

## New Protective Measures for Cooling Systems

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Cooling water treatments have been updated and improved during the last few years. Particularly important are the nontoxic programs which conform plant cooling water effluents to local water quality standards without expenditures for capital equipment.

The relationship between scaling and corrosion in natural waters has been recognized for many years. This relationship is the basis for the Langelier Saturation Index control method which was once widely applied to reduce corrosion in cooling water systems. It used solubility characteristics to maintain a very thin deposit on metal surfaces for preventing corrosion. This technique was rarely successful.

That is, the solubility of calcium carbonate and most other inorganic salts depends on temperature. If good control exists on cold surfaces, excessive deposition results on the heat transfer tubes. Also, because water characteristics normally vary in a typical cooling system, precise control of scaling at both hot and cold surfaces is virtually impossible.

Until the last few years, acid was normally used for most recirculating cooling water systems to decrease the pH to a level where calcium carbonate scaling was no longer a problem. That approach made excellent corrosion inhibitor formulations necessary. Most of such formulations were chromatebased. However, more recent legislation prohibiting the discharge of toxic materials to navigable water ways has made it impossible to use chromates in some areas of the United States. This restriction resulted in the development of a new technology and many new corrosion inhibiting formulations to satisfy environmental nontoxic criteria.

### New technique eliminates need for acid

Combining deposit control agents and newer nonchromate inhibitor formulations now provides excellent corrosion control without scaling in a pH range that would have been unmanageable from a scaling standpoint five years ago. This new technique is exactly the reverse of traditional approach.

Instead of lowering the pH to avoid scaling and then treating to prevent corrosion, the pH is elevated to a range of 7.5 to 9.0 to minimize corrosion. The

system is then treated to control scaling and deposition, corrosion being the relatively minor problem. With this new technology, many plants can now operate without using acid.

### Laboratory evaluations

Several experimental procedures were used to evaluate the new technology.

**Rapid Screening Test**—This test exposed preweighed corrosion test coupons (AISI 1085 steel) attached to a rotating holder in a 22 liter glass vessel containing the solution under study. The solution was constantly aerated and maintained at a uniform temperature of 120F, using a thermostatically controlled heater.

Total Hardness, as CaCO <sub>3</sub>	280
Calcium, as CaCO <sub>3</sub>	170
Magnesium, as CaCO <sub>3</sub>	110
Chloride, as Cl	119.4
Sulfate, as SO <sub>4</sub>	105.5
Copper, as Cu	0.2
(all values in parts per million)	

Fig. 1—Composition of simulated cooling water used for laboratory evaluations of new nontoxic treatments.

A simulated cooling water was utilized in all studies, unless otherwise indicated. pH was adjusted to the desired value with sodium bicarbonate or sulfuric acid.

Tests were conducted over a three-day period. Two corrosion test coupons were removed, cleaned and weighed after the first and third day. The weight loss between one and three days was used to calculate the corrosion rate in thousandths of an inch penetration per year.

**Recirculating System**—This system utilized automatic pH and temperature control. Treatment and makeup water were added to the system continuously, using Precision chemical feed pumps. The blowdown was the overflow from the sump of the system.

Since rates could be varied from 0.5 to 14 feet per second past the coupons, the system allowed studies at flow rates typical of industrial heat exchangers. The system was also equipped with a heat exchanger so heat transfer 'U' coefficients could be calculated. Hot water at 180-200F was utilized on the hot side of the exchanger. A typical temperature difference of 4-10F existed between the outlet and inlet of the cold water side. Measuring the change of 'U' coefficient with time provided a fouling factor.

**Test Cooling Tower**—The Lillie Hoffman CU50 cooling tower was rated at five tons of cooling at a circulation rate of 3 gallons per minute per ton. A heat load supplied by steam to three heat exchangers provided a 5-10F temperature rise ( $\Delta T$ ) across the tower. Corrosion data was obtained by use of coupons and a corrosion probe installed in a test specimen bypass.

**Electrochemical Tests**—Potentiodynamic polarization studies using a previously developed technique were utilized.

### Results and discussion

The phosphonates, particularly nitrilotris (methylenephosphonic acid) abbreviated as AMP, have been widely accepted in water treatment during the past few years. These materials prevent the precipitation of undesirable scales. They also have corrosion inhibiting properties.

Corrosion inhibition obtained with AMP alone is shown in Fig. 3

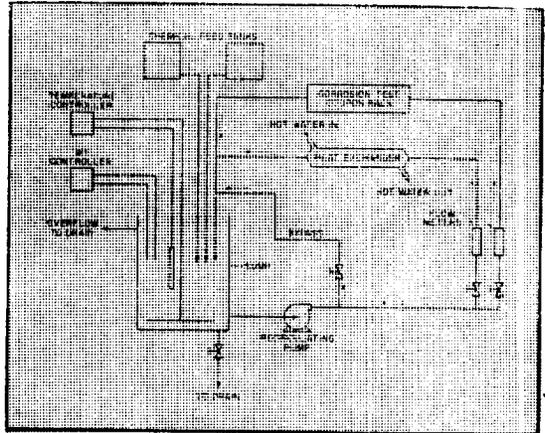


Fig. 2 Schematic diagram of the recirculating cooling system used for laboratory evaluations.

A similar behavior was exhibited at both pH 7 and 8. A minimum treatment level of 25 ppm provided acceptable corrosion rates. In addition, pitting was exhibited at both pH 7 and absent at pH 8. Although the exact mechanism of corrosion inhibition with AMP is unknown, cathodic inhibition from either calcium phosphonate salt is more evident at high pH than at a low pH. Results of potentiodynamic cathodic polarization studies covered by Figure 4 seem to confirm this.

An increase in pH increased the cathodic inhibition under the same conditions. At the same pH, an increase in calcium concentration also increased the

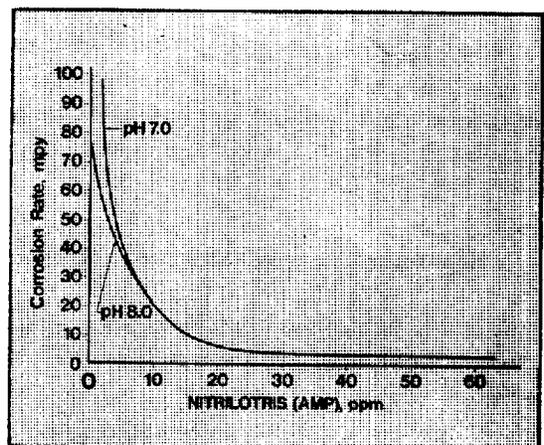


Fig. 3 Evaluation of the effect of nitrilotris (AMP) concentrations on the corrosion rate of high carbon steel in the simulated cooling water using the screening test.

cathodic inhibition. Based on this data, it seems that AMP alone provides adequate corrosion inhibition in cooling waters containing high levels of calcium. However, further study of the system indicated that the treatment was unacceptable.

Without heat transfer, the corrosion rate in the recirculating system was 16 mils per year (mpy). This rate resulted from the increased flow (2 ft/sec) as compared to the screening test. Within ten minutes of utilizing the heat transfer tube, insoluble iron oxide appeared in the system due to corrosion. This also occurred with a drop of pH to 5.0 for a halfhour without heat transfer. Another disadvantage, reported by Hatch et al and confirmed by BETZ, is that the phosphonates alone are aggressive to copper and copper alloys.

Nitritoltris (AMP), ppm	Calcium, ppm CaCO <sub>3</sub>	pH	Cathodic Inhibition, percent
50	37	6.5	-50
50	500	6.5	+70
20	500	6.5	+20
20	500	8.0	+40
20	170	8.0	+10

Fig. 4—Potentiodynamic cathodic polarization tests for AMP in the simulated cooling water.

It was noticed in all tests conducted with AMP that the corrosion coupons did not have a visible film on the surface. With chromate-based treatments, however, interference colors, indicating an adherent protective film, are usually present. Apparently the film with phosphonates alone is thin, probably only several molecules thick. This film breaks down rapidly under such severe conditions as high flow rates, low pH or high heat transfer.

To overcome these inherent disadvantages, the phosphonates were formulated with such corrosion inhibitors as zinc and/or organic nitrogen-containing agents. Some of the same disadvantages were evident with these new formulations. However, these treatments are effective in air conditioning systems utilizing copper heat transfer tubes.

The pH is critical in phosphonate-based treatments. There is a minimum pH for any particular conditions

at which adequate corrosion inhibition can be obtained. Normal range of operation is pH 7.5 to 9.0, a level which allows most recirculating cooling systems to operate without acid feed.

Inhibitor Concentration, ppm	pH	Testing Procedure	Corrosion Rate, mpy
25	8.0	Screening	4
25	8.0	Recirculating System Without Heat Transfer	16
25	8.0	Recirculating System with Heat Transfer	43

Fig. 5—Corrosion inhibition performance of AMP with various testing procedures.

Additional studies have developed several proprietary formulations based on phosphates. Combining rate control and dispersant technology with nonchromate inhibitor developments resulted in corrosion rates of less than 3 mpy, without pitting and harmful deposition. Protection resulted even at high pH and in high hardness waters.

Fig. 6 shows the results of studies of several proprietary formulations containing phosphates, phosphonates and organic heterocyclic compounds. These tests were conducted with a 5-10 ppm phosphate (PO<sub>4</sub>) at high pH without deposition problems. All corrosion rates are as acceptable as rates for many of the chromate-based treatments.

Inhibitors A, B and C are all phosphonate/phosphate

Inhibitor	Concentration, ppm	pH	Calcium, ppm CaCO <sub>3</sub>	Testing Procedure	Corrosion Rate, mpy
A	150	8.5	340	screening	1
A	150	8.5	700	tower	1-3
B	150	8.5	170	recirculating	2
B	150	8.5	700	recirculating	1.5
C	1000	8.0	170	screening	1.5

Observations: None of the coupons suffered pitting or heavy deposition. In the case of the cooling tower test for inhibitor A, appearance of the heat transfer tube was excellent.

Fig. 6—Results of laboratory evaluation tests for various proprietary formulations.

organic treatments designed for recirculating cooling systems. A is used where chlorine is not being used for microbiological control. Treatments B and C can be used in the presence of chlorine. C is designed for systems not having good control of feed rates and other operating parameters of the tower.

These formulations offer several advantages in that they:

- 1) satisfy environmental criteria of being non-chlorinate and nonzinc treatments,
- 2) eliminate the need for the precise control required with other phosphate-based treatments since reversion creates no deposition problems,
- 3) can be used when chlorine is used as a biocide,
- 4) eliminate the need for acid feed in most systems, and
- 5) work effectively under heat-transfer conditions, with no deposition or pitting attack occurring.

But there are other combinations of phosphates with deposit control agents that can also give acceptable corrosion rates without deposition at high pH.

### Case history:

#### large chemical corporation

The process tower, with a circulation rate of 10,000 gpm, operates at 4 cycles of concentration on the new phosphate/phosphonate organic treatment program.

Typical Tower Water Analysis (pH 7.5-8.0) ppm	
Total Hardness, as CaCO <sub>3</sub>	600
Calcium, as CaCO <sub>3</sub>	400
Magnesium, as CaCO <sub>3</sub>	200
Alkalinity, as CaCO <sub>3</sub>	120
Sulfate, as SO <sub>4</sub>	95
Chloride, as Cl	240

This plant has been operating with phosphate control limits of 4-6 ppm for over a year with acceptable corrosion rates (less than 4 mpy). No pitting or deposition problems have been experienced. Previously, corrosion rates above 10 mpy, possibly associated with poor control of pH, occurred.

### Summary

Acceptable control of corrosion and scaling can now be accomplished using treatments containing no chromate or zinc. One such treatment program, based on phosphates in combination with phosphonates and organics, has proven its effectiveness in many industrial systems. Others, based on phosphonates without phosphates, can be used successfully in air conditioning systems.

More recent treatments with polymeric compounds may eventually eliminate phosphorus-containing treatments, and thereby satisfy further pollution standards.