in southern China has four open recirculating cooling systems. Makeup water is clarified river water, which has very low calcium, alkalinity and conductivity (See Table 6). In order to eliminate the impact of phosphorus on the seawater, the cooling water program is strictly limited to <1 mg/L of total phosphate and <1 mg/L of zinc.

4.1.2 Treatment program

AEC/Zinc non-phosphorus program has been applied in this plant. The program provides both corrosion and deposition control by utilizing: AEC to control calcium carbonate scaling and inhibit steel corrosion, a sulfonated copolymer (HPS-1) to prevent zinc precipitation and disperse particulate solids (clays, silt, iron oxides, etc.), zinc to inhibit steel corrosion and HRA to prevent copper alloy corrosion. Sodium hypochlorite solution is used as the oxidizing biocide, supplemented with a bio-dispersant and a non-oxidizing biocide for microbial control.

4.1.3 Treatment results

After the precleaning and prefilming operation, the cooling water systems underwent about 3 to 5 months transitional period with little heat load. During this time, the cooling water calcium hardness was below 40 mg/L for an extended period. Caustic soda was added to increase the cooling water pH to 8.4~8.7. Coupon corrosion test showed excellence performance. Corrosion rates were below 0.4 mpy (0.01 mm/y) for carbon steel and below 0.2 mpy (0.005 mm/y) for admiralty brass during the transitional stage.

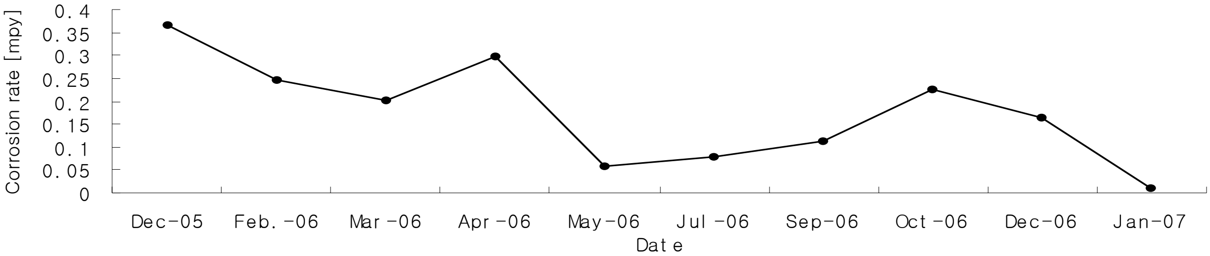

Fig. 2. Carbon steel coupon corrosion rate in CT1&2

During the normal operation with heat load, the cooling water chemical dosages and treatment cost were optimized based on excellent performance. Cooling tower cycles were controlled at 8 to 10 based on the silica calculation. The average cooling water data in 2006 are in Table 6. As can be seen, the cooling water total phosphate and zinc are both below 1 ppm, which meets the demand of the first grade wastewater discharge standard.

The lower calcium hardness makes it very corrosive for ferrous metal. Meanwhile, high cycles systems with long retention time stressed both scale and corrosion control. The low iron level of the cooling water indicated that the system was being protected. For more than 12 months normal operation, coupon corrosion results demonstrated excellence performance. (Please see the carbon steel coupon corrosion rate tendency for cooling tower 1&2 in Fig. 2.) Corrosion rate were consistently below 0.5 mpy (0.013 mm/y) for carbon steel and below 0.2 mpy (0.005 mm/y) for admiralty brass. The equipment inspections also showed excellent scale, corrosion and biological control.

4.2 Case history-2

4.2.1 Background

In a new large Ethylene plant in eastern China, the makeup water for open recirculating cooling systems is clarified river water, which has moderate calcium, alkalinity and high chloride (See the average make up water in 2006 in Table 7). In order to eliminate the impact of wastewater on nearby coastal area, total phosphate and zinc were required to be less than 1.5 and 2 ppm respectively in the cooling water blowdown. There are many high temperature, low water velocity heat exchangers in this cooling water system. Meanwhile, the large system volume resulted in a long retention time, which increased the treatment difficulty under harsh conditions.

4.2.2 Treatment results

The treatment program is the same as the previous case history. Cycles of concentration were limited to 4 to maintain a site imposed chloride limitation less than 500 ppm. Cooling water has moderate calcium and high chloride level (See average cooling tower water in 2006 in Table 7).

Table 7. Cooling system make up and tower water data

Items	Unit	Makeup Water	Cooling Tower Water
pH		7.3	8.5
Total Hardness	mg/L as $CaCO_3$	198	737
Calcium Hardness	mg/L as $CaCO_3$	130	510
Magnesium Hardness	mg/L as $CaCO_3$	68	227
Total Alkalinity	mg/L as $CaCO_3$	115	194
Conductivity	μS/cm	856	3100
Turbidity	FAU	0.5	5
Chloride	mg/L	117	481
Sulfate	mg/L	127	761
Silica	mg/L as SiO_2	5.3	18
Iron	mg/L	0.02	0.09
Zinc	mg/L		0.88

Through continuous improvement using GE 6 sigma tools, water control limit, chemicals dosage and treatment cost were optimized in condition of excellence performance. GE Water and Process Technologies has treated this system for more than 24 months. The corrosion rate and deposit rate are tested by coupons and bypass monitor tubes once every month. The average corrosion rate and deposit rate data are presented in Table 8. The carbon steel corrosion rate tendency is shown in Fig. 3. Both Table 8 and Fig. 3 show excellent corrosion and scale control performance. From the table 7 water data, we also see excellent corrosion control, since the iron concentration of the cooling water closely tracked its theoretical value, based on the iron level of the make up water and the cycles of concentration. The equipment inspections also showed excellent scale, corrosion and microbial control.

5. Conclusions

(1) AEC, a patent non-phosphorous calcium carbonate scale inhibitor, has demonstrated better scale inhibition abilities than traditional phosphonates. In addition to its scale inhibition properties, AEC inhibits carbon steel cor-

Table 8. Average corrosion and deposit rate

Material	Coupon Corrosion Rate [mpy] (mm/y)	Monitor Tube Corrosion Rate [mpy] (mm/y)	Monitor Tube Deposit Rate [mg/cm^2/month]
Carbon Steel	0.22 (0.0056)	0.95 (0.0242)	5.81
Stainless Steel	0.004 (0.0001)		
Brass	0.013 (0.0003)		

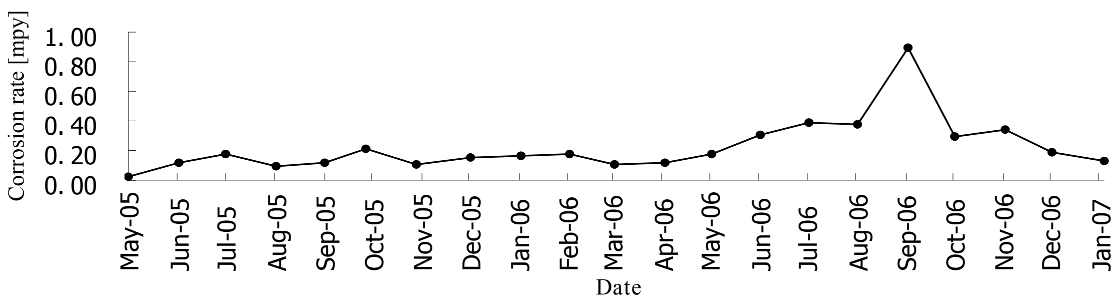

Fig. 3. Carbon steel coupon corrosion rate

rosion when used at high dosages.

(2) AEC can be combined with zinc to form a non-phosphorous program to provide an environmentally acceptable program, which complied with the first grade standard of wastewater discharge limitations.

(3) AEC/Zinc combinations have been found to be highly effective in controlling the corrosion of ferrous metals. AEC can provide good corrosion inhibition at high concentrations, 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.

Acknowledgments

The authors would like to acknowledge the efforts of Luo Hailong and Xu Jie of GE Water and Process Technologies for their hard work in the areas of monitor and control the projects. We would also like to acknowledge the efforts of Raymond Post, Gary Geiger and Heo JuCheol of GE for coordinating the writing of this technical paper.

References

1. V. Jovancicevic, The NACE International Annual Conference and Exposition, p. 226 (1996).
2. Roy Holliday, *8th European Symposium on corrosion inhibitors*, **17**, 493 (1995).
3. G. E. Geiger, International Water Conference, Pittsburgh, Pennsylvania (1995).
4. Carey William S, United States Patent, 5,871,691 (1999).
5. Xie Xiao, *Industrial Water Treatment*, **21**, 36 (2001).
6. He Jixing, *Petrochemical Technology*, Vol.30 Supplement, 836 (2001).
7. "Integrated wastewater discharge standard" (GB 8978 1996).
8. Xiong Rongchun, *Chinese Chemical Letters,* **14**, 955 (2003).
9. Zhang Bingru, *Industrial Water Treatment*, **26**, 53 (2006).