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Evolution of a Cooling Water Treatment
Program at a Chemical Processing Plant

BY

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RESEARCH REPORT

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ABSTRACT

During the construction of a chemical processing plant, a polyphosphate product was selected for use as a corrosion inhibitor in the open recirculating cooling tower system. After several months of operation, problems in the system made evident the fact that polyphosphate as a corrosion inhibitor was not acceptable. An organic corrosion inhibitor was substituted for the phosphate, resulting in improved corrosion protection and the elimination of phosphate fouling.

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INTRODUCTION

In 1978 the National Association of Corrosion Engineers reported that the estimated cost of corrosion and corrosion control for the year was \$50 billion (1). Since then this cost has surely increased, particularly in the area of corrosion control. A large part of this cost increase is due to government regulations that have made many of the traditional corrosion inhibitors environmentally unacceptable. The conventional zinc-chromate program, once the industry standard, is becoming a thing of the past (2,3).

Corrosion in aqueous systems takes many forms (4), and water treatment is a necessary part of a corrosion control program. The majority of plants in the chemical industry have established water treatment programs to control their water related corrosion problems. These programs include treatment of steam generating systems, open recirculating systems, and closed systems.

This paper will cover the treatment of an open recirculating cooling water system at a large chemical processing plant. This includes the implementation of a water treatment program and the changes needed before the optimum treatment program was established.

In the latter part of 1975, Degussa Corporation announced that it would build a chemical complex in Theodore, Alabama. This complex was to be constructed in stages, beginning with a utilities area and eventually ending with about forty individual plants. Because the utilities area was the first to be constructed, a water treatment program was among the first things to be considered.

The goals of a water treatment program are:

- to minimize corrosion
- to keep the system free of deposits
- to provide adequate microbiological control

These three topics are covered in more detail by Nestor and Cappeline in their paper Water Related Problems of Evaporative Cooling (5). In the case of Degussa Corporation, a corrosion rate of 5.0 mils per year (mpy) was established as the maximum acceptable corrosion rate for the system. The system was to be kept free of deposits, and no more than 50,000 microorganisms per ml were to be allowed in the tower water.

In order to monitor the program, corrosion coupons (6,7) and a magna corrotor (7) were installed in the return water line. Visual inspections would take place every time a piece of equipment was opened.

The circulating water which is cooled by evaporation in an induced draft cooling tower removes heat from compressors, chillers, and process heat exchangers. The circulation rate of the tower is 34,000 gallons per minute (gpm) and the average temperature drop is ten degrees F. (Reference 8 is a basic description of cooling towers, including the terms and diagrams necessary for an understanding of their workings.) The makeup water to this tower is supplied by the city of Mobile, Alabama.

The Initial Program

The choice of corrosion inhibitors was made on the basis of environmental impact and cost effectiveness. The Alabama Water Improvement Commission (A.W.I.C.) would not allow chromate to be present in the plant's effluent. Since chromate removal was considered to be too costly (3), this left polyphosphate or organic corrosion inhibitors as the only viable candidates. Because of the lower cost, the polyphosphate inhibitor was chosen.

The choice of a polyphosphate corrosion inhibitor as a replacement for chromate is becoming more widespread. Many studies have shown polyphosphate to be an excellent corrosion inhibitor, and almost as effective as chromate (9,10).

In addition to being proven corrosion inhibitors, studies have shown that polyphosphates are effective scale inhibitors and dispersants (11).

In addition to the polyphosphate corrosion inhibitor, the treatment program included a dispersant for mud, silt, and organic matter. For microbiological control, gaseous chlorine was selected as the primary biocide and was supplemented with a polychlorophenate compound. Sulfuric acid and caustic were used as needed for pH control. A description of the products used along with feeding information and control limits is contained in Table I.

DISCUSSION AND RESULTS

Results of the Phosphate Treatment Program

The corrosion rate in the treated system was very low, only 0.8 mpy average (Table II). This was well below the allowed maximum limit of 5.0 mpy. However, there was fouling in several of the compressors and some of the oil coolers. Results from the analyses of these deposits showed them to be primarily phosphate sludge, probably caused in part by the treatment program. Table III shows the results of analyses on these deposits.

Table I

Polyphosphate Treatment Program
of Cooling Tower Water

Chemical	Control Limits	Method and Point of Feed
Drewgard 180 (polyphosphate corrosion inhibitor)	orthophosphate 3-7 ppm polyphosphate 6-10 ppm total phosphate 10-15 ppm	Continuously to the cooling tower basin
Drewspense 738 (nonionic polymeric dispersant)	25 ppm as product	Continuously to the cooling tower basin
Biocide 207 (polychlorophenolate biocide)	30 ppm as product	Slug fed to cooling tower basin once per week
Gaseous Chlorine	free residual chlorine of 0.1-0.5 ppm	Residual obtained every shift. Fed to the cooling tower basin.
caustic or sulfuric acid	pH 7.0-7.5	Slug fed to cooling tower basin

Table II
Corrosion Rates Using the Polyphosphate Corrosion Inhibitor.

Date Coupon Installed	Date Coupon Removed	Corrosion Rate (mpy)
9/20/77	11/1/77	0.5
9/20/77	11/1/77	0.6
9/20/77	11/1/77	0.6
9/20/77	11/1/77	0.7
11/1/77	1/26/78	1.9

Table III

Composition of Deposits Obtained During the Use of the Polyphosphate Corrosion Inhibitor. All analyses are weight percent.

<u>Test</u>	<u>Sample 1*</u>	<u>Sample 2*</u>	<u>Sample 3*</u>
Silica as SiO ₂	4.0	5.1	17.0
Phosphorus as P ₂ O ₅	10.0	14.0	13.0
Calcium as CaO	6.7	4.8	1.5
Iron as Fe ₂ O ₃	60.0	63.0	48.0
Loss on Ignition	9.6	7.6	13.0

* Carbonate, sulfur, magnesium, copper, zinc, chromium, and chloroform extractables all less than one percent.

Sample 1: south nitrogen compressor; 11/11/77

Sample 2: south nitrogen compressor; 2/13/78

Sample 3: oil cooler on air compressor; 10/13/78

Note: the south nitrogen compressor was acid cleaned after the sampling on 11/11/77.

In considering the results presented in Table III, several points are noteworthy:

- all of the deposits are virtually identical, indicating only one cause for the deposition.
- the deposits consist of calcium phosphate, iron phosphate, sand, and rust.

The conclusions drawn from the results are:

- the polyphosphate in the corrosion inhibitor reverted to orthophosphate because of high temperatures in the heat exchangers.
- the orthophosphate then reacted with calcium and iron to form calcium phosphate and iron phosphate deposits.
- corrosion took place under the deposits producing iron oxide.

These conclusions were confirmed when visual inspection of the south nitrogen compressor revealed, after cleaning, the pitting attack that is associated with under-deposit corrosion.

Microbiological control was very good, with little growth seen on the tower or in any of the equipment, but process contamination from one of the production plants was causing severe pH excursions. This particular plant was releasing silicon tetrachloride into the air, where it was being pulled into the cooling tower and dissolving in the water. The reaction that took place,



lowered the pH of the tower water.

In addition to the SiCl_4 contamination there was a history of iron contamination following the start up of new plants. As each of the new plants came on line, the rust from the pipes was dumped into the cooling water system. This iron was present in sufficient quantities to cause iron deposits on the corrosion coupons and in heat exchange equipment (Table IV).

Deposits 4 and 5 consist primarily of iron phosphate, along with an abundance of iron oxide. The phosphate is again from the corrosion inhibitor, but the iron must have come from another source.

Evaluation of the phosphate treatment program showed two areas where improvement was desired. The first area of concern was the phosphate sludge that was fouling the compressors. This sludge was resulting in a steady decrease in efficiency that culminated in having to shut down and clean the equipment. The second area of concern was the iron fouling from the rust in the pipes. Iron deposits are very insulating and are potentially detrimental to the system.

Because of these two problem areas, in March of 1978 it was decided to make two changes in the water treatment program. The first change was to replace the polyphosphate corrosion inhibitor with a totally organic corrosion inhibitor. The second change was to begin continuous feed

Table IV

Composition of Deposits from Corrosion Coupons. Analyses are weight percent.

Test	Sample 4 *	Sample 5 *
silica as SiO ₂	2.6	1.8
phosphorus as P ₂ O ₅	2.6	6.7
iron as Fe ₂ O ₃	89.0	58.0
loss on ignition	15.0	----

* Carbonate, sulfur, calcium, magnesium, copper, zinc, chromium, and chloroform extractables less than one percent.

Sample 4: From corrosion coupon #6929; 9/14/78

Sample 5: From corrosion coupon #8467; 12/4/78

of a dispersant designed to solubilize and disperse the rust so that it could be removed by bleeding off some of the concentrated cooling water.

The Organic Treatment Program

The new inhibitor formulation contains hydroxyethylidene-1,1 Diphosphonate (HEDP); benzotriazole; a sulfonated wood derivative; and Isoquest (R).

HEDP has proven to be both a corrosion inhibitor and a scale preventative (3,9-12). Benzotriazole is recognized as one of the most effective copper corrosion inhibitors available today, as well as enhancing corrosion control on mild steel when used in conjunction with other inhibitors. Benzotriazole's tenacious film acts as a corrosion inhibitor even when the benzotriazole is not being added continuously (13-15). The carboxylic-substituted polymers, such as Isoquest, are very effective as both corrosion inhibitors and scale inhibitors (12).

The addition of a dispersant for iron was determined to be necessary because of the addition of new pieces of process equipment due to the rapid growth of the plant and because of the realization that the iron levels in the Mobile city water were greater than originally expected.

The iron dispersant used in the treatment program consists of aminomethylenephosphonate (AMP) and nitrilotriacetic acid (NTA). These compounds sequester iron and solubilize it so that it can be removed from the system by bleed (11,12). Table V shows the water treatment program as it currently exists.

Results of the Organic Treatment Program

After the change to the organic corrosion inhibitor, the corrosion rate was measured by corrosion coupons to be an average of 1.2 mpy. A two-year history of corrosion rates during the organic treatment program is given in Appendix A. The average corrosion rate is slightly higher than when using the polyphosphate corrosion inhibitor, but still less than the maximum acceptable level of 5.0 mpy.

Phosphate deposits are no longer visible in the nitrogen or air compressors. Some phosphate deposits were found in other pieces of equipment, but these had never been cleaned, and the deposits were determined to be old deposits retained from the phosphate treatment program.

There was no change in microbiological control, and it appeared that the optimum water treatment program had finally been achieved.

Table V

Organic Treatment Program

Chemical	Control Limits	Method and Point of Feed
Drewgard 187 (organic corrosion inhibitor)	150-300 ppm as product	continuously to the cooling tower basin
Drewperse 738 (nonionic polymeric dispersant)	25 ppm as product	continuously to the cooling tower basin
Biocide 207 (polychlorophenolate biocide)	30 ppm as product	slug fed to the cooling tower basin
Gaseous Chlorine	free residual chlorine of 0.1-0.5 ppm	Residual obtained every shift. Fed to cooling tower basin.
caustic or sulfuric acid	pH 7.5-8.5	slug fed to the cooling tower basin
Drewperse 744 (iron dispersant)	25 ppm as product	continuously to the cooling tower basin

On August 2, 1978, a mechanical failure caused water from another system to be dumped into the cooling water system. This water contained 12% ethylene glycol by weight. Experience had shown that uninhibited ethylene glycol is corrosive to mild steel, so several precautions were taken to protect the system.

The first precaution was to double the concentration of corrosion inhibitor. As can be seen from the corrosion data in Appendix A, this had very little effect, and the corrosion rate increased to an average of 19.6 mpy.

Since ethylene glycol is a nutrient, the chlorination cycle was extended and the polychlorophenate biocide was added twice each week. In spite of this, severe microbiological deposits appeared in many pieces of equipment and on the corrosion coupons.

Because of the increased corrosion due to the ethylene glycol and because of the under-deposit corrosion caused by the microbiological growth, iron fouling increased. The dosage of the iron dispersant, Drewperse 734, was doubled in an effort to remove the iron from the system.

On October 1, 1978, repairs were completed and the ethylene glycol was no longer being dumped into the cooling tower. The corrosion rate began to decrease immediately, but took almost eight months to reach an

acceptable level. As the corrosion rate decreased, so did the microbiological growth and the iron fouling.

By the end of 1979 all systems were in excellent condition. The current corrosion rate is consistently less than one mpy and the system is free of deposits. There is little microbiological growth in the tower and none in the equipment that has been inspected. At this time, all of the goals of the water treatment program are being realized.

PROJECT OVERVIEW

The choice of polyphosphate as the initial corrosion inhibitor was the correct one, given the information available at the time. The fouling and contamination problems were completely unforeseen, given the newness of the equipment.

The phosphate fouling had many causes. Polyphosphates will revert to the simpler orthophosphate with time, high temperatures, and low pH values. The skin temperatures in the compressors were causing reversion to orthophosphate and the formation of calcium phosphate and iron phosphate deposits. This explains why the deposits were seen only in the compressors and not in other heat exchange equipment or piping.

Some reversion to orthophosphate was also occurring due to pH values as low as 3 and was aggravated by the long retention time caused by the partial heat load on the tower. This phosphate would deposit in low flow areas of the system. Calculations showed that the nitrogen compressors had a very low flow: less than one foot per second. This combination of high temperatures and low flow rates made the nitrogen compressors extremely susceptible to phosphate fouling.

When fouling in the nitrogen compressors became a problem, many possible solutions were considered. The three most reasonable possibilities were:

- to install a booster pump to increase water flow through the compressor
- to feed a dispersant directly into the compressor, hoping that it would keep the phosphate from settling there
- to eliminate the phosphate from the treatment program

The installation of a booster pump or feeding a dispersant directly to the compressors would probably help the problem but would not cure it. Therefore, the decision to change corrosion inhibitors would be the best course of action.

After the change of corrosion inhibitors was completed the corrosion rate increased. This rate increase was expected, because studies have shown organic corrosion inhibitors to be slightly less effective than phosphates (10). Recent results, however, show an average corrosion rate of only 0.5 mpy (Appendix A). These results are better than those obtained using phosphate, and are the result of the combined effects of the corrosion inhibitor and dispersants. Many of the compounds in the dispersant products also act as corrosion inhibitors (3,9-12),

thus helping to achieve the low corrosion rates that are currently being measured.

CONCLUSIONS

1. In 2½ years of plant operations using two different corrosion inhibitors, an organic corrosion inhibitor has been more effective than a polyphosphate corrosion inhibitor, and not subject to the fouling problems associated with a phosphate program.
2. Because the corrosion rates being obtained using this program are much better than studies of organic inhibitors show should be expected, the entire program, not just the type of corrosion inhibitor, should be considered when designing a water treatment program.
3. Changes in water characteristics can have a substantial impact on the corrosion control program.
4. Because of individual system characteristics, dynamics, and operating parameters, effective cooling water treatment requires close monitoring of results and modifications based on scientific evaluation and the application of available technology.

APPENDIX A

Corrosion Coupon Results Using the Organic Corrosion Inhibitor

<u>Date Coupon Installed</u>	<u>Date Coupon Removed</u>	<u>Corrosion Rate (mpy)</u>
3/20/78	CHANGED TO DREWGARD 187 PROGRAM	
3/20/78	4/3/78	0.6
3/20/78	4/10/78	0.8
3/20/78	5/11/78	1.3
5/11/78	7/28/78	1.3
5/11/78	7/28/78	1.2
6/23/78	7/28/78	2.1
8/2/78	BEGAN DUMPING WATER (with ethylene glycol) INTO THE COOLING TOWER	
8/7/78	9/14/78	24.9
8/7/78	9/25/78	21.3
8/7/78	10/9/78	19.0
8/7/78	10/16/78	16.2
9/14/78	10/16/78	18.6
9/25/78	10/30/78	18.1
10/1/78	STOPPED DUMPING WATER (with ethylene glycol) INTO THE COOLING TOWER	
10/9/78	11/8/78	13.9
10/23/78	11/8/78	9.8
10/23/78	11/8/78	9.8
10/30/78	11/8/78	11.0
11/8/78	11/24/78	10.9

<u>Date Coupon Installed</u>	<u>Date Coupon Removed</u>	<u>Corrosion Rate, mpy</u>
11/8/78	12/4/78	8.9
11/8/78	12/11/78	7.3
11/26/78	12/11/78	1.2
12/4/78	1/8/79	1.4
12/11/78	12/26/78	2.3
12/11/78	1/22/79	2.2
12/26/78	1/8/79	13.2
12/26/78	1/22/79	12.8
1/8/79	2/26/79	3.4
1/22/79	1/29/79	4.6
1/22/79	2/26/79	7.0
1/22/79	2/26/79	6.0
1/29/79	2/26/79	5.3
3/19/79	4/11/79	9.8
3/19/79	4/11/79	8.5
3/19/79	4/11/79	9.7
4/11/79	5/14/79	3.9
4/11/79	5/22/79	1.3
4/11/79	5/22/79	4.8
5/14/79	6/11/79	1.0
5/14/79	6/4/79	1.4
5/22/79	6/18/79	1.0
5/22/79	6/28/79	0.4

<u>Date Coupon Installed</u>	<u>Date Coupon Removed</u>	<u>Corrosion Rate, mpy</u>
6/4/79	7/12/79	0.8
6/11/79	7/30/79	0.3
6/18/79	8/9/79	0.2
6/28/79	8/9/79	0.3
7/30/79	8/27/79	0.7
8/9/79	8/27/79	0.7
8/9/79	8/27/79	0.5
10/25/79	11/12/79	0.9
10/25/79	12/6/79	0.5
10/25/79	12/6/79	0.5
10/25/79	12/6/79	0.5
11/12/79	1/7/80	0.5
12/6/79	1/31/80	0.5
12/6/79	1/31/80	0.5
12/6/79	1/31/80	0.4
1/7/80	2/28/80	0.3
1/31/80	3/27/80	0.3

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