

Non-Chromate Treatment of Cooling Water

Technique uses viable alternative chemical materials to help reduce or eliminate increasing problems from heavy metals in cooling system effluents.

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Cooling water systems can be protected successfully with a non-chromate kind of approach, mainly phosphate and phosphonate, which can also permit a reduction in unwanted environmental pollution problems.

The use of blended chromate, phosphate and zinc treatment has for years been proving to be the best approach to the control of corrosion in cooling water systems where steel heat exchange equipment is used. In recent years, deposit control agents have been applied with a corrosion inhibitor to improve system cleanliness and maintain heat transfer efficiency.

This treatment program has been highly successful, especially in ammonia plants and refineries, in extending periods between turnarounds and providing protection at an economical cost. A development of Betz Laboratories, it has the registered trade name of "Dianodic."

To meet the environmental standards governing discharge regulations requires close analysis of cooling tower blowdown streams. In most instances, hexavalent chromium must be maintained below 0.05 ppm in plant effluent. This restriction severely limits the level of chromate that can be used in the cooling system without special treatment of the cooling tower blowdown to remove chromate.

To comply with the environmental regulations and maintain an effective treatment program, several alternatives are available. A partial listing of approaches in use today includes:

1. Chemical reduction and precipitation.
2. Electrochemical reduction.
3. Chromate recovery by ion exchange.
4. Makeup pretreatment with minimum blowdown.
5. Blowdown softening and recycle.
6. Ultra low chromate treatment.
7. Non-chromate treatment.

Each discharge problem must be considered independently and an evaluation of each alternative made. Such factors as

makeup water quality, system design, and existing waste treatment facilities can all influence the best approach. A qualified water treatment consultant can provide practical guidance in this important area.

Because of the many factors which can affect the results, each plant's problems must be considered independently. However, it may be helpful to examine more carefully the non-chromate approach which has proven to be a viable alternative in recent years.

Considerable experience has been gained in recent years with treatments that employ phosphate and phosphonate. These programs have met environmental standards and provided industry with protection approaching that of chromate based treatment. The basic program employs phosphate and phosphonate with pH ranging from 6.5 to 8.5. Typical orthophosphate and total phosphate levels are 2 to 10 ppm, and 4 to 15 ppm, respectively. Where copper or copper alloys exist in a system, a specific corrosion inhibitor is included for these metals. In many systems, polymers and surfactants are used to aid in deposit control.

Specific guidelines were developed

Various aspects of this program have been examined through both laboratory and field data from actual case histories to provide specific guidelines for the application of the program. A thorough system review is required to establish proper control limits and treatment particulars. The following data should be reviewed prior to the establishing of a program and its startup.

Water characteristics are the most important assessment. The total treatment program, including the selection of control parameters and type of deposit control agent, is designed around the composition of the water. The following is a listing of critical parameters, the exact details of which can be obtained from a careful analysis plus knowledge of the

system: calcium, silica, iron, aluminum, pH, and dissolved solids.

Calcium functions effectively as a cathodic corrosion inhibitor by precipitating at the high pH sites of the cathodic reaction. Several species of calcium salts play an important role in cathodic inhibition with the phosphate/phosphonate program. To effectively combat this treatment's reduced effectiveness in low calcium concentration waters (<100 ppm. Ca as CaCO₃), other cathodic corrosion inhibitors, such as zinc, can be used. The addition of low levels of zinc is frequently successful in eliminating pitting attack encountered with low hardness waters, as shown in Table 1.

Table 1. Effect of hardness on phosphate/phosphonate treatments

Phosphate concentration, ppm.	Total hardness pH as CaCO ₃ , ppm.	Calcium as CaCO ₃ , ppm.	Corrosion rate, mil/yr.
6	8.0	0	50
6	8.0	110	50
6	8.0	195	0-5
6	8.0	380	0-5
6	8.0	450	0-5
6	8.0	570	0-5
6	8.0	610	0-5

Need both corrosion and deposit control

A phosphate/phosphonate program requires a balance between corrosion and deposit control. Control of calcium carbonate, calcium sulfate, and calcium phosphate scale formation is accomplished through the activity of the phosphonates and polymers, and maintenance of specific solubility limits. A maximum Langelier Saturation Index of +2.5 should be maintained for the control of calcium carbonate. Control of calcium phosphate involves a saturation index of less than 1.5 and the use of polymers in conjunction with the phosphonate for dispersion.

Silica. The potential for silica and magnesium silicate to form is considerably increased as the pH rises above 8.0. A maximum of 200 ppm. silica is suggested. If the silica level is above 100 ppm., a pH of 7.5 or less is preferred. Magnesium silicate deposition depends on several factors, a very important one being the history and form of the silica in the circulating water. Deposit control agents containing acrylate polymers reduce the tendency for magnesium silicate to form.

Iron levels above 0.5 ppm. require a phosphonate/polymer treatment to control iron deposition. Where heavy iron contamination is experienced (greater than 3 ppm.) higher levels of phosphonate will be required due to adsorption of the phosphonate on iron. Iron removal should be considered if the concentration will approach 10 ppm. in the recirculating water.

Aluminum. Even low levels of aluminum can cause deposition problems. Carryover of soluble aluminum from clarifiers using alum should be minimized. Aluminum in the

circulating water should be less than 1 ppm.

pH. The operating pH range will be determined primarily by the various saturation indices which must be maintained. Other factors influencing pH include design considerations, microbiological control and system metallurgy. Typically these programs are operating within the broad range of 6.5 to 8.5. The control of pH for a given system should not vary more than 0.2 units from a set point. Automatic pH control is required to obtain this close degree of control when feeding acid.

Dissolved solids. Waters with conductivities greater than 4,000 micromhos are extremely corrosive, and this can cause marginal to poor results for a non-chromate program. To use a non-chromate treatment with this type of water, a high pH should be maintained to help reduce the corrosion load. Also, if copper alloys are present, a specific copper inhibitor such as benzotriazole should be used because high solids water will accelerate copper corrosion.

The design of a plant should be thoroughly studied before applying a phosphate/phosphonate program. Adverse factors such as low water velocities and shell-side cooling may exist, and these can increase the potential for deposit problems. Modified control parameters and treatment composition and practices must be established which take this increased potential for fouling and corrosion into consideration.

The conversion of a system from a chromate based program to a phosphate/phosphonate treatment generally results in an increase in biological activity. The removal of chromate from the water is one reason for this, because the chromate ion exhibits a certain level of toxicity to some bacteria and algae. Also, the pH control range is frequently altered to favor algae growth.

Non-oxidizing biocides should be selected on the basis of their effectiveness within the operating pH range. Our work has shown that methylene bithiocyanate based biocides are generally not as effective with the pH in the range of 7.5-8.5 as they are with the pH below this level. Likewise, chlorophenolate based biocides lose effectiveness as the pH is increased, as illustrated in Figure 1.

Chlorination is being used successfully in numerous instances, although high pH systems will require a longer

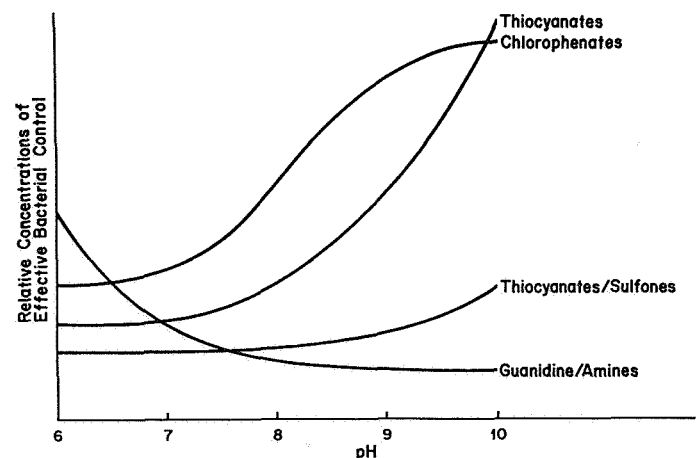


Figure 1. Curves show relative effectiveness of several families of compounds used to control bacteria.

contact time. Despite the change in HOCl/OCl ratio with change in pH, as shown in Figure 2, changing a system from a low pH to a high pH program normally does not seem to result in a major increase in chlorination requirements.

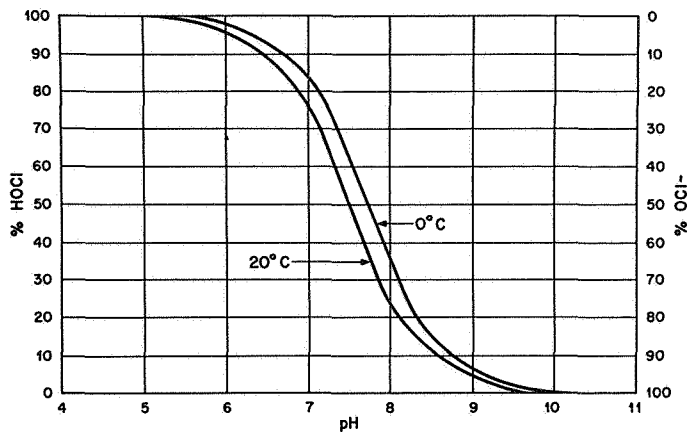


Figure 2. Relative amounts of HOCl and OCl present at various pH values.

Plant control practices

It is imperative that the plant maintain good control of the critical parameters of pH and treatment level, otherwise the program will produce poor results. Automatic control of pH is recommended. Either the orthophosphate or total phosphate test is used for treatment control. A photometric method is normally suggested for control of low levels of orthophosphate or total phosphate. Close control over cycles of concentration is also important as it directly affects inhibitor balances.

Whenever a chromate program is being replaced by a phosphate/phosphonate program it is usually sufficient simply to phase in the new program. Where the system is not well passivated, however, pretreatment with a specific pretreatment compound is strongly recommended. Chromate-based and phosphate-zinc formulations are used for this purpose. Pretreatment should also follow acid cleaning or accidental low pH upsets.

In January, 1974, a "Dianodic" treatment was replaced with a phosphate/phosphonate ("Polynodic") program at a midwestern ammonia facility. Before the conversion, several means of eliminating chromate from the plant's effluent were considered. Chromate reduction by chemical means was considered too expensive because of capital costs. Also, state authorities would have required a chromate reduction facility that provided a 30-min. residence time in reduction, neutralization, and surge tanks. A clarifier was required in addition to sludge dewatering equipment.

The possibility of cold lime softening for the makeup water and operating the cooling tower with windage loss only was considered. Windage loss of approximately 0.2% would have resulted in 10 cycles of concentration. Even with the improved makeup water quality, it was recommended that the system not exceed six cycles of concentration due to the high level of dissolved and suspended solids which would develop. Operating at this level would have resulted in a hexavalent chromium concentration of 0.7 ppm. in the plant

effluent. It was at this point that it was decided to go to a non-chromate program. Table 2 indicates the makeup and circulating water analyses.

Table 2. Water analysis report

	Well	makeup	Circulating
Total hardness, as CaCO ₃ , ppm.	278	1,128	
Calcium, as CaCO ₃ , ppm.	190	824	
Magnesium, as CaCO ₃ , ppm.	88	304	
Phenolphthalein alkalinity, as CaCO ₃ , ppm.	0	0	
Methyl Orange alkalinity, as CaCO ₃ , ppm.	220	46	
Sulfate, as SO ₄ , ppm.	55	950	
Chloride, as Cl, ppm.	10	87	
Silica, as SiO ₂ , ppm.	13.5	56.7	
Total phosphate, as PO ₄ , ppm.	0.0	9.0	
Total inorganic phosphate, as PO ₄ , ppm.	0.0	5.7	
Orthophosphate, as PO ₄ , ppm.	0.0	3.3	
pH	8.3	7.4	
Specific conductance, micromhos, 18 C	500	1,900	
Total copper, as Cu, ppm.	0.02	0.05	
Total iron, as Fe, ppm.	0.05	0.6	

This plant is currently operating a 25,000-gal./min. cooling tower with a 20°F temperature drop. Cycles of concentration are controlled in the range of 3.0 to 4.0, and pH is maintained at 7.2 to 7.4. Total inorganic phosphate residual is held at 3-5 ppm. A proprietary formulation is fed to provide the polyphosphate, phosphonate, and copper corrosion inhibitor. At present, a deposit control agent containing polymer and surfactants is topping off the program. Microbiological control is with intermittent chlorination and weekly additions of non-oxidizing biocides.

Results of the treatment program are closely monitored with a continuing corrosion coupon study, test heat exchanger, microbiological (MB) testing, and visual inspection of the cooling tower. Mild steel corrosion coupons indicate corrosion rates consistently in the range of 2 mil/yr. Initial coupon data revealed low overall corrosion rates; however, substantial pitting type attack was observed. Recent changes have improved this condition considerably.

Corrosion rates are also monitored in the makeup water because this is used for cooling of six trim coolers on a once-through basis. We should note that the treatment is applied at the well pump discharge so that a low level of treatment is present at this point. Corrosion rate measurements reflect a possible increase in corrosion rate in the once-through exchangers, over previous treatment with chromate. Equipment inspections scheduled for the fall of the year will provide additional insight into this problem area.

Equipment inspections during the past two years have revealed overall conditions in some areas to equal or exceed those of the previous chromate program. In high heat transfer areas, such as a four-pass monoethanolamine (MEA) solution cooler, excessive calcium phosphate buildup has been observed. The inspection of this unit in June, 1976, revealed

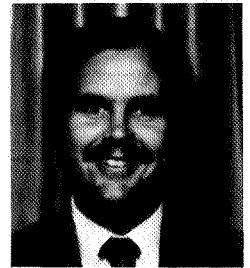
considerable improvement with very little deposition observed and the presence of a uniform film. This is attributed to the recent addition of the polymer-surfactant based dispersant to the program.

Biological control over this period has been generally good, with the exception of a few outbreaks of slime and algae growth. In some instances this has been associated with leakage of a process stream into the system. In general, the system has been brought under control by the removal of process contamination and increased frequency of biocide addition.

Conclusions

The need to remove heavy metals from plant effluents can be achieved by several methods. Each facility has its own set

of conditions, and the solution to each problem will vary. Non-chromate treatment is one of the viable alternatives. Experience over the past several years has given additional insight into the limitations of the phosphate/phosphonate program. With close attention to control practice and monitoring of results, reliable performance has been consistently achieved. #



RUE, J. R.

DISCUSSION

BOB OSMAN, Exxon Chemical Co.: Do you have much experience with this system in services where there are large numbers of carbon steel heat exchangers with cooling water on the shell side, and also do you have any successful experience where the cooling water contains significant amounts of ammonia?

RUE: Yes, we do have considerable experience with shell side cooling. As I mentioned before, the control parameters have to take into account shell side cooling because of the low water velocity encountered with shell side cooling. The tendency is to use a lower pH program to avoid any significant buildup of phosphate deposits in that area.

As far as the ammonia contamination, I myself do not have any specific case histories to relate to, with a high level of ammonia. Generally where you have high levels of ammonia, an increase in biological activity would be anticipated.

Q: Isn't it also true that we all depend on chromate systems for so long that we really didn't do the monitoring of those systems that we probably should have, and that Betz is now on a strong program for actually comparing penetration with chromate vs. penetration with non-chromate. I don't believe that we had the background data in the past. We all just accepted the chromate system.

RUE: That's true. The surveillance of cooling systems has significantly increased with the conversion to a non-chromate system. As Bill mentioned, the pitting function is an example. It was often thought it was not necessary to monitor pitting type attack on corrosion coupons where a chromate based program is employed. So any comparison of the pitting function with the previous chromate based system is not possible in many cases. There was not a lot of background information being obtained on chromate based sys-

tems, as we are doing today with non-chromate systems.

GEORGE OSTROOT, Monsanto: Is there any limitation on temperature of the heating surface at which the phosphate treatment is not effective -skin temperature?

RUE: A maximum skin temperature of 200 degrees.

OSTROOT: All right.

ARTURO RIOJAS, Amoco Oil Co.: Do you have any information you could give us about chlorine dioxide? I understand that it's much more effective than chlorine at higher pHs.

RUE: We don't have a lot of experience with chlorine dioxide. It's relatively new on the market. Where it is being publicized as an effective biocide is in systems where high levels of ammonia are known to be present. The significant advantage there is that the chlorine dioxide does not react with the ammonia, as would be expected with chlorine.

In this instance the chlorine dioxide may be cost competitive with chlorination.

RIOJAS: Okay, another question. You mentioned that where silica might be a problem, that cold lime softening would reduce the silica content of the water. I would think that if there are large concentrations of silica in the water that cold lime softening might not be the answer since you wouldn't get as much silica removal as say with hot lime softening.

RUE: That is correct. If silica is a limiting factor, the higher temperature will help achieve a greater silica reduction.

RIOJAS: For your test equipment, you had a corrosion meter and a test heat exchanger. On the corrosion meter, aren't those electrodes supposed to be submerged in the water for a period of several days or something before you can get results that you can naturally believe?

RUE: The probes themselves are going to require

sufficient time to establish passivation. After a 48-hour period results should be representative of the system.

RIOJAS: I've seen some other test heat exchangers on the market that have a glass shell, and cooling waters on the shell side. I would think that under high pH conditions that this might be advantageous over an exchanger that has water on the tube side where you can't see what's really going on. You have to actually pull the tubes to see what's going on.

RUE: We have both shell side and tube side test heat exchangers that can be used.

RIOJAS: Have you had any problem with reversion of phosphonates to orthophosphate?

RUE: A problem that is realized. We know that inorganic polyphosphates are going to revert in a cooling system, and we control the tricalcium phosphate problem by maintaining the orthophosphate level in a range where the phosphonates are effective. In fact the orthophosphate itself is acting as a corrosion inhibitor in this corrosion inhibition system.

KEES VAN GRIEKEN, UKF: We had problems with a closed cooling circuit with low chromate inhibitors when we had oil leakage in that cooling water.

RUE: Well depending on the nature of your oil leakage, you may have encountered periods where the chromate was being reduced to the trivalent form, where it would be insoluble and form a sludge in the cooling

system and no longer provide the corrosion inhibition that the hexavalent chromium does. That may have been a problem.

Also, oil coating the metal surfaces can set up localized corrosion cells.

VAN GRIEKEN: So you think that even this type of inhibitor won't work in this case.

RUE: I would say that steps need to be taken to correct the oil leak and provide an emergency procedure to remove the oil as fast as possible from the system. Frequently, surfactants are used for oil removal.

BILL WESTBROOK, Standard Oil Co., Pascagoula: With regard to chlorine dioxide, due to the presence of ammonia in our cooling water we have in the past had difficulty with excessive bacteria growth. This summer we started using chlorine dioxide and have found it to be very effective.

ANON: I think it may be well to bring out that in a non-chromate system, if you were designing for a non-chromate system from scratch, that water velocity through the exchangers is extremely important.

RUE: That's correct. With a non-chromate inhibitor there is a greater tendency in low velocity areas for excessive film buildup. So if one was designing a plant with the knowledge that a non-chromate system were to be employed, higher water velocities would be an advantage.