

Molybdate and Non-Molybdate Options for Closed Systems

Association of Water Technologies
(AWT)
2005

Warning and Disclaimer

This document is designed to provide information regarding the subject matter presented. It is produced with the understanding that neither the AWT nor the authors (or other contributors) are rendering legal, medical, engineering, or other professional services. Neither the AWT nor the authors (or other contributors) shall be liable for damages, in any event, for incidental or consequential damages caused, or alleged to be caused, directly or indirectly, by the use of any information disclosed in this document, including the use of any recommendations, methods, products, services, instructions, or ideas.

Forward

The Association of Water Technologies (AWT) is an international trade association founded to serve the interests of regional water treatment companies and to advance the technologies of safe, sound and responsible water treatment practice. The AWT is a non-profit organization providing education and training, public awareness, networking, research, industry standards and resource support. Association activities serve to benefit members, as well as advance the arts and sciences of the water treatment industry. Moreover, the AWT makes a commitment to the public as a Responsible Care® Partner Association.

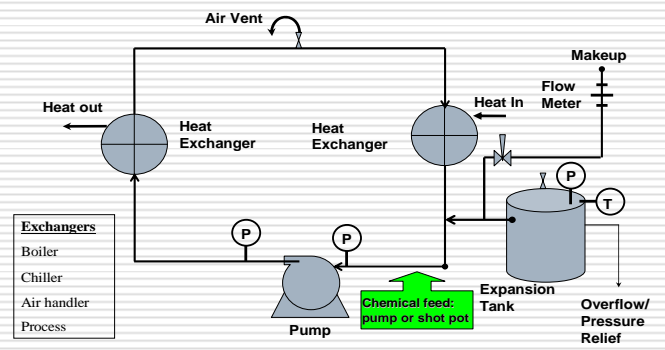
Abstract

Treatment of closed loops, since the enactment of regulations restricting the use of chromates, has typically relied on the use of a select few list of corrosion inhibitors. Sodium molybdate has become a particularly common replacement for chromate because: 1.) it is a very good steel corrosion inhibitor; 2.) it is relatively persistent unless water losses occur; 3.) there is a reliable field test readily available; and 4.) unlike nitrite, sodium molybdate does not contribute nutrients, which can exacerbate microbiological activity in a closed loop. However, over the previous five years, there has been a slow but consistent trend by municipal wastewater treatment facilities to restrict, and in some cases ban, the discharge of sodium molybdate to the sanitary sewer. Moreover, recently the water treatment industry has had to deal with a significant rise in the purchase cost of sodium molybdate raw material. These market trends have forced water treaters to evaluate alternative treatment methods. The goal of this paper is to review the treatment of closed loops with an emphasis on corrosion inhibitor selection and use. Consequently, molybdate alternatives can be evaluated.

Section One-Closed System Design & Operation

Closed recirculating systems or closed hydronic loops utilize a water-based solution to transfer heat. The most common distinction defining a closed system is the fact that the method of cooling is non-evaporative. Minimal water loss/makeup requirement and minimal air contact are two additional conditions typically associated with closed loops. Closed systems are so diverse in application that it can be difficult to suggest a standard set of operating conditions and design. Figure 1 shows a simple illustration conceptualizing the closed loop system.

Closed Loop Systems - System Anatomy



The heat transfer will typically be indirect utilizing some type of heat exchanger. One or more exchangers will take on heat and one or more heat exchangers will give off heat, thus maintaining heat balance. Heat transfer surfaces must be maintained in a clean condition to ensure efficient and reliable operation. The distribution system can be simple as shown above or it can be complex; for example, a high rise HVAC distribution system can be complex since it is integrated with the building infrastructure making maintenance/pipe replacement complicated and expensive. Materials of construction can be diverse, but typically the materials are steel piping and tanks, and stainless steel or copper/copper alloy exchangers. Aluminum, galvanized steel, and other exotic alloys, can be used as well. In many cases, these systems are designed with a surge tank or expansion tank. This tank can operate at atmospheric pressure or at elevated pressure and utilize a pressure relief device to prevent over-pressurization. Air vents are used to help remove oxygen and other non-condensable gases from the system at startup and whenever water is added to the system. Pumps are used to recirculate the water-based solution throughout the distribution system.

Operating conditions associated with closed loops, such as, little to no evaporation (i.e., no cycling of chemistry), minimal water losses and minimal air contact should allow for near zero corrosion and fouling rates to be achieved. However, these operating conditions are not always present and consequently this can significantly influence the treatment program selection process. Below are some key operating and design elements that can greatly influence the choice of chemical treatment:

- Degree of Air Contact or Ingress (atmospheric vs. pressurized)
- Water Loss (<1%/month vs. >1%/month)
- Temperature (chilled water vs. hot water)
- Heat Transfer Solution Chemistry (Conductivity Sensitive Loops, Brine Loops, Glycol Loops, etc.)
- Makeup Water Chemistry (hardness, suspended solids, microbiological activity, etc.)
- Materials of Construction (steel, copper, aluminum, other)
- System Cleanliness (new, clean, fouled)
- System Size (volume, large, small, etc.)

Degree of Air Contact or Ingress & Water Loss –it is expected that a pressurized closed loop with minimal water loss will have minimal oxygen content after operating for a period of time. Generally, the tighter the system the easier it is to maintain effective treatment. It is important to understand the quantity of makeup water and the amount of oxygen ingress that may be occurring (versus what is expected) as these parameters will potentially affect treatment cost and performance. Obviously, if water loss and oxygen ingress can be reduced, this should be done. In order to effectively track water losses, each closed loop should have a makeup flow totalizer and the meter reading should be monitored routinely. Water losses can occur for various reasons, such as, pump seal leakage(s), improper level control or improper pressure control, invasive system maintenance or intentional water draw. Air in leakage can be associated with makeup water ingress or it can occur in the absence of water losses such as with faulty air vents. Air and water ingress can affect the selection of a closed loop treatment inhibitor. For example, silicates can be an excellent choice for high makeup systems because they are low cost (especially in comparison to molybdate treatment), can function in the presence or absence of oxygen, protect multiple metallurgies and do not contribute nutrient that can exacerbate microbiological activity.

Vapor phase corrosion inhibitors (VCIs) can be an excellent choice where oxygen ingress is a particular issue as the VCI products protect the metal surface in the water, water-vapor interface and in the vapor phase. On the flip side, nitrites may be avoided in high makeup systems where microbiological activity is difficult to control or where oxygen ingress is notable.

Temperature & Chemistry – closed loops can be categorized by the system's operating temperature; for example, chilled water systems will typically operate at or below room temperature (i.e. <72 °F). Hot water loops can be further categorized by temperature. For example, hot water systems operating at or well above 212 °F may be referred to as high temperature hot water systems, while moderate temperature hot water loops will tend to operate below 212 °F. Water temperature, besides impacting the corrosion potential, can dictate the preference and limitation of various treatments. For example, under hot water conditions nitrites are particularly appealing because they are effective in the absence of oxygen, do not contribute to sludge loading, are relatively inexpensive and due to the water temperature there is little concern for microbiological control. Sulfites may be used instead of nitrites for high temperature loops. Silicates are often avoided at temperature greater than 180 °F due to concern with deposition. Under chilled water conditions, nitrites (while still cost-effective) lose some of their appeal since they contribute nutrient that can aid microbiological growth. Silicates and particularly molybdates are common alternative choices to nitrites when microbiological issues are chronic. Dual temperature loops will operate at times in the chilled water mode (typically during the cooling months) and at times in the hot temperature mode (typically during the heating months). Depending on the piping configuration (i.e., two pipe versus four pipe system), part or nearly all of this system may utilize the same recirculating water for both operating conditions – this will need to be factored when deciding upon a treatment.

The recirculating water chemistry (excluding the treatment chemicals added) should be similar or identical to the makeup water source chemistry since little to no evaporation is expected. Recirculating water chemistry requirements can drive the treatment selection process. For example, conductivity sensitive closed loops will typically require all-organic based treatments that can provide effective performance while contributing little conductivity to the water.

For brine solution loops (specifically calcium-based brine) one must consider the potential for calcium deposition as well as corrosion. Consequently, these treatments must perform in aggressive conditions at only slightly alkaline pH (preferably <8.5). Buffered molybdate treatments have been used with some success and newer organic-phosphate treatments have had success.

For glycol-based loops one must consider if the glycol is preformulated with treatment and with what type of treatment. Treatment (preformulated or otherwise) should consider the quality of solution water used with the glycol and the materials of construction. Glycol manufacturers will typically provide water quality specifications for the dilution water for their glycol. Hardness in particular should be scrutinized when using monophosphates (typically dipotassium phosphate/DKP), although polymers have increased the tolerance for hardness.

The reason that ethylene or propylene glycol is added to a closed system is to freeze-proof the system. Examples of systems requiring freeze proofing include systems in which pipes are exposed to cold air and ice and snow melting systems. Glycol concentrations can run from 20% to 50%, with the actual glycol concentration of a particular system being selected based on the desired freeze point of that system. For a given freeze point, a lower percentage of ethylene glycol is needed than propylene glycol. However, as indicated in Table 3, ethylene glycol is toxic to humans. Interestingly, the Oral LD50 (rat) is very high for ethylene glycol indicating low toxicity to rats, yet it is very toxic to humans. This contradiction illustrates that sometimes the results of animal toxicity testing cannot be extrapolated to humans. In contrast, propylene glycol is much less toxic to humans and therefore the use of propylene glycol is increasing.

Glycol concentrations should not be allowed to fall below 20%. One reason is that glycols become nutrients for microbes when the concentration falls below 20%, whereas glycols become biostatic at concentrations above 20%. A second reason is that freeze protection will not be adequate at low levels of ethylene or propylene glycols. Graphs or charts of glycol concentration versus freeze point are available from glycol manufacturers and can be used to select the correct concentration to obtain a desired level of freeze proofing.

Inhibited glycols contain dipotassium phosphate for buffering the system at pH 9.0 to 10.5 and for preventing mild steel corrosion. Molybdate, nitrite, or molybdate/nitrite programs are often added to uninhibited glycol to control mild steel corrosion. Azoles are usually added for controlling yellow metal corrosion and for complexing any copper impurities

Materials of Construction – It is critical to understand the materials of construction present in the closed loop when considering the chemical treatment program. When chromates were used, there was little need for multi-component inhibitor formulations regardless of the material of construction. With the elimination of chromates there was a need to consider formulating multiple inhibitor components based on material of construction. Today it is very common to use multi-component formulations to optimize the protection of multi-metal systems. Certain metallurgies, such as aluminum will require special consideration in choosing a treatment program. The use of azole is common and is recommended for almost all closed loop treatment formulations just in case there is copper metallurgy or in the event that copper is a contaminant to the system. Table 1 summarizes a list of commonly used inhibitors and the applicable metallurgies they protect.

System Cleanliness – to achieve effective treatment performance, the system metal surfaces must be clean. Use of an effective cleaning solution along with side stream filtration should be considered for new and old systems alike that may require cleaning. Special care should be given to addressing microbiological control prior to treatment with nitrite-based formulations and then again as needed.

Treatment formulations may include deposit control inhibitors to help maintain clean surfaces and to prevent under-deposit attack. The installation of side stream filtration is a relatively low cost add-on that can pay dividends down the road. If filtration equipment design incorporates backwashing, be sure that fresh makeup water is used and not closed recirculating water.

System Volume – knowledge of system volume is critical to ensuring adequate chemical dosing. Additionally, the size of the system may impact on the choice of treatment, particularly if the system volume is significant and/or has notable water loss. Water losses, barring uncontrolled and controlled leaks, should be essentially zero for most systems.

Consequently, in tight systems, the initial cost of a well designed treatment program will pay dividends in the long run – do not compromise. System volume measurements and trending of water losses are essential pieces of information. This data can be achieved by relatively simple methods that will not be addressed in this document. When assessing system volume, be sure that the entire volume is accounted for, i.e., parts of the system that may be idle during volume assessment should be operated and/or accounted for.

Section Two–Review of Corrosion Inhibitor Types

Introduction

The first use of molybdate as a corrosion inhibitor can be traced to 1939, when two patents issued claiming the use of molybdate for corrosion protection in alcohol-water antifreeze for automotive cooling systems.^{1,2,3} Investigation of molybdate as a corrosion inhibitor continued in the 1940's leading to the publication of the first fundamental study of corrosion inhibition by molybdate in 1951.⁴ In this study, in addition to proposing a mechanism of inhibition, Robertson reported that molybdate was as efficient as nitrite and chromate for inhibiting mild steel corrosion in aerated, distilled water. Two years later in 1953, Pryor and Cohen reported that while molybdate is effective in aerated, distilled water, it is not effective in deaerated water.⁵ In the next four decades, further electrochemical and surface studies were undertaken and the results published. While the identification of molybdate as a corrosion inhibitor, the anodic mechanism, and the window of performance were of interest to corrosion specialists, molybdate was not commonly used in the 1950's and 1960's, since chromate was already in use and since chromate was very effective and inexpensive. Then in the 1970's, the carcinogenic nature of chromate became known driving the market to shift away from chromate chemistry to other chemistries such as nitrite, molybdate, and combinations of the two. Recently market forces have once again changed as the price of molybdate has rapidly escalated due to the demand for molybdate in steel production in support of the growing Chinese infrastructure.

The high cost of molybdate has left water treaters scrambling to reduce or eliminate molybdate as a closed system inhibitor, as a pitting inhibitor, as product tracer in open recirculating cooling systems, and as a product tracer in low pressure boiler products.

This section of the paper covers the strengths and weaknesses of closed system inhibitor options and provides useful application information. Armed with this information, water treaters can then price out viable molybdate and non-molybdate options for their customers.

Molybdate

Molybdate is classified as an anodic, oxidizing inhibitor. Molybdate is not effective in the absence of oxygen, but works in conjunction with oxygen to form a protective oxide layer on ferrous metals.⁵ As ferrous ions are formed at the anode ($\text{Fe}^0 \rightarrow \text{Fe}^{+2} + 2\text{e}^-$), molybdate ions react with the ferrous ions to form a non-protective ferrous molybdate complex. This complex is then oxidized by dissolved oxygen to form an insoluble and protective ferric molybdate complex in combination with ferric oxide.⁶ Furthermore, molybdate is believed to strengthen the outermost hydrated iron oxide layer by hydrogen bonding to hydroxide groups on the surface thus imparting a negative surface charge which impedes aggressive chloride and sulfate ions from approaching the metal surface and ferrous ions from leaving the metal.⁷ Lastly, molybdate helps to retard the growth of pits because as a break in the protective film occurs, absorbed molybdate is released and concentrates inside the pit precipitating as either FeMoO_4 ⁸ or as a condensed molybdate species.⁹

In addition to use for ferrous metal corrosion control, molybdate is commonly used as an aluminum corrosion inhibitor. However, the mechanism for aluminum corrosion control is much less defined, but molybdate is believed to be incorporated into the protective film as a hydrated aluminum molybdate¹⁰. When yellow metals are present, azoles are usually added for yellow metal corrosion control.

From a practical standpoint, the absorbance of molybdate onto the outer hydrated iron oxide layer means that when molybdate is fed to a poorly maintained system containing old corrosion products, it will be consumed, leaving the water treater wondering how it “disappeared”.¹¹ Therefore prior to using a molybdate based treatment in a fouled system, the system should be cleaned to remove existing corrosion products. Another implication of the molybdate mechanism is that oxygen must be present (or another oxidant such as nitrite) if a molybdate treatment program is to be most effective.

Therefore, if a system is “tight”, i.e. if there is no ingress of dissolved oxygen from make-up water addition or leaks, the molybdate program performance will be compromised and/or will require increased dosage. While the exact concentration of oxygen needed may vary based on the corrosion potential and temperature, some experts suggest that a minimum of about 1 ppm dissolved oxygen is required when molybdate is used (without nitrite) to achieve optimum results.

Use guidelines for molybdate are given in Table 1. The dose range for molybdate is broad, because the effective concentration of molybdate increases substantially as the chloride, and to a lesser extent sulfate, concentration increases¹². For example, 70 ppm molybdate (as Mo^{+6}) may be effective in deionized or low electrolyte waters, whereas 466 ppm molybdate (as Mo^{+6}) may be needed when the chloride level is 200 ppm.¹³ To convert from molybdate as Mo^{+6} to molybdate as MoO_4^{-2} multiply by 1.67. To convert from molybdate as Mo^{+6} to molybdate as $\text{Na}_2\text{MoO}_4^{-2}$ multiply by 2.15. Refer to Table 2 for conversions that are useful when formulating with molybdate raw materials.

Typically, systems treated with molybdate, nitrite, molybdate/nitrite combinations or HPA/triazine combinations will be buffered to or controlled at pH 8.5 to 10.5, since this pH range is optimal for controlling both ferrous and yellow metal corrosion and these metals are most prevalent in closed systems in North America. However, when aluminum is present, the system pH should be maintained at pH less than 9.0 and ideally between 7.8 to 8.3. At lower pH, metal loss via the anodic reaction will be accelerated; at higher pH aluminum hydroxide forms, also accelerating metal loss.

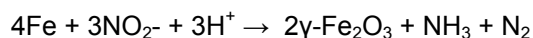
Molybdate is not a nutrient for microbes and is often used when controlling microbiological growth is difficult (i.e. conditions of low flow, low temperature, contamination) thereby precluding the use of nitrite, nitrite/molybdate combinations, and possibly organic-based components as well.

Molybdate is compatible with the non-oxidizing biocides that are commonly used for closed systems and with ethylene and propylene glycols. It has been used in sodium chloride brines as a replacement for chromate with some success. However, external control measures including sidestream filtration, nitrogen capping, and tight pH control may be required to obtain good results.

Increasingly, treatment toxicity is becoming a concern to the customer. Based on acute animal and aquatic toxicity data, molybdate would be considered only slightly toxic. (See Tables 3, 4, and 5). The main toxicity concern with molybdate use is the possibility of its accumulation in waste treatment plant sludge that is spread on agricultural land that may be used for animal feed crops. Animals feeding on these crops may be subject to molybdenum poisoning, which interferes with copper metabolism, and liver and kidney function. At this point in time, however, based on the low acute animal and aquatic toxicity of molybdate, its use has been restricted in only a few areas of the US.

Nitrite

Nitrite is an oxidizing, anodic inhibitor that has been in use for many years^{14, 15}. With the present high cost of molybdate, nitrite is often the most effective and least expensive option for controlling mild steel corrosion, when no other factors prevent its use. Nitrite works by promoting the formation of a passive $\gamma\text{-Fe}_2\text{O}_3$ film by the following reaction^{16, 17}:



Unlike molybdate, nitrite does not need the presence of dissolved oxygen.

As shown in Table 1, the recommendations for the dosage range vary somewhat depending on the source, but in summary the range runs from a low of 700 ppm as NaNO_2 to a high of 1,800 ppm as NaNO_2 . For a given system, the required dose will depend on the concentration of aggressive ions (i.e. chloride and sulfate ions) and the system temperature. Sulfate ions interfere with corrosion protection by nitrite more than chloride ions do. A recommendation based on aggressive ion content is that for low levels of aggressive ions, the ppm sodium nitrite should equal the ppm chloride ion plus 250 to 500 ppm more than the ppm sulfate ion^{16, 18}. Doses for chilled loops will tend to be at the low end of the range while doses for hot loops will fall at the high end of the range, since corrosion increases with increasing temperature. As with all anodic inhibitors, under dosing nitrite can cause severe pitting. Too little nitrite can be worse than no nitrite.

Nitrite is not effective for controlling aluminum corrosion. If aluminum is present, an aluminum inhibitor such as silica or nitrate will be needed. Azoles are added when yellow metal protection is needed. Nitrite is compatible with glycol systems and commonly used non-oxidizing biocides.

A shortcoming of nitrite treatment is the propensity to promote microbiological growth. This will be more of a problem in chilled loops than in hot loops, since bacteria and mold will not grow at temperatures exceeding 140 °F.¹¹ Nitrifying bacteria will oxidize nitrite to nitrate, while denitrifying bacteria will reduce nitrite to either nitrogen gas or ammonia ($\text{NO}_2^- + 5\text{H}^+ + 6\text{e}^- \rightarrow \text{NH}_3 + 2\text{OH}^-$)¹⁹. In addition to the loss of protection as a result of the loss of nitrite, nitrate is also a nutrient for bacteria and ammonia is aggressive to yellow metals. Diligent use of a non-oxidizing biocide regime is imperative when using a nitrite program. Some commonly used non-oxidizing biocides are glutaraldehyde, isothiazolin and tris nitro (tris nitro is particularly effective at higher pH and against nitrifiers and denitrifiers). Potassium dimethyldithiocarbamate and polyquats are also used. Often, the use of multiple non-oxidizing biocides provides best results. Conversely, oxidizing biocides should not be used since they will oxidize nitrite to nitrate. To monitor the success of the biocide treatment, bio counts should be measured at least once a month.

Air ingress can be another problem with the use of nitrite, since dissolved oxygen can cause nitrite to be oxidized to nitrate ($2\text{NO}_2^- + \text{O}_2 \rightarrow 2\text{NO}_3^-$). Therefore, in systems having much air ingress, more nitrite than expected may be needed and microbiological control may be difficult.

Toxicity can be a concern with nitrite programs as nitrite is more toxic than other closed system inhibitors. This is illustrated in Table 3 with sodium nitrite having the lowest Oral LD50 (rat) among closed system inhibitors and an estimated lethal dose by ingestion for humans of 1 to 2 g. Furthermore, sodium nitrite has a CERCLA discharge limit of 100 lb, therefore discharges into the environment exceeding 100 lb (dry weight) must be reported to the EPA.

Molybdate/Nitrite

The combination of molybdate and nitrite has been shown to be synergistic and prior to the escalation of molybdate pricing, the combination was considered by many to be the treatment of choice for closed systems. When using the combination, nitrite takes the place of oxygen in forming the protective oxide film. Molybdate forms a protective ferric complex which becomes incorporated as part of the oxide layer and/or it absorbs onto the ferrous hydroxide surface layer thus imparting a negative surface charge which repels aggressive ions (i.e. chloride and sulfate).

Molybdate helps to retard the growth of pits as discussed earlier.

The ratio of sodium molybdate to sodium nitrite giving the lowest mild steel corrosion rate was shown experimentally to be 50:50 to 60:40.²⁰ Some water treaters have formulated their products accordingly with an approximate 1:1 ratio of sodium molybdate to sodium nitrite. Following this train of thought, typical use rates are 150 ppm Na_2MoO_4 plus 150 ppm NaNO_2 to 400 ppm Na_2MoO_4 plus 400 ppm NaNO_2 . Other water treaters have weighted their products more towards sodium nitrite likely as a cost cutting consideration. Along this vein, the AWT Technical Manual indicates that the molybdate level can be reduced to as low as 161 ppm Na_2MoO_4 with 525 to 750 ppm nitrite as NaNO_2 .

The benefits of molybdate/nitrite programs include enhanced corrosion control, a reduced propensity for pitting over nitrite alone, and both mild steel and aluminum corrosion control. (As in the case of molybdate and nitrite alone, azoles will be needed for yellow metal corrosion control.) Disadvantages of molybdate/nitrite programs include a higher cost since molybdate is still a significant component, possible microbiological control difficulties associated with nitrite, and possible toxicity concerns associated with nitrite. Molybdate/nitrite programs are compatible with commonly used non-oxidizing biocides as well as ethylene and propylene glycol.

Silicates

Silicates are commonly used for ferrous metal and yellow metal corrosion control in soft, potable water applications where no heat transfer is involved. In fact, the first proposal for using silicates for the protection of an entire water system was made by Thresh in 1922 and silicates have been in use since the 1920's.²¹

Silicates are occasionally employed for multimetal protection in high temperature systems that use deionized water, since at low hardness, calcium and magnesium silicate will not form and at low chloride and sulfate concentrations, the protective film can form over time.

Silicates are considered to be anodic, filming inhibitors. They have a variable composition of $n \text{Na}_2\text{O} : m \text{SiO}_2$. Generally a ratio of m/n of 2.5 - 3.0 is effective.¹⁶ With a silicate treatment, the protective film develops slowly and may take weeks to form. The film is believed to consist of silica gel along with ferric hydroxide precipitates.

Silicates provide protection for mild steel, yellow metals, and aluminum.

Other than for potable water systems, silicates are not commonly used as stand alone corrosion inhibitors for mild steel protection. However, they are often added either for aluminum corrosion control and/or to augment the performance of other mild steel corrosion inhibitors. The recommended dose for silicates is 50-100 ppm as SiO_2 when used alone for multi-metal corrosion control and 10-25 ppm as SiO_2 as adjunct for Al and Cu alloys.

For closed systems having both ferrous metals and yellow metals, the operational pH should be 8.5 to 10.5. As discussed earlier, if aluminum is present, the pH should be maintained at less than 9.0 and ideally between 7.8 to 8.3.

One advantage of silicates is that they do not act as a nutrient for microbes and are therefore an option where microbiological control is difficult. A disadvantage of using silicates is the tendency for silica deposition to occur if the product is overfed or used with hard water at higher temperature or where pH is not properly controlled. For example, if silica is used for aluminum corrosion control and the pH gets too high, aluminum silicate deposition may occur, which can plug nozzles, etc.

Silicates are considered to be relatively non-toxic. The Oral LD50 (rat) value of 800 mg/Kg probably reflects the high pH of sodium metasilicate and overstates the toxicity of silicates at use levels.

Nitrate

While molybdate/nitrite and nitrite/silicate are the most commonly used combinations for controlling both mild steel and aluminum corrosion, occasionally sodium nitrate is used in conjunction with sodium nitrite to provide the aluminum corrosion control that nitrite alone does not offer. In fact, while nitrite is an effective mild steel corrosion inhibitor, it can be antagonistic to aluminum corrosion. However, the addition of nitrate overcomes this effect.²²

Nitrate works as an anodic, oxidizing inhibitor to control the growth of the aluminum hydroxide film and also works as a pitting inhibitor by the preferential reaction of nitrate with the active surface.^{10, 23} A study of aluminum pitting inhibition, indicated that $\text{NO}_3^- > \text{MoO}_4^{-2} > \text{SiO}_3^{-2}$ in effectiveness;²² however, a study of aluminum film growth inhibition indicated $\text{SiO}_3^{-2} > \text{MoO}_4^{-2} > \text{NO}_3^-$ in effectiveness.¹⁰

The recommended dose rate for controlling both aluminum and mild steel corrosion is 685 to 1,371 ppm sodium nitrate in combination with 750 to 1,500 ppm sodium nitrite. If yellow metals are present, an azole is recommended, since neither nitrite nor nitrate provide protection against yellow metal corrosion.

Nitrate is considered less toxic than nitrite, with its toxicity stemming from the conversion of nitrate to nitrite in the digestive tract. This conversion occurs to a greater extent in infants and nitrite has been associated with "Blue Baby Syndrome" or methemoglobinemia, a decreased oxygen-carrying capacity of the blood resulting in shortness of breath and bluish colored skin, other symptoms, and possibly death.

HPA-Triazine Stand Alone & Combination

HPA (Hydroxyphosphonoacetic acid) was patented in 1987 for controlling ferrous metal corrosion and scaling.²⁴ Electrochemical studies performed at the time determined that HPA operates via a cathodic control mechanism.²⁵ At cathodic sites on a mild steel surface, the pH is raised due to the formation of hydroxide ions ($1/2 O_2 + H_2O + 2e^- \rightarrow 2OH^-$). Calcium/HPA salt forms and precipitates at the cathodic sites due to the localized high pH. Over time, the mild steel surface becomes covered with a thin calcium/HPA film which stifles the cathodic reaction by preventing oxygen from reaching the metal surface, but is so thin that heat transfer is not affected. The suggested HPA dose is 50-100 ppm as HPA (30-122 ppm organic phosphate as PO_4^{-3}). The low calcium level in some closed systems may limit the effectiveness of HPA alone for controlling mild steel corrosion, though product literature suggests that in low calcium waters HPA can directly absorb onto the iron oxide layer.²⁶

While HPA containing formulations have not found wide use, they have found use in calcium chloride brine systems at 240 to 1,000 ppm HPA.²⁷ In these systems, calcium chloride is used to enable very low operating temperatures. Chromate is the most effective multi-metal treatment for calcium chloride brine systems, but the restrictions on chromate have minimized its use. Since there are few effective options for brine systems, treatment with HPA is beginning to find use. As with other nonchromate treatments, external control measures including sidestream filtration, nitrogen capping, and tight pH control may be required to obtain good results.

The combination of HPA and Tris-(aminopentamethylenecarboxylic acid)-triazine containing formulations can offer a broader window of performance compared to HPA alone. Tris-(aminopentamethylenecarboxylic acid)-triazine was commercialized in the late 1980's and has been marketed for use in closed systems with and without HPA. However, for more aggressive applications, the combination has been recommended. In contrast to HPA, the substituted triazine works by forming a ferrous triazine complex at anodic sites.¹⁹ This complex eventually coats the surface with a very thin, chemisorbed film. When both HPA and the substituted triazine are present, both cathodic and anodic corrosion inhibition is afforded and performance is enhanced. The recommended ratio of HPA to substituted triazine is 1:1 by weight. The suggested feedrate is 100-150 ppm total actives. For monitoring purposes, this would correspond to an organic phosphate level of 30-50 ppm as PO_4^{-3} . When aluminum is present, an aluminum corrosion inhibitor such as a silicate should be used, as the substituted triazine does not provide protection for aluminum (or yellow metals).

HPA and the substituted triazine are considered to have low toxicity and to be environmentally friendly. HPA does contain phosphorus, and in some areas of the country, the use of phosphorus containing products is regulated.

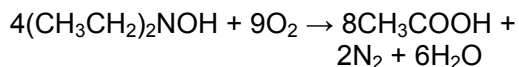
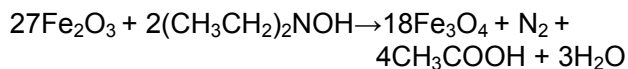
The HPA/substituted triazine combination provides an alternative to traditional chemistries such as molybdate, nitrite, and their combination and at this point in time, the HPA/substituted triazine combination has found use mainly where a non-molybdate, non-nitrite product is desired. In the past, "all organic" programs such as HPA/substituted triazine have been considered pricey, thus often keeping them from consideration. With the changing market, these chemistries are becoming increasingly cost-competitive.

As with all organic-based programs, controlling microbiological growth is a critical consideration. As phosphonates, such as HPA breakdown, they release orthophosphate, a nutrient for bacteria and mold. Likewise, as carboxylic acids break down, they release carbon-based moieties that can be nutrients for microbiological species. The presence of such nutrients provides a growth media, when temperatures are below 140 °F.¹¹

Thus microbiological control will be more difficult in chiller waters and hot water loops that operate at the lower end of the range for hot water loops.

DEHA

Some closed systems require the cooling water to have a low conductivity (the upper limit following in the range of 40 to 500 umhos). These systems may include induction heating circuits and weld gun cooling circuits. Other closed systems are considered high temperature hot water systems with temperatures that can range from 212 °F to 400 °F. These systems may cool plastic molding operations, B.O.F. furnace hoods, tire curing operations, etc. For both low conductivity and high temperature systems, DEHA (diethylhydroxylamine) can be used for controlling ferrous metal corrosion. DEHA acts as a passivator, converting hematite to magnetite, oxygen scavenger, and pH buffer. A DEHA treated system would typically be buffered to about pH 9.5 to 10.0, sometimes by formulating a low level of a neutralizing amine with DEHA. The passivation and oxygen scavenging reactions with DEHA, respectively, are as follows:²⁸



When initially fed, DEHA will react with existing corrosion products producing a haze to the water. To remove the haze caused by suspended solids, side stream filtration or bleeding of the system may be required. In the process, DEHA will be consumed, thus an initial feed of about 200 ppm DEHA will be needed as compared to a maintenance dose of about 125 ppm DEHA.

DEHA (or sometimes carbonylhydrazide) presents one of the few options for low conductivity and/or high temperature systems. The chief disadvantage of a DEHA program is that DEHA will not be effective in a system that is not "tight" (i.e. has leaks or uses much make-up) therefore allowing the ingress of oxygen into the system. In theory, 1.24 ppm DEHA scavenges 1 ppm oxygen, but in practice the ratio is 3.0 ppm DEHA to 1 ppm oxygen.²⁸ If there is much oxygen ingress, the DEHA will be consumed and corrosion protection compromised.

DEHA is not effective for yellow metal corrosion control; consequently, an azole is needed when yellow metals are present.

Since DEHA tends to be used in systems with temperatures exceeding 140 °F, microbiological growth is not usually a problem.

DEHA is considered to be slightly toxic based on animal toxicity studies. Based on fish kill studies, it would be considered to have moderate aquatic toxicity.

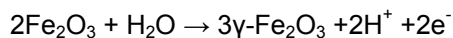
VCI/Organic Contact Film Formers

VCIs (Vapor Phase Corrosion Inhibitors) are organic chemicals that inhibit the corrosion of ferrous and/or non-ferrous metals in a confined space by volatilizing and then condensing on the metal surface. In the presence of moisture, the crystals ionize and react with the metal surface, imparting a protective film.²⁹ The film builds over time as more inhibitor volatilizes and condenses on the metal surface. In contrast, organic contact film formers are organic molecules that react with metal surfaces in contact with the water in which they are dissolved to form a protective film. These types of inhibitors have been more commonly used as "rust preventatives", i.e. in the treatment of metal parts prior to storage preceding assembly. In the last 10 years, VCIs and organic contact film formers or combinations of the two are beginning to find use in water treatment applications. Manufacturers of such products have given limited information about their content, but a quick summary of possible chemistries follows.

One of the earliest volatile corrosion inhibitors, dicyclohexylammonium nitrite (DICHAN), was reported on in 1951.³⁰ Sodium benzoate was suggested as a contact rust inhibitor while esters of benzoic acid were suggested as volatile corrosion inhibitors by Stroud and Vernon in 1952.³¹ Later that same year, Stroud and Vernon reported the use of a series of amine carbonates as VCIs.³² Also in 1952, the use of amines, alkyloamines, and amine acid complexes was claimed for packing steel materials and for preventing rust in steam systems.³³ More recently, Miksic and company have claimed the use of Vapor Phase Corrosion Inhibitor (VPCI)/film former blends of ammonium benzoate, sodium benzoate, sodium sebacate, monoethanolammonium benzoate, benzotriazole, and cyclohexylammonium benzoate for use as lay-up treatments for systems including boilers and cooling systems.³⁴ In addition, triethanolammonium tolyltriazole is listed as a building block for VPCI applications.³⁵

Commonly used organic film former additives (“rust preventatives”) include triethanolamine, monoethanolamine, amine borates, and alkylcarboxylates such as heptanoic acid or octanoic acid.

DICHAN works as a VCI by contributing its nitrite ion to condensed or absorbed moisture on the metal surface.²⁹ In comparison, aminobenzoates work by promoting the formation of γ -Fe₂O₃ through the following reaction:



Aminobenzoates act as electron acceptors and the oxide layer as an electron donor.²⁹ Alkylamines, on the other hand, absorb on metal surfaces by donating unshared electron pairs on the nitrogen atom to unoccupied electronic orbitals or through defects present in the oxides on metals with fully occupied orbitals or in some cases by an electron exchange between the metal and the inhibitor molecule.²⁹ Alkylamines form barrier films that prevent oxygen from reaching the metal surface, thus inhibiting the cathodic reaction.

Alkylcarboxylates absorb onto metal/metal oxide surfaces, possibly through hydrogen bonding. The hydrophobic hydrocarbon tail provides a barrier, which prevents water and hence dissolved oxygen from reaching the metal surface, thus preventing corrosion. The optimization of the chain length for straight chain alkylmonocarboxylates and dicarboxylates was studied in the mid 1990's.³⁶ To reflect typical application conditions, pH 8.4 water containing 300 ppm chloride ion and 100 ppm sodium bicarbonate was used. The results of this study showed that the optimal chain length for straight chain aliphatic monocarboxylates is ($6 \leq N \leq 10$) for controlling mild steel control, ($10 \leq N \leq 17$, or more - highest tested) for controlling copper corrosion, and $N = 10$ or 11 for controlling aluminum pitting. In contrast, the optimal chain length for straight chain α,ω -dicarboxylates ($\text{OOC}(\text{CH}_2)_n\text{COO}^-$) is ($4 \leq N \leq 12$) for mild steel and ($11 \leq N \leq 14$, or more – highest tested) for controlling copper corrosion and aluminum pitting. The optimal chain length for straight chain alkyl mono and dicarboxylates is a function of competing reactions involving adsorption and complexation at the metal/metal hydroxide-oxide surface, solubility, and micelle formation in solution.

Most combinations of VCIs and film formers are formulated to provide multimetal protection.

Feedrates for commercially available VCI/film former blends are typically 1,000+ ppm for dry products and 2,000+ ppm for liquid products. At the recommended treatment levels, the pH falls at about 8.5 to 10.5 with the dry products and 8.0 to 9.0 with liquid blends.

Combinations of VCIs and/or organic film formers are now being commercialized for use in closed systems including hot water, chilled water, brine, and low conductivity systems with anecdotally good results as indicated by case histories. As a rule, recently marketed VCI/organic film former blends are nitrite free and are touted to have low toxicity and to be environmentally friendly. This makes them attractive to customers concerned about health, safety, and environmental issues or constrained by regulations.

The fact that the VCI/organic film former blends are organic in nature would imply that product components or breakdown species may be nutrients for microbes and possibly promote microbiological growth. The use of oxidizing biocides would not be recommended, due to possible oxidation of product components. Before using non-oxidizing species, the water treater should clear their use with the product manufacturer. Several non-oxidizing biocides that are commonly used for closed loop treatment have been shown to be compatible with recently marketed VCI/film former products.

In the past, the higher cost of VCI/organic film former programs relative to treatments such as nitrite or nitrite/molybdate and the lack of experience with VCI/organic film former products has limited their use. With the changing market conditions, this is starting to change.

Dipotassium phosphate

Dipotassium phosphate (DKP) is commonly used in glycol systems for controlling mild steel corrosion. DKP serves as a buffer as well to inhibit pH depression as the glycol degrades to organic acids.

Orthophosphate is an anodic inhibitor. In the presence of dissolved oxygen, the protective film that forms is γ -Fe₂O₃.³⁹ Magnetite is sometimes found underneath the γ -Fe₂O₃ film, and is believed to be a partially oxidized intermediate layer.¹³ The γ -Fe₂O₃ film is porous, with many voids and cavities. Orthophosphate works by forming ferric phosphate, dihydrate that fills the voids and cavities, eliminating unprotected sites where the anodic reaction could occur.⁴⁰

Orthophosphate is not effective in the absence of oxygen, since it cannot oxidize iron to $\gamma\text{-Fe}_2\text{O}_3$ and form the primary film.¹³

Phosphates are generally fed at 1,000 to 5,000 ppm in glycol systems. Phosphates can be used in glycol systems, since at >20% glycol, these systems become biostatic to microbes. Phosphates are a nutrient for microbes, therefore if used in water-based systems at such high concentrations, control of microbiological growth would likely be problematic.

Phosphates are inexpensive and have low toxicity, unless ingested in large quantity. However, they are a nutrient for microbes and cause algae blooms in surface waters, which can cause eutrophication of ponds and lakes.

Azoles

In the 1950s, azoles began to be used in closed systems for controlling yellow metal corrosion. Today, tolyltriazole (TT) and benzotriazole (BT) are the most commonly used azoles, however, mercaptobenzotriazole (MBT) is occasionally used.

Typical active azole doses are 10 to 50 ppm as the sodium salt. The azole requirement increases with increasing concentration of chloride and sulfate ions.

TT and BT work by reacting with cuprous ions at cathodic sites to form a chemisorbed monolayer of cuprous azole, which acts as a barrier to the oxygen reduction reaction. Bridged by cuprous ions, the TT or BT molecules form a polymeric structure across the metal surface in which the ring is believed to be parallel to the metal surface.³⁷ MBT initially reacts with cuprous ions at cathodic sites forming a monolayer of cuprous MBT. Unlike TT or BT, the film can grow to a 1000 molecular layer thickness as follows. As cuprous ions form, they diffuse through the Cu_2O layer and $\text{Cu}(1)\text{MBT}$ film, then bridge molecules of MBT to form a three dimensional polymeric structure. Again the rings are believed to be oriented in a parallel fashion to the metal surface.³⁸

MBT films form most quickly, forming a film several hundred molecules thick in 30 seconds,³⁸ whereas TT or BT films takes hours to form. However, TT and BT are more tolerant to oxidation by chlorine than MBT, and hence are more commonly used. TT has become the inhibitor of choice because TT films provide better

corrosion protection during chlorination than BT films.⁴¹ New substituted azoles have been developed for controlling aluminum corrosion in addition to yellow metals, but these have not seen wide use in closed systems, in part due to cost.

In addition to controlling yellow metal corrosion, azoles react with cuprous ions in solution and prevent them from plating out on mild steel or aluminum surfaces, which causes pitting to occur. Pitting occurs because as more and more surface becomes covered with copper metal, the electron flow from the larger more inert copper cathodic area must be balanced by electron flow from the smaller, anodic area where the metal loss occurs.

Azoles are moderately toxic to animals and have moderate aquatic toxicity, but usually comprise such a small percentage of a typical closed system formulation that the toxicity level is not problematic.

Adjuncts

In addition to corrosion inhibitors, buffers and dispersants are usually added to closed system inhibitor packages. Borate is the most commonly used buffer since has a relatively high buffering capacity and because it buffers out at a higher pH (pH 9.3 to 9.5). Dipotassium phosphate is commonly used as a buffer and anodic corrosion inhibitor for glycol systems as discussed earlier. Carbonates are sometimes used in nuclear power cooling systems, since borates are not permitted for use in such systems. Amines are used for buffering low conductivity and/or high temperature systems. They are often used to buffer systems treated with VCI/organic contact film former blends as well.

Dispersants are usually fed at 10 ppm to 20 ppm to prevent deposition of corrosion products or contaminants that could cause under-deposit attack. Typically, an AA/AMPS based copolymer is used. In the past maleic acid/sulfonated styrene (MA/SS) copolymers were commonly used and still are occasionally used, but they are being supplanted by the more effective AA/AMPS copolymers.

TABLE 1: Recommended Inhibitor Levels for Closed Systems

Inhibitor	Metal(s) Protected	Typical pH Range****	Active Dose (mg/L)
Molybdate, Alone	Fe, Al	8.5-10.5 Fe 7.8-8.3 (<9.0) Al	150-1,000 as Na ₂ MoO ₄ *, ref. 3 (177-777 as MoO ₄ ⁻²) (70-466 as Mo ⁺⁶)
Nitrite	Fe	8.5-10.5 Fe	500-1,000 NO ₂ ⁻ or 750-1,500 as NaNO ₂ , ref. 1 600-1,200 NO ₂ ⁻ or 900-1,800 as NaNO ₂ , ref. 2 467- 800 NO ₂ ⁻ or 700-1,200 as NaNO ₂ , ref. 4
Molybdate/Nitrite	Fe, Al	8.5-10.5 Fe 7.8-8.3 (<9.0) Al	50:50 - 60:40 Na ₂ MoO ₄ :NaNO ₂ Ratio, ref. 6 150+150 - 400+400 Na ₂ MoO ₄ +NaNO ₂ , typical Low Moly: 161 Na ₂ MoO ₄ + 525-750 NaNO ₂ , ref.1
Nitrite/Nitrate	Fe + Al	7.8-8.3 (<9.0) Al	500-1,000 NO ₂ ⁻ + 500-1,000 NO ₃ ⁻ , ref. 2 (750-1,500 as NaNO ₂ + 685-1,371 NaNO ₃)
Silicate	Fe**, Al, Cu	8.5-10.5 Fe 7.8-8.3 (<9.0) Al	50-100 as SiO ₂ alone for multimetals, ref. 1 10-25 as SiO ₂ adjunct for Al and Cu alloys
Hydroxyphosphonoacetic acid (HPA)	Fe	8.5-10.5 Fe	50-200 HPA, ref. 4 (30-122 Organic Phosphate as PO ₄ ⁻³)
Hydroxyphosphonoacetic acid (HPA)/Tris-(aminopentamethylene-carboxylic acid)-triazine***	Fe	8.5-10.5 Fe	100-150 actives, ref. 5 (35-50 ppm Organic Phosphate as PO ₄ ⁻³)
DEHA	Fe	9.5-10.0 Fe	200 ppm initially; 125 pm maintenance, typical
VCI/Organic Filmer Blends	Fe, Cu, Al	8.5-10.5 powder 8.0-9.0 liquid	1000+ ppm for powder products 2000+ ppm for liquid products
Orthophosphate (Glycol Systems)	Fe	9.0-10.5 Fe	1,000- 5,000 as PO ₄ ⁻³ , ref. 4
TT/BT	Cu	8.5-10.5 Cu with Fe	10-50, ref. 1
Dispersants	All surfaces	7.5-10.5 Fe 7.8-8.3 (<9.0) Al	10-20 ppm (typical)

* Actual dose dependent on electrolyte concentration of closed system and requires water to have ≥1 ppm D.O.

** No heat load with soft or deionized water OR high temperature with deionized water only

1:1 Ratio *Ref. 4 for Fe and Cu

TABLE 2: Molybdate/Nitrite Conversion Factors

Component	% Na ₂ MoO ₄ *2H ₂ O	% Na ₂ MoO ₄	% MoO ₄ ⁻²	% Mo ⁺⁶
Sodium molybdate dehydrate (Na ₂ MoO ₄ *2H ₂ O)	100.0	85.1	66.1	39.7
Sodium Molybdate Liquid	41.1	35.0	27.2	16.3
Sodium Nitrite		%NaNO ₂ * 0.667 = % NO ₂		

TABLE 3: Toxicity of Closed System Treatment Components

Test Material	Oral LD50 (rat) (mg/Kg)	Dermal LD50 (rabbit) (mg/Kg)	Inhalation LC50 (rat) (as indicated)
Sodium molybdate dihydrate	4,233	>2,000	>1.93 mg/L/4H
Sodium nitrite	180	N.A.	5,500 ug/m ³ /4H
Sodium metasilicate	800	N.A.	N.A.
Sodium nitrate	1,267	N.A.	N.A.
Hydroxyphosphonoacetic acid (HPA), 50%	2,750	N.A.	N.A.
Tris-(aminopentamethylene-carboxylic acid)-triazine, 63%	>5,000	N.A.	N.A.
Diethylhydroxylamine (DEHA), 85%	2,190	1,300	3,140 mg/L/4H
VCI/Organic filmer blends	See manufacturer for data.		
Dipotassium phosphate (DKP)	>500	>300	N.A.
Sodium tolyltriazole (TTNa), 50%/ Tolyltriazole (TTA), 100%	920, male 640, female (TTNa, 50%)	>2,000 (TTA, 100%)	N.A.
Benzotriazole (BT)	560	>2,000	1,910 mg/m ³ /3H
Sodium tetraborate pentahydrate	3,200-3,400	>2,000	N.A.
60/40 AA/AMPS* Copolymer, 28%	>5,000	>2,000	N.A.
AA/AMPS/SS**	N.A.	N.A.	N.A.
Ethylene glycol	6,000-13,000	>22,270	>3.95 mg/L/7H
Propylene glycol	20,000-34,000	>10,000	N.A.

*60/40 AA/AMPS: 60 Acrylic acid/40 acrylamidomethylpropylsulfonic acid

**AA/AMPS/SS: Acrylic acid/acrylamidomethylpropylsulfonic acid/sulfonated styrene

Humans:

Sodium Nitrite: The estimated lethal dose in humans is 1 to 2 g.

Ethylene glycol versus propylene glycol:

The lethal dose of ethylene glycol in humans is 100 mL (3-4 oz). In comparison, propylene glycol is relatively non-toxic. Ingestion of a sizable amount of propylene glycol (over 100 mL) may cause some gastrointestinal upset and temporary central nervous system depression. The effects appear more severe in individuals with kidney problems.

TABLE 4: Toxicity Classes: Hodge and Sterner Scale

Tox. Rating	Commonly Used Term	Oral LD50 (rat) (mg/Kg)*	Dermal LD50 (rabbit) (mg/Kg)**	Inhalation LD50 (rat) (ppm)***	Probable Lethal Dose For Man
1	Extremely Toxic	1 or less	5 or less	10 or less	a grain, a taste, a drop
2	Highly Toxic	1-50	5-43	10-100	4 mL (1 tsp)
3	Moderately Toxic	50-500	44-340	100-1,000	30 mL (1 fl oz)
4	Slightly Toxic	500-5,000	350-2,810	1,000-10,000	600 mL (1 pt)
5	Practically Non-toxic	5,000-15,000	2,820-22,590	10,000-100,000	1 L (1 qt)
6	Relatively Harmless	15,000 or more	22,600 or more	100,000	1 L (1 qt)

*Single dose to rats;

**Single application to skin of rabbits;

***Exposure of rats for 4 hr

Reference: CCOHS (Canadian Center for Occupational Health and Safety) Website,

www.ccohs.ca/oshanswers/chemicals/ld50.html (2005).

TABLE 5: Aquatic Toxicity of Closed System Treatment Components

Test Material	Aquatic Toxicity Data (mg/L)
Sodium molybdate dihydrate	48 hr EC50 (Daphnia magna): 330 96 hr LC50 (Rainbow trout): 7,600 72 hr IC50 (Algae): >100
Sodium nitrite	24 hr NOEC (Minnow): 17.1 48 hr TLm (Mosquito fish): 7.5
Sodium metasilicate (Na ₂ SiO ₃)	48 hr LC50 (Water flea): 113 96 hr LC50 (Mosquito fish): 530
Sodium nitrate	96 hr LC50 (Water flea): >1,000 mg/L 96 hr LC50 (Fathead minnow): >1,000 mg/L
Hydroxyphosphonoacetic acid (HPA), 50%	24 hr EC50 (Daphnia magna): 140 96 hr LC50 (Rainbow trout): 180 96 hr LC50 (Zebra fish): >820 as solids
Tris-(aminopentamethylene-carboxylic acid)-triazine, 63%	96 hr LC50 (Zebra fish): >1,000
Diethylhydroxylamine (DEHA), 85% Diethylhydroxylamine (DEHA), 85%, neutralized	48 hr EC50 (Daphnia magna): 111 96 hr LC50 (Guppy): 150
VCI/Organic filmer blends	See manufacturer.
Dipotassium phosphate (DKP)	48 hr EC50 (Daphnia magna): >100 mg/L 96 hr LC50 (Rainbow trout): >100 mg/L
Sodium tolyltriazole, 50% solution	48 hr LC50 (Daphnia magna): 245.7 96 hr LC50 (Bluegill sunfish): 191.2 96 hr LC50 (Rainbow trout): 23.7
Sodium benzotriazole (BT)	48 hr LC50 (Daphnia magna): 141.6 96 hr TIm (Minnow): 28 96 hr TIm (Bluegill sunfish): 28 96 hr LC50 (Trout): 39 96 hr EC50 (Algae): 15.4
Sodium tetraborate pentahydrate	24 hr EC50 (Daphnia magna): 1,631 3 day LC50 (Goldfish): 478 24 day LC50 (Rainbow trout): 593 96 hr EC10 (Algae): 162
60/40 AA/AMPS*, as active	48 hr LC50 (Daphnia magna): 2,800 96 hr LC50 (Bluegill sunfish): >10,000 96 hr LC50 (Rainbow trout): 4,900
AA/AMPS/SS**, 48%	48 hr EC50 (Daphnia): >1,529 96 hr LC50 (Rainbow trout): >1,079 96 hr LC50 (Algae): >1,049 and <2,120
Ethylene glycol	LC50 (Daphnia magna): 46,300-51,100 LC50 (Fathead minnow): 51,000 LC50 (Bluegill): 27,540 LC50 (Rainbow trout): 18,000-46,000
Propylene glycol	Acute LC50 (Daphnia magna): 4,850-34,400 Acute LC50 (Fathead minnow): 46,500-54,900 Acute LC50 (Guppy): >10,000 Acute LC50 (Rainbow trout): 44,000

*60/40 AA/AMPS: 60 Acrylic acid/40 acrylamidomethylpropylsulfonic acid

**AA/AMPS/SS: Acrylic acid/acrylamidomethylpropylsulfonic acid/sulfonated styrene

Section Three – Performance Monitoring

Water treatment needs to be a conservative business. The potential consequences of failure of these closed loops can be costly for the owner/operator. For example, the cost of downtime, equipment repair and replacement, and collateral damage (i.e., water leak damage, etc) can easily run hundreds of thousands of dollars! The water treatment service company may be held liable for part or all of these expenses, regardless of fault, if proper monitoring and documentation are not maintained.

The key objectives to implementing a proper monitoring program are:

- System knowledge
- Field testing of critical performance criteria
- Documentation of observations and recommendations

System Knowledge – before taking the responsibility and accountability of treating a system be sure to walk the system and review the operational and design characteristics.

Know (to the best of your ability) the metallurgies present, the system’s operating volume, temperature and pressure, and the system’s treatment and performance history.

Field Testing – critical performance criteria should include corrosion monitoring, fouling monitoring and chemical residual testing (please refer to the monitoring matrix shown below as a guide). Corrosion monitoring should try to represent all or at least the most critical metallurgies present in the system. Refer the Cooling Technology Institute’s standard for coupon testing to ensure proper corrosion testing procedures is followed.⁴² A guide for rating performance based on coupon corrosion rates is listed in Table 7.

Documentation – be sure to effectively document your knowledge of the system, your field testing results, and any observations and recommendations you provide to the customer. Verbal communication of critical observations and recommendations must be confirmed in writing. It is also a good idea to document (as explicitly as possible) the consequences of not heeding these observations and recommendations.

TABLE 6: Monitoring Matrix

System Type	Critical Test Parameters						
	Inhib. Conc.	pH	Fe/Cu	Coupons/Probes	MB Testing	Buffer Cap.	Other
Hot Water	X	X	X	X			
Chilled Water	X	X	X	X	X		
Glycol	X	X	X	X	X	X	% glycol

TABLE 7: Quantitative Classification of Corrosion Rates for Closed Systems*

Description	Carbon Steel (mpy)	Copper Alloys (mpy)
Excellent	≤ 0.2	≤ 0.10
Good	0.2 to 0.5	0.10 to 0.25
Moderate	0.5 to 0.8	0.25 to 0.35
Poor	0.8 to 1.0	0.35 to 0.50
Very Poor to Severe	≥1.0	≥0.5

*Boffardi, B.P. (2000). “Standards for Corrosion Rates”, *The Analyst*, Vol. 7, No.2, p. 61.

Conclusion

There is no treatment program that effectively controls corrosion and deposition in every application, but more often than not, there is more than one option available for a given application. It is up to the water treater to: 1.) obtain the appropriate information on the closed system to be treated; 2.) consider which options will work effectively, customer concerns and preferences, regulatory issues, and product pricing; and 3.) to follow up with proper monitoring.

Information has been provided in this paper to help the water treater to meet these objectives in this difficult business climate.

Special Acknowledgements

This document was produced by the Cooling Water Subcommittee of the AWT Technical Committee and was authored by Susan Rey and Gary Reggiani. Special thanks is given to Ben Boffardi, Al Bassett, and Jay Farmerie for their gracious contribution of time and expertise in reviewing this paper.

References for Paper:

1. Vukasovich, M.S.; Farr J.P.G. (1986). "Molybdate in Corrosion Inhibition - A Review." Materials Performance, Vol. 25, No. 5, pp. 9-18.
2. Bayes, A.L. U.S. Patent 2,147, 395, 1939.
3. Lamprey, H. U.S. Patent 2,147,409, 1939.
4. Robertson, W.D. (1951). "Molybdate and Tungstate as Corrosion Inhibitors and the Mechanism of Inhibition." Journal of the Electrochemical Society, Vol. 98, No. 3, pp. 94-100.
5. Pryor, M.J.; Cohen, M. (1953). "The Inhibition of the Corrosion of Iron by Some Anodic Inhibitors." Journal of the Electrochemical Society, Vol.100, No. 5, pp. 203-215.
6. Lizlovs, E.A. (1976). "Molybdates as Corrosion Inhibitors in the Presence of Chlorides." Corrosion, Vol. 32, No. 7, pp. 263-266.
7. Sakashita, M.; Sato, N. (1977). "The Effect of Molybdate Anion on the Ion-Selectivity of Hydrous Ferric Oxide Films in Chloride Solutions." Corrosion Science, Vol. 17, p. 473-486.
8. Kodama, T.; Ambrose, J.R. (1977). "Effect of Molybdate Ion on the Repassivation Kinetics of Iron in Solutions Containing Chloride Ions." Corrosion, Vol. 33, No. 5, pp. 155-161.
9. Ogura, K.; Ohama, T. (1984). "Pit Formation in the Cathodic Polarization of Passive Iron IV. Repair Mechanism by Molybdate, Chromate and Tungstate." Corrosion, Vol. 40, No. 47, pp. 47-51.
10. McClune, R.C.; Shilts, R.L; Ferguson, M.S. (1982). "A Study of Film Formation on Aluminum in Aqueous Solutions using Rutherford Backscattering Spectroscopy." Corrosion Science, Vol. 22, No. 11, pp. 1049-1065.
11. Hartwick, D.; Hutchinson, D.; Langevin, M. "A MultiDiscipline Approach to Closed System Treatment." Paper No. 322, pp. 1-15, presented at the National Association of Corrosion Engineers Conference, March, 2004.
12. Armour, A.W.; Robitaille, D.R. (1979). "Corrosion Inhibition by Sodium Molybdate." Journal of Chemistry, Technology, and Biotechnology, Vol. 29, pp. 619-628.
13. Boffardi, B.P. (late 1980's). Fundamentals of Cooling Water Treatment, Calgon Corporation Publication No. 11-431A, Calgon Corporation, Pittsburgh, PA, pp. 47-53.
14. Cohen, M.; Pyke, R.; Marier, P. (1949). "The Effect of Oxygen on Inhibition of Corrosion by Nitrite." Journal of the Electrochemical Society, Vol. 96, No.4, pp. 254-261.
15. Beck, A.; Cohen, M.; Mellor, G.; (1958). "A Study of the Effect of Chloride Ion on Films Formed on Iron in Sodium Nitrite Solutions." Journal of the Electrochemical Society, Vol. 105, No. 6, pp. 332-338.
16. Boffardi, B.P. "Corrosion Control of Industrial Cooling Water Systems." Paper No. 274, pp. 1-11, presented at the National Association of Corrosion Engineers Conference, April, 1983.
17. Cohen, M. (1952). "An Electron Diffraction Study of Films Formed by Sodium Nitrite Solution on Iron." Journal of Physical Chemistry, Vol. 56, No. 4, pp. 451-453.
18. Conoby, J.F.; Swain, T.M. (1967). "Nitrite as a Corrosion Inhibitor." Materials Protection, Vol. 6, No. 4, pp. 55-58.
19. Hartwick, D. (2001). "Water Treatment in Closed Systems." ASRAE Journal, Vol. 43, No. 2, pp. 30-38.
20. Robitaille, D.R. (1976). "Sodium Molybdate as a Corrosion Inhibitor in Cooling Water." Materials Performance, Vol. 15, No. 11, pp. 40-44.

21. Thresh, J.C. (1922). The Analyst, Vol. 47, pp. 459-468, 500-505.
22. Wiggle, R.R.; Hospadaruk, V.; Styloglou, E.A. (1981). "The Effectiveness of Automobile Engine Coolant Inhibitors." Materials Performance, Vol. 20, No. 6, pp. 13-18.
23. Heinrich, H.; Kanini, N.; Feller, H.G. (1978). Aluminum, Vol. 54, p. 198.
24. Cook, B; Richardson, N.; Tames, J. U.S. Patent 4,689,200, 1987.
25. "The New Standard: Belcor 575", (1988). Belgram, March, 1988 Edition, Ciba Geigy Publication No. A-5322M38, Ciba Geigy Water Chemicals Group, Hawthorne, NY.
26. "All Organic Corrosion Inhibitors for Closed Systems." (1990's). BioLabs Power Point Presentation [BS93], Slides 1-31, BioLabs, Inc., Lawrenceville, GA.
27. U.S. Patent 5,292,455, 1994.
28. "Give Your Entire Steam Boiler System a 'Rust-proof' Vest with Pennstop DEHA Water Treatment." (2003). Atofina Publication, Atofina Chemicals, Inc., Philadelphia, PA.
29. Subramanian, A.; Natesan, M.; Muralidharan, V.S.; Balakrishnan, K.; Vasudevan, T. (2000). "An Overview: Vapor Phase Corrosion Inhibitors." Corrosion, Vol. 56, No. 2, pp. 144-155.
30. Wachter, A.; Skei, T.; Stillman, N. (1951). "Dicyclohexylammonium Nitrite, A Volatile Inhibitor for Corrosion Preventative Packaging." Corrosion, Vol. 7, No. 9, pp. 284-294.
31. Stroud, E.G.; Vernon, W.H.J. (1952). "The Prevention of Corrosion in Packaging. I. The Use of Sodium Benzoate as a Corrosion-Inhibitor in Wrappings." Journal of Applied Chemistry, Vol. 2, No. 4, pp. 166-172.
32. Stroud, E.G.; Vernon, W.H.J. (1952). Journal of Applied Chemistry, "The Prevention of Corrosion in Packaging. III. Vapor-Phase Inhibitors." Vol. 2, No. 4, pp. 178-183.
33. Jacoby, A.L. U.S. Patent 2,580,923, 1952.
34. Miksic, B.A.; Kharshan, M. U.S. Patent 6,085, 905, 2000.
35. "Vapor Corrosion Inhibiting Additives." (1998). Revised 4/98-10M, Cortec Publication, Cortec Corporation, White Bear Parkway, MN.
36. Hefter, G.T.; North, N.A.; Tan, S.H. (1997). "Organic Corrosion Inhibitors in Neutral Solutions; Part 1 – Inhibition of Steel, Copper, and Aluminum by Straight Chain Carboxylates." Corrosion, Vol. 53, No. 8, pp. 657-667.
37. Boffardi, B.P. (1980's). Copper Corrosion in the Utility Industry." Calgon Publication No. 11-258, Calgon Corporation, Pittsburgh, PA. pp. 1-8.
38. Ohsawa, M.; Suetaka, W. (1979). "Spectro-Electrochemical Studies of the Corrosion Inhibition of Copper by Mercaptobenzothiazole." Corrosion Science, Vol. 19, pp. 709-722.
39. Pryor, M.J.; Cohen, M. (1953). "The Inhibition of the Corrosion of Iron by Some Anodic Inhibitors." Journal of the Electrochemical Society, Vol. 100, No. 5, pp. 203-215.
40. Pryor, M.J.; Cohen, M.; Brown, F. (1952). "The Nature of Films Formed by Passivation of Iron with Solutions of Sodium Phosphate." Journal of the Electrochemical Society, Vol. 99, No. 12, pp. 542-545.
41. Hollander, O.; May, R. "The Chemistry of Azole Copper Corrosion Inhibitors in Cooling Water." Paper 310, pp. 1-7, presented at the National Association of Corrosion Engineers Conference, April, 1983.
42. "Corrosion Testing Procedures – Corrosion Coupon Testing and Test Devices." Revision Date: October, 2000, CTI Code Std – 149(00), Cooling Tower Institute.

References for Table 1 - Recommended Inhibitor Levels for Closed Systems:

1. AWT (Association of Water Technologies) Reference and Training Manual, 1st Edition, Chapter 4, Cooling Water, pp. 74-83.
2. Kessler, S.M. "An All Organic Treatment Approach to Closed Loop Cooling Water Applications." Paper No. 218, p. 1-19, presented at the National Association of Corrosion Engineers Conference, March, 1983.
3. Boffardi, B.P. (late 1980's). Fundamentals of Cooling Water Treatment, Calgon Publication No. 11-431A, Calgon Corporation, Pittsburgh, PA, pp. 47-53.
4. Hartwick, D.; Fortin, G. "Advances in Closed System Inhibitors." Paper 659, pp.1-19, presented at the National Association of Corrosion Engineers Conference, March, 2000.
5. "Belcor® 593 – Corrosion Inhibitor for Closed Water Systems", (2003). Waterfront, BioLab Publication, BioLab Water Additives, Lawrenceville, GA.
6. Robitaille, D.R. (1976). "Sodium Molybdate as a Corrosion Inhibitor in Cooling Water." Materials Performance, Vol. 15, No.11, pp. 40-44.

References for Tables 3 - Animal Toxicity Studies and Human Toxicity:

Sodium molybdate: Sodium Molybdate Dihydrate MSDS, Revision 5-21-2003, Climax Molybdenum.

Sodium nitrite: Sodium Nitrite MSDS, Version 002, Effective Date: 6-22-1999, Vopak USA, Inc.

Sodium metasilicate pentahydrate: Sodium Metasilicate Pentahydrate MSDS, Version 006, Effective Date: 12-18-1998, Vopak USA, Inc.

Sodium nitrate: Sodium Nitrate MSDS, Revision No. 11, Date: 1-14-2005, Fisher Scientific.

Hydroxyphosphonoacetic acid: Belcor 575 MSDS, Revision No. 4, Date: 12-27-1999, Bio-Labs, Inc.

Tris-(aminopentamethylenecarboxylic acid)-triazine: "Belcor® 593 – Corrosion Inhibitor for Closed Water Systems", (2003). Waterfront, BioLab Publication, BioLab Water Additives, Lawrenceville, GA.

Diethylhydroxylamine (DEHA): Pennstop 85% MSDS, Revision No. 2, Date: 6-16-2000, ATOFINA Chemicals, Inc.

Dipotassium Phosphate: Dipotassium Phosphate MSDS, Version 003, Date: 9-29-1998, Univar, U.S.A.

Sodium tolyltriazole: Cobratec®TT-50S MSDS, Current Date: 9-12-2002, PMC Specialties Group, Inc., Oral LD50 (Rat).

Tolyltriazole: Cobratec®TT-100 MSDS, Current Date: 9-19-2003, PMC Specialties Group, Inc., Dermal LD50 (Rabbit).

Benzotriazole: Cobratec®99 Flake MSDS, Current Date: 9-25-2003, PMC Specialties Group Inc., Oral LD50 (Rat), Dermal LD50 (Rabbit).

Benzotriazole: Benzotriazole MSDS, Effective Date 9-16-2002, Mallinckrodt Baker, Inc., Inhalation LC50 (Rat).

Sodium Tetraborate Pentahydrate: Borax 5 mole MSDS, Version 002, Effective Date: 5-2003, Univar USA, Inc.

60/40 AA/AMPS Copolymer: TRC-233 MSDS, Issue Date: 10-30-1996, Calgon Corporation.

AA/AMPS/SS Copolymer: "Dispersing & Sequestering with Good-Rite® K-700 Dispersants." (1997). B.F. Goodrich Publication, B.F. Goodrich Company Specialty Chemicals Division, Cleveland, OH, p. 10.

Ethylene Glycol: Ethylene Glycol MSDS, Version 006, Date: 8-12-2002, Univar USA, Inc.

Propylene Glycol: Propylene Glycol MSDS, Effective Date: 1-16-2001, Univar USA, Inc.

References for Table 5- Aquatic Toxicity Studies:

Sodium molybdate: Sodium Molybdate Dihydrate MSDS, Revision 5-21-2003, Climax Molybdenum.

Sodium nitrite: Sodium Nitrite MSDS, Current Issue Date: May, 1999, General Chemical Corporation.

Sodium metasilicate pentahydrate: Sodium Metasilicate Pentahydrate MSDS, Version 006, Effective Date: 12-18-1998, Vopak USA, Inc.

Sodium nitrate: Sodium Nitrate MSDS, Revision No. 11, Date: 1-14-2005, Fisher Scientific.

Hydroxyphosphonoacetic acid: Belcor 575 MSDS, Revision No. 4, Date: 12-27-1999, Bio-Labs, Inc.

Tris-(aminopentamethylenecarboxylic acid)-triazine: "Belcor® 593 – Corrosion Inhibitor for Closed Water Systems", (2003). Waterfront, BioLab Publication, BioLab Water Additives, Lawrenceville, GA.

Diethylhydroxylamine (DEHA): Pennstop 85% MSDS, Revision No. 2, Date: 6-16-2000, ATOFINA Chemicals, Inc.

Dipotassium Phosphate: Dipotassium Phosphate MSDS, Version 003, Date: 9-29-1998, Univar, U.S.A.

Sodium tolyltriazole: Cobratec®TT-50S MSDS, Current Date: 9-12-2002, PMC Specialties Group, Inc.

Benzotriazole: Cobratec®99 Flake MSDS, Current Date: 9-25-2003, PMC Specialties Group Inc.

Sodium Tetraborate Pentahydrate: Borax 5 mole MSDS, Version 002, Effective Date: 5-2003, Univar USA, Inc.

60/40 AA/AMPS Copolymer: pHreeGUARD 4500 MSDS, Issue Date: 5-19-1997, Calgon Corporation.

Ethylene Glycol: Ethylene Glycol MSDS, Version 006, Date: 8-12-2002, Univar USA, Inc.

Propylene Glycol: Propylene Glycol MSDS, Effective Date: 1-16-2001, Univar USA, Inc.