Molybdate and Non-Molybdate Options for Closed Systems – Part II

Susan Rey, The National Colloid Company and
Gary M. Reggiani, Eastern Technologies, Inc.

In part I, the authors discussed the physical attributes of a closed system. In part II, the authors present the various chemistries used in closed cooling water systems to control system metallurgies. They also describe the strengths and weaknesses of closed system inhibitor options and provide useful application information.

Introduction

The first use of molybdate as a corrosion inhibitor can be traced to 1939, when two patents were issued claiming the use of molybdate for corrosion protection in alcohol-water antifreeze for automotive cooling systems.[1-3] 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, a mechanism of inhibition was proposed by Robertson. He also reported that molybdate was as efficient as nitrite and chromate for inhibiting low carbon 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, 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.

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 ($Fe^0 \rightarrow Fe^{+2} + 2e^-$), 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 surface.[7] Lastly, molybdate helps to retard pit growth. When 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 is believed to be incorporated into the protective film as a hydrated aluminum molybdate.[10] When yellow metals are also present in the system, azoles are usually added for their corrosion protection.

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, molybdate 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 ingression 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 dosage of 1 mg/L 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 chloride ions and to a lesser extent, sulfate ion concentration increases.[12] For example, 70 mg/L molybdate (as Mo^{+6}) may be effective in deionized or low electrolyte waters, whereas 466 mg/L molybdate (as Mo^{+6}) may be needed when the chloride level is 200 mg/L.[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 Na_2MoO_4-multiply by 2.15. Refer

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_2MoO_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_2MoO_4:$NaNO_2$ Ratio, ref. 6 150+150 - 400+400 Na_2MoO_4+$NaNO_2$, Low Moly: 161 Na_2MoO_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 as $NaNO_3$)
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 as 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 Organic Phosphate as PO_4^{-3})
DEHA	Fe	9.5-10.0 Fe	200 initially, 125 mg/L maintenance is typical
VCI/Organic Filmer Blends	Fe, Cu, Al	8.5-10.5 powder 8.0-9.0 liquid	1000+ for powder products 2000+ 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 is typical

* Actual dose dependent on electrolyte concentration of closed system and requires water to have ≥1 mg/L 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	% $Na_2MoO_4 \cdot 2H_2O$	% Na_2MoO_4	% MoO_4^{-2}	% Mo^{+6}
Sodium molybdate dehydrate ($Na_2MoO_4 \cdot 2H_2O$)	100.0	85.1	66.1	39.7
Sodium molybdate, liquid	41.1	35.0	27.2	16.3
Sodium nitrite	% $NaNO_2$ x 0.667 = % NO_2			

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 or controlled at pH 8.5 to 10.5, since this pH range is optimal for controlling both ferrous and yellow metal corrosion. 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 within the range of 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 side stream 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 as shown by the data in 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 fee ing on these crops may be subject to molybdenum poisc ing, which interferes with copper metabolism, liver and ki ney functions. At this point in time, however, based on t low acute animal and aquatic toxicity of molybdate, its u has been restricted in only a few areas of the U.S.

Table 3 - Toxicity of Closed System Treatment Components

Test Material	Oral LD$_{50}$ (rat) (mg/Kg)	Dermal LD$_{50}$ (rabbit) (mg/Kg)	Inhalation LC$_{50}$ (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% acetic 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 aerosol
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

Table 4 - Toxicity Classes: Hodge and Sterner Scale

Tox. Rating	Commonly Used Term	Oral LD$_{50}$ (rat) (mg/Kg)*	Dermal LD$_{50}$ (rabbit) (mg/Kg)**	Inhalation LD$_{50}$ (rat) (mg/L)***	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) Wesite, www.ccohs.ca/oshanswers/chemicals/ld50.html (2005).

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 low carbon steel corrosion when no other factors prevent its use. Nitrite functions by promoting the formation of a passive γ-Fe_2O_3 film by the following reaction:[16, 17]

$$4Fe + 3NO_2^- + 3H^+ \rightarrow 2\gamma\text{-}Fe_2O_3 + NH_3 + N_2$$

Table 5 - Aquatic Toxicity of Closed System Treatment Components

Test Material	Aquatic Toxicity Data (mg/L)
Sodium molybdate dihydrate	48 hr EC$_{50}$ (Daphnia magna): 330 96 hr LC$_{50}$ (Rainbow trout): 7,600 72 hr IC$_{50}$ (Algae): >100
Sodium nitrite	24 hr NOEC (Minnow): 17.1 48 hr TLm (Mosquito fish): 7.5
Sodium metasilicate (Na_2SiO_3)	48 hr LC$_{50}$ (Water flea): 113 96 hr LC$_{50}$ (Mosquito fish): 530
Sodium nitrate	96 hr LC$_{50}$ (Water flea): >1,000 mg/L 96 hr LC$_{50}$ (Fathead minnow): >1,000 mg/L
Hydroxyphosphono-acetic acid (HPA), 50%	24 hr EC$_{50}$ (Daphnia magna): 140 96 hr LC$_{50}$ (Rainbow trout): 180 96 hr LC$_{50}$ (Zebra fish): >820 as solids
Tris-(aminopentamethylene-carboxylic acid)-triazine, 63%	96 hr LC$_{50}$ (Zebra fish): >1,000
Diethylhydroxylamine (DEHA), 85% Diethylhydroxylamine (DEHA), 85%, neutralized	48 hr EC$_{50}$ (Daphnia magna): 111 96 hr LC$_{50}$ (Guppy): 150
VCI/Organic filmer blends	See manufacturer.
Dipotassium phosphate (DKP)	48 hr EC$_{50}$ (Daphnia magna): >100 mg/L 96 hr LC$_{50}$ (Rainbow trout): >100 mg/L
Sodium tolyltriazole, 50% solution	48 hr LC$_{50}$ (Daphnia magna): 245.7 96 hr LC$_{50}$ (Bluegill sunfish): 191.2 96 hr LC$_{50}$ (Rainbow trout): 23.7
Sodium benzotriazole (BT)	48 hr LC$_{50}$ (Daphnia magna): 141.6 96 hr Tlm (Minnow): 28 96 hr Tlm (Bluegill sunfish): 28 96 hr LC5$_{50}$ (Trout): 39 96 hr EC$_{50}$ (Algae): 15.4
Sodium tetraborate pentahydrate	24 hr EC$_{50}$ (Daphnia magna): 1,631 3 day LC$_{50}$ (Goldfish): 478 24 day LC$_{50}$ (Rainbow trout): 593 96 hr EC$_{10}$ (Algae): 162
60/40 AA/AMPS®*, as active	48 hr LC$_{50}$ (Daphnia magna): 2,800 96 hr LC$_{50}$ (Bluegill sunfish): >10,000 96 hr LC$_{50}$ (Rainbow trout): 4,900
AA/AMPS®/SS**, 48%	48 hr EC$_{50}$ (Daphnia): >1,529 96 hr LC$_{50}$ (Rainbow trout): >1,079 96 hr LC$_{50}$ (Algae): >1,049 and <2,120
Ethylene glycol	LC$_{50}$ (Daphnia magna): 46,300-51,100 LC$_{50}$ (Fathead minnow): 51,000 LC$_{50}$ (Bluegill): 27,540 LC$_{50}$ (Rainbow trout): 18,000-46,000
Propylene glycol	Acute LC$_{50}$ (Daphnia magna): 4,850-34,400 Acute LC$_{50}$ (Fathead minnow): 46,500-54,900 Acute LC$_{50}$ (Guppy): >10,000 Acute LC$_{50}$ (Rainbow trout): 44,000

Unlike molybdate, nitrite does not require dissolved oxygen to function as a passivating inhibitor.

As shown in Table 1, the recommended dosage depends on the water source, but in summary the range is from a low of 700 mg/L as $NaNO_2$ to a high of 1,800 mg/L 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 to a greater extent with corrosion protection by nitrite than with chloride ions. A recommendation based on aggressive ion content is that for low levels of aggressive ions, the mg/L sodium nitrite should equal the mg/L chloride ion plus 250 to 500 mg/L more than the mg/L 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 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 required. Nitrite is compatible with glycol systems and commonly used non-oxidizing biocides. An inadequacy of nitrite treatment is the propensity to promote microbiological growth. This will be more of a concern 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.[19]

$$NO_2^- + 5H^+ + 6e^- \rightarrow NH_3 + 2OH^-$$

In addition to the loss of protection as a result of the loss of nitrite, nitrate is also a nutrient for bacteria, whereas ammonia is aggressive to some 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, isothiazolone and trisnitro, [tris(hydromethylnitromethane)]. Trisnitro is particularly effective at higher pH and against nitrifying and denitrifying bacteria. 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 with nitrite treatments, since they will oxidize nitrite ions to nitrate ions.

Air ingress can also oxidize nitrite ions to nitrate ions:

$$2NO_2^- + O_2 \rightarrow 2NO_3^-$$

Therefore, in systems having much air ingress, higher levels of nitrite may be needed, making biological control more 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 LD_{50} (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 of nitrite into the environment exceeding 100 lb (dry weight) must be reported to the EPA.

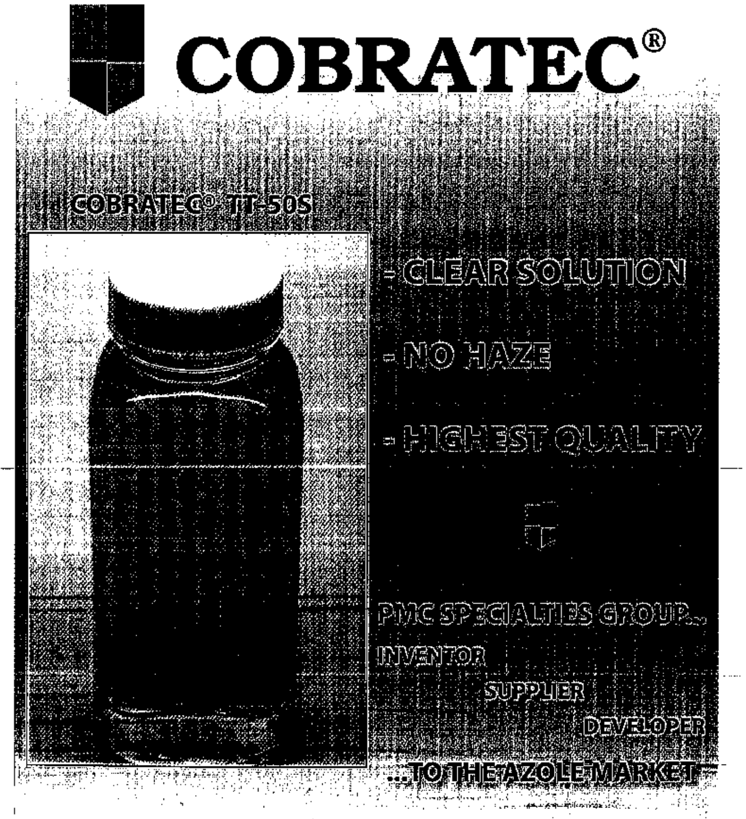
Humans: Sodium Nitrite: The estimated lethal dose in humans is 1 to 2 g.

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.

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 is absorbed onto the ferrous hydroxide surface layer of the metal. The absorption imparts a negative surface charge which repels aggressive ions (i.e., chloride and sulfate). Molybdate also helps to retard the growth of pits as discussed above.

The ratio of sodium molybdate to sodium nitrite giving the lowest low carbon 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 mg/L Na_2MoO_4 plus 150 mg/L $NaNO_2$ to 400 mg/L Na_2MoO_4 plus 400 mg/L $NaNO_2$. Other water treaters have weighted their products more towards sodium nitrite likely as a cost



cutting consideration. Along this vein, the AWT Technical Reference & Training Manual indicates that the molybdate level can be reduced to as low as 161 mg/L Na_2MoO_4 with 525 to 750 mg/L nitrite as $NaNO_2$.

The benefits of molybdate/nitrite programs include enhanced corrosion control, a reduced propensity for pitting over nitrite alone, and both low carbon 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. Also, microbiological control may be difficult due to the nitrite component. Toxicity is also a concern. Molybdate/nitrite programs are compatible with commonly used non-oxidizing biocides as well as ethylene and propylene glycols.

Silicates

Silicates are commonly used for both ferrous and yellow metal corrosion control in soft potable water applications, where minimal 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 then.[26]

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 $nNa_2O: mSiO_2$. Generally, a ratio of m/n of 2.5 -3.0 is effective.[16] With silicate treatments 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 low carbon steel, yellow metals, and aluminum.

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

For closed systems having both ferrous 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 pHs 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, 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 exceeds the 9.0 limit, aluminum silicate deposition may occur, which can plug nozzles and other small orifices, etc.

Silicates are considered to be relatively non-toxic. The oral LD_{50} (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 low carbon steel and aluminum corrosion, occasionally sodium nitrate is used in conjunction with sodium nitrite to provide the aluminum corrosion control. In fact, while nitrite is an effective low carbon steel corrosion inhibitor, it can be antagonistic to aluminum corrosion. However, the addition of nitrate overcomes this antagonism.[22]

Nitrate functions by controlling the growth of the aluminum hydroxide film and also as a pitting inhibitor by the preferential reaction of nitrate with the active surface.[10, 23] A study of aluminum pitting inhibition indicated that

$NO_3^- > MoO_4^{-2} > SiO_3^{-2}$ in effectiveness.[22]
However, a study of aluminum film growth inhibition indicated
$SiO_3^{-2} > MoO_4^{-2} > NO_3^-$ in effectiveness.[10]

The recommended dose rate for controlling both aluminum and low carbon steel corrosion is 685 to 1,371 mg/L sodium nitrate in combination with 750 to 1,500 mg/L sodium nitrite. If yellow metals are present, an azole is recommended, since neither nitrite nor nitrate provides 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. Nitrite has been associated with "Blue Baby Syndrome" or methemoglobinemia, a decreased oxygen-carrying capacity of the blood resulting in shortness of breath, bluish colored skin, other symptoms, and possibly death.

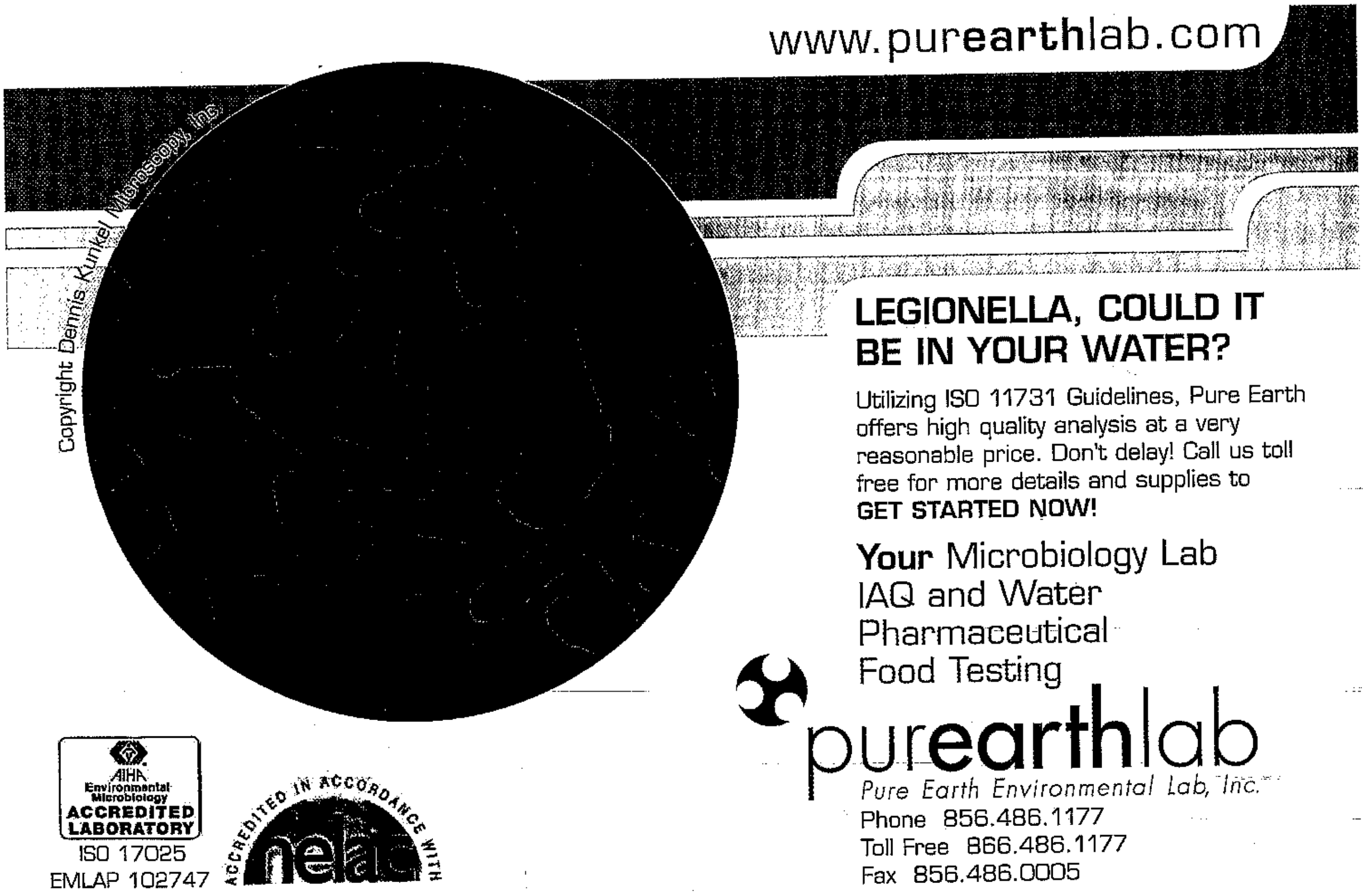
HPA-Triazine Stand Alone and Combination

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 low carbon steel surface, the pH is increased 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 low carbon steel surface becomes covered with a thin calcium/HPA film, which stifles the cathodic reaction by preventing oxygen from reaching the metal surface. The film is extremely thin and does not interfere with heat transfer. The suggested dosage is 50-100 mg/L as HPA (30-122 mg/L organic phosphate as PO_4^{-3}). The low calcium level in some closed systems may limit the effectiveness of HPA alone for controlling low carbon 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 mg/L HPA.[27] In these systems, calcium chloride is used to enable very low operating temperatures. Chromate is the most effective multimetal 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 non-chromate treatments, external control measures including side stream 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 functions 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 mg/L total actives. For monitoring purposes, this would correspond to an organic phosphate level of 30-50 mg/L 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 and nitrite. 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 expensive, 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 ions, a nutrient for bacteria and mold growth. Likewise, the decomposition of carboxylic acids provides 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 both chiller 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 μmhos). These systems may include induction heating 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, besides being an oxygen scavenger and pH buffer. A DEHA treated system would typically be buffered to approximately a pH of 9.5 to 10.0, by formulating a low level neutralizing amine. The passivation and oxygen scavenging reactions with DEHA, are respectively:[28]

$$27Fe_2O_3 + 2(CH_3CH_2)_2NOH \rightarrow 18Fe_3O_4 + N_2 + 4CH_3COOH + 3H_2O$$

$$4(CH_3CH_2)_2NOH + 9O_2 \rightarrow 8CH_3COOH + 2N_2 + 6H_2O$$

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 mg/L DEHA will be required as compared to a maintenance dose of about 125 mg/L DEHA.

DEHA (or sometimes carbohydrazide) presents one of the few options for low conductivity and/or high temperature systems. The chief disadvantage of a DEHA program is that it will not be effective in a system that is not "tight," (i.e., has leaks or uses much make-up). In theory, 1.24 mg/L DEHA scavenges 1 mg/L oxygen, but in practice the use ratio is 3 mg/L DEHA to 1 mg/L oxygen.[28] If there is much oxygen ingress, the DEHA will be consumed and corrosion protection will be 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. Fish kill studies indicate that DEHA is considered to have moderate aquatic toxicity.

VCIs/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 forming a thin film 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 films 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, alkyl amines, 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 functions as a VCI by contributing its nitrite ion to condensed or absorbed moisture on the metal surface.[29] In comparison, aminobenzoates functions by promoting the formation of $\gamma\text{-}Fe_2O_3$

Aminobenzoates act as an electron acceptor and the oxide layer as an electron donor.[29] Alkylamines 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] Alklyamines form barrier films that prevent oxygen from reaching the metal surface, thus inhibiting the cathodic reaction.

Akylcarboxylates 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 inhibiting 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 mg/L chloride ion and 100 mg/L sodium bicarbonate was used. The results of this study showed that the optimal chain length for straight chain aliphatic monocarboxylates is ($6 \le n \le 10$) for controlling low carbon steel control, ($10 \le n \le 17$, or more - highest tested) for controlling copper corrosion, and n = 10 or 11 for controlling aluminum pitting. In contrast, the optimal chain length for strait chain α,ω-dicarboxylates [$^{-}OOC(CH_2)_nCOO^{-}$] is ($4 \le n \le 12$) for low carbon steel and ($11 \le n \le 14$, or more – highest tested) for controlling copper corrosion and a
minum pitting. The optimal chain length for straight ch
alkyl mono and dicarboxylates is a function of comp
ing reactions involving adsorption and complexation
the metal/metal hydroxide/oxide surface, solubility, a
micelle formation in solution.

Most combinations of VCIs and film formers are forn
lated to provide multimetal protection. Feedrates for co
mercially available VCI/film former blends are typica
1,000+ mg/L for dry products and 2,000+ mg/L for liq
products. At the recommended treatment levels, the
falls at about 8.5 to 10.5 with the dry products and 8.0
9.0 with liquid blends.

Combinations of VCIs and/or organic film formers are n
being commercialized for use in closed systems includ
hot water, chilled water, brine, and low conductivity syste
with anecdotally good results as indicated by case histor
As a rule, recently marketed VCI/organic film former ble
are nitrite free and are touted to have low toxicity and to
environmentally friendly. This makes them attractive to c
tomers concerned about health, safety, and environmer
issues or constrained by regulations.

The fact that the VCI/organic film former blends
organic in nature would imply that product component
breakdown species may be nutrients for microbes and p
sibly promote microbiological growth. The use of oxidiz
biocides would not be recommended, due to possible c
dation of product components. Before using non-oxid
ing species, the water treater should clear their use w
the product manufacturer. Several non-oxidizing bioci
that are commonly used for closed loop treatment h
been shown to be compatible with recently marketed V
film former products.

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

Dipotassium phosphate

Dipotassium phosphate (DKP) is commonly used in g
col systems for controlling low carbon steel corrosion. D
serves as a buffer, as well to inhibit pH depression as
glycol degrades to organic acids.

Orthophosphate ion is an anodic inhibitor. In the presence of dissolved oxygen, the protective film that forms is γ-Fe_2O_3.[39] Magnetite is sometimes found underneath the γ-Fe_2O_3 film, and is believed to be a partially oxidized intermediate layer.[13] The γ-Fe_2O_3 film is porous with many voids and cavities. Orthophosphate ion functions 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 γ-Fe_2O_3 and form the primary film.[13]

Phosphates are generally fed at 1,000 to 5,000 mg/L 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 high concentrations the control of microbiological growth would likely be problematic.

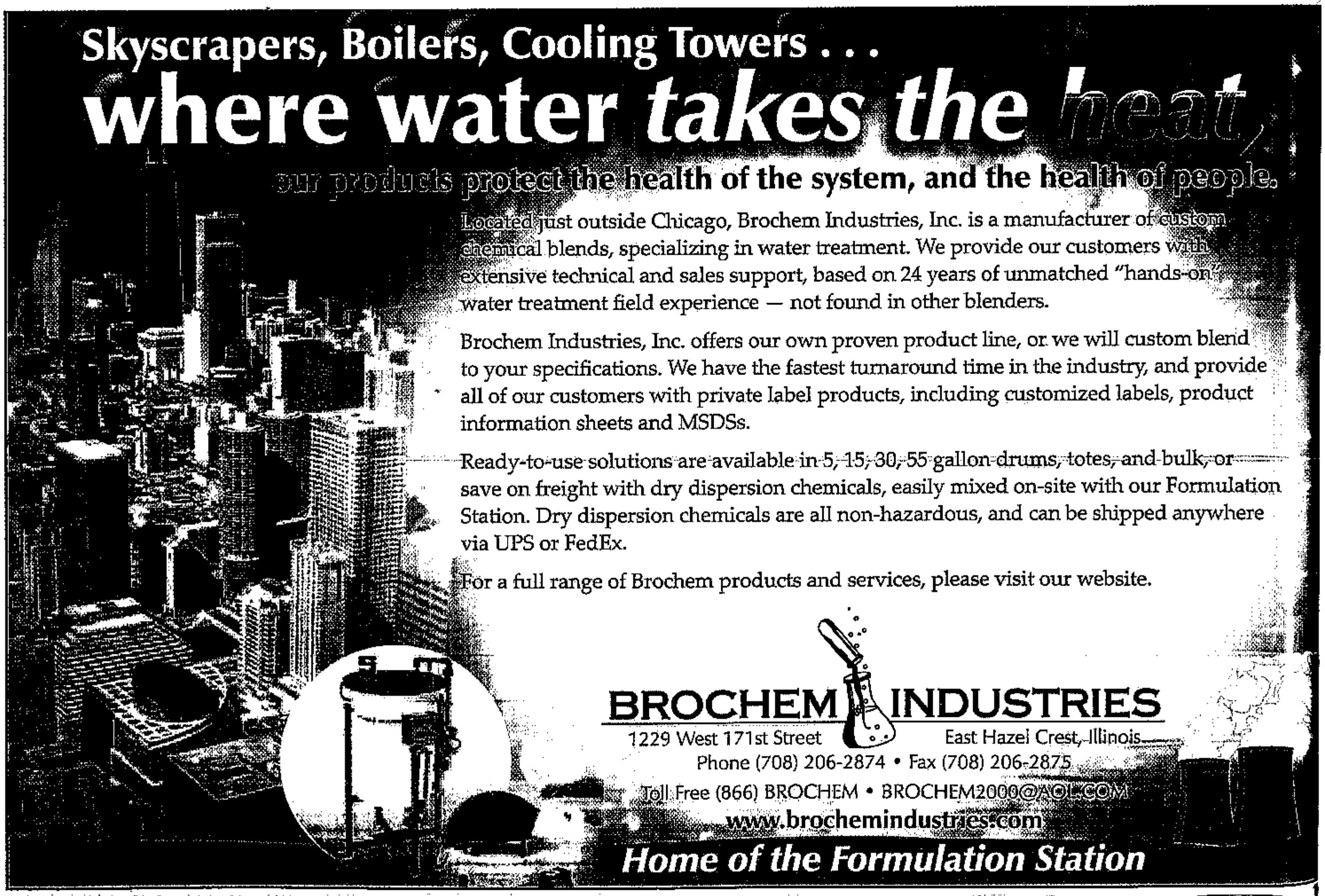
Phosphates are inexpensive and have low toxicity, unless ingested in large quantity. However, they are a nutrient for microbes and cause algae blooms in surface waters, which can cause eutrophication of ponds and lakes.

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 mg/L as the sodium salt. The azole requirement increases with increasing concentration of chloride and sulfate ions.

TT and BT function 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 Cu(1)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.

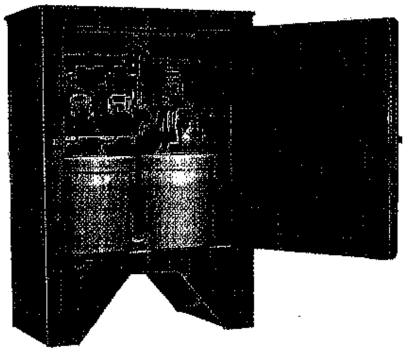
In addition to controlling yellow metal corrosion, azoles react with cuprous ions in solution and prevent them from plating out on low carbon steel or aluminum surfaces, which causes pitting to occur. Pitting occurs because as more and more surface becomes covered with copper metal, the electron flow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

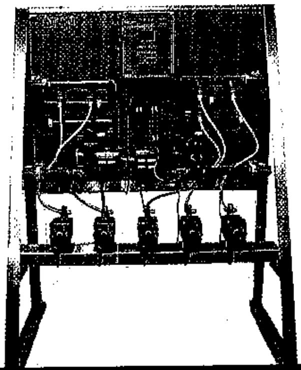
Azoles are moderately toxic to animals and have moderate aquatic toxicity, but usually comprise such a small percentage of a typical closed system formulation that the toxicity level is not problematic.

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 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 waters 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 mg/L to 20 mg/L to prevent deposition of corrosion products or contaminants that could cause underdeposit attack. Typically, an AA/AMPS® based copolymer is used. In the past, maleic acid/sulfonated styrene (MA/SS) copolymers were commonly used and are occasionally in use, but they are being supplanted by the more effective AA/AMPS® copolymers.





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 cost 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 (refer to Table 6, 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 the system parameters, field testing results, and any observations and recommendations provide by the customer. Verbal communication of critical observations and recommendations must be confirmed in writing. It is also a good practice to document (as explicitly as possible) the consequences of not heeding these observations and recommendations.

Table 6 - Monitoring Matrix

System Type	Critical Test Parameters						
	Inhibitor Conc.	pH	Fe/Cu	Coupons/Probes	MB Testing	Buffer Capacity	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	Low 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, VII, 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 article to help the water treater to meet these objectives in this difficult business climate. ♦

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Susan Rey is the Technical Manager at The National Colloid Company. Ms Rey can be reached at srey@natcoll.com. Gary Reggiani is the Director of Sales and Technical Marketing for Eastern Technologies, Inc. Mr. Reggiani can be reached at greggiani@aol.com

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