Water Treatment In Closed Systems

By Darrell Hartwick

Closed systems are commonly classed by their function — either heating (hot water) or cooling (chilled water). They typically rely on water or water-based solutions as their heat transfer fluid.

While various ways exist to classify water treatment product technologies, one of the simplest is whether the primary corrosion inhibitors are reducing agents, oxidizing agents, or film formers.

In addition to the primary corrosion inhibitors, factors such as fluid pH and copper ions also affect corrosion. Supplemental agents are used to buffer/control pH and minimize yellow metal corrosion. The primary corrosion inhibitors, which focus on ferrous alloys, and the supplemental inhibitors comprise the total treatment package.

Reducing Agents

Reducing agents are not commonly used due to inherent limitations with available chemicals. Reducing agents work by removing oxygen from solution so it is not available to corrode metals.

Although rarely seen nowadays, tannins have been used both to remove oxygen and form an iron-tannin film on steel surfaces. Tannins are low cost, easy to formulate, testable, and readily available. The drawbacks for tannins include their tendency to form organic deposits on heat exchange surfaces. These deposits may eventually require chemical cleaning to remove. More significantly, while they do scavenge oxygen, the rate of reaction is not rapid. It is common to have oxygen corrosion in spite of maintaining a reasonable tannin residual.

Sulphite is another type of reducing agent treatment that still shows up from time to time. The reaction of sulphite with oxygen has been well studied. It is generally recognized that the reaction proceeds via a free radical mechanism. The overall equation is:

$$\tfrac{1}{2}\,O_2 + Na_2SO_3 \rightarrow Na_2SO_4 \qquad (1)$$

With this technology, sufficient sulphite must be present at all times. Otherwise free oxygen will exist and the boiler metal will corrode. The normal approach involves maintaining an excess of sulphite (30 – 50 mg/L Na_2SO_3) in the water. The sulphite residual acts as a "sponge" to react with oxygen that enters the system. Without regular testing, the risk of corrosion is quite high, since even temporary losses of the sulphite residual can lead to corrosion.

A secondary drawback is that as sulphite is fed to the system (to cope with the ongoing ingress of oxygen), the concentration of sulphate builds. Increasing sulphate increases the conductivity of the water and its corrosivity as well as the potential for SRB (sulphate reducing bacteria) growth.

Organic reducing agents such as hydrazine (N_2H_4) and DEHA (diethylhydroxylamine) have been used. However, decomposition (catalyzed by copper) and health concerns for hydrazine have largely eliminated their use. In the case of hydrazine, its breakdown to ammonia has resulted in failures related to intensive copper corrosion by the following mechanism.

$$3\,N_2H_4 + 6\,OH^- \rightarrow 2\,NH_3 + 2\,N_2 + 6\,H_2O \qquad (2)$$

$$NH_3 + Cu^{+2} \rightarrow Cu\,(NH_3)^{+2} \qquad (3)$$

Both hot and cold loops have all the conditions for these reactions to take place, including the oxygen needed to oxidize the copper metal and ammonia that dissolves copper oxide. The dissolved copper is free to plate on to steel surfaces in the system where it can cause galvanic corrosion. When the copper plates out, it releases the ammonia, which is free again to repeat the cycle. As a result, ammonia will rapidly corrode copper (and its alloys).

Oxidizing Agents

In contrast to reducing agents, oxidizers either react directly with the metal surface (chromate and nitrite) or work in conjunction with oxygen (molybdate) to achieve a passive film on the metal.

The standard inhibitor in this category, nitrite, has been used to inhibit corrosion of mild steel for many years[1, 2] in neutral or alkaline aqueous solutions. Nitrite is the only remaining anodic oxidizing inhibitor that can still be used. Unlike molybdate, another anodic inhibitor, nitrite does not need oxygen.[3] For this reason, it is very effective in closed systems.

It has been proposed that nitrite protects ferrous metal by an oxidation-reduction process where ferrous hydroxide forms a passive magnetite layer.[4] The

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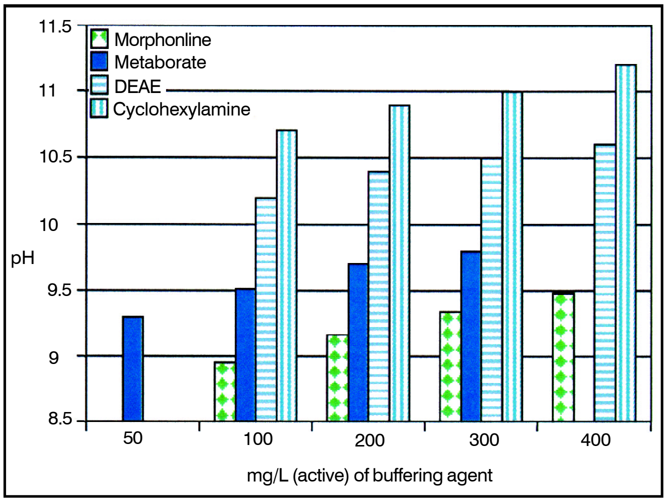

Figure 1: pH curves for different buffering agents as a function of their concentration in DI water.

overall reaction is:

$$9Fe(OH)_2 + NO_2^- \rightarrow 3Fe_3O_4 + NH_4^+ + 2OH^- + 6H_2O \tag{4}$$

Whether nitrite is used alone or in conjunction with pH buffering agents, relatively high concentrations are needed to establish a protective film, usually on the order of 700 to 1200 mg/L to completely inhibit pitting corrosion. Once the protective film has been established, the nitrite concentration can be lowered slightly to 700 to 1000 mg/L . Some sources have stated that the required nitrite level is influenced by the amount of chloride and sulphate present in the water[5,6] because they can affect the stability of the magnetite layer. As with all anodic inhibitors, severe pitting can occur at low concentrations (<500 mg/L as $NaNO_2$). In other words, too little nitrite is actually worse than none at all because low levels of nitrite will speed up the corrosion process.

Loss of nitrite can occur via electrochemical and biological processes. In the former case, if corrosion continues, nitrite can be reduced at the cathode to form ammonia[7] according to the equation:

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

In chilled water loops (or hot water systems, that are not in operation) exposure to bacteria has the potential to oxidize nitrite to nitrate or reduce it to ammonia or nitrogen. Controlling biological activity is difficult because oxidizing biocides (like chlorine) will oxidize the nitrite to nitrate, and the efficacy of non-oxidizing biocides tends to be less certain. Difficulty in preventing biological degradation of nitrite has always been a serious limitation.

The use of molybdate for corrosion protection in cooling water, either open recirculating or closed loop, systems[8, 9, 10] is well documented. While molybdate is not as strong an oxidizing agent as chromate, it can function in this role in the presence of oxygen.

In the presence of oxygen, molybdate will convert hematite (Fe_2O_3 or red rust) to magnetite (Fe_3O_4 or magnetic black rust). This process is quite visible as boilers (either hot water or steam) change from a reddish color to black when treated with molybdate. This mechanism predominates at higher concentrations (>50 mg/L as Mo). By contrast, molybdate's efficacy as an anodic (or pitting) inhibitor is related to its ability to accumulate within the acidic part of a pit and block the corrosion process. Use of molybdate alone at <20 mg/L will reduce the risk of pitting type attack but will not offer good general corrosion protection.

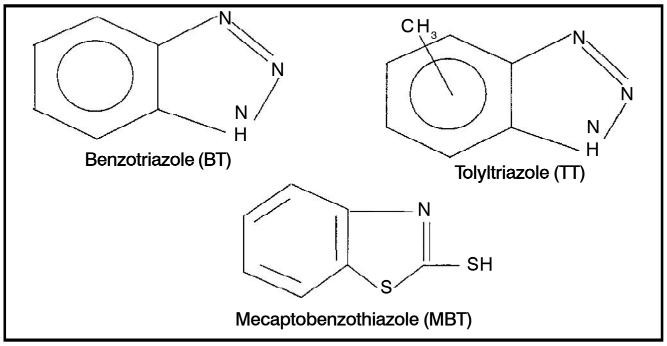

Figure 2: Commonly used copper inhibitors.

Regardless of the mode of action at low concentrations, at elevated levels (>50 mg/L as Mo), molybdate (in the presence of oxygen) is capable of passivating boiler metal.

The only concern regarding molybdate use is related to its accumulation in sludge from waste treatment plants if the sludge is spread on agricultural land. However, based on its low human and aquatic toxicity, molybdate is not severely restricted in most areas of North America.

The last oxidizer is hexavalent chromium, or chromate, which, while a very effective corrosion inhibitor, is seldom used due to concerns of health/environmental effects.[11] Being a strong oxidizing agent, chromate is capable of converting hematite to magnetite. The reduced chromium becomes incorporated into the resultant oxide layer.[8]

Film Formers

Among the four filmers used, ortho-phosphate is the most common. Glycol manufacturers widely use ortho-phosphate in the dual role of corrosion inhibitor and pH buffer in their formulations. At normal use concentrations (1000 to 5000 mg/L as PO_4), phosphate protects against corrosion on ferrous and non-ferrous alloys. The primary mode of action is via precipitation at the anode to form insoluble metal phosphates. This low solubility of phosphate salts is why manufacturers recommend using good quality (i.e., soft or distilled/deionized) water[12] for diluting phosphate containing products like glycols.

The ability of phosphate to form a protective film by directly precipitating is both its strength and weakness. While it will film the metal surfaces, it will just as readily precipitate with metal ions or hardness salts in the bulk water. This competition between useful and non-productive reactions is the major liability associated with phosphate. Since ortho phosphate is an anodic inhibitor, if the concentration falls below the critical level (200 to 300 mg/L), rapid corrosion attack will occur.

Phosphonates are related to inorganic phosphates, which include ortho and polyphosphate. HPA (hydroxy-phosphonoacetic acid) is the best example of a phosphonate. These chemicals are effective cathodic inhibitors. HPA can be employed where a prod-

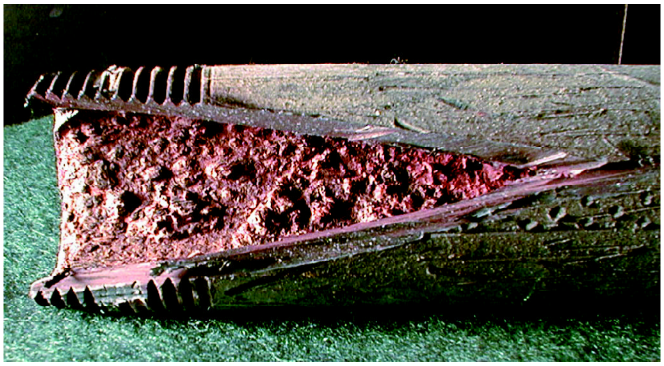

Figure 3: Rapid corrosion to piping, with extensive pitting type attack, is a risk of failing to treat closed loops.

uct with a low environmental impact is preferred. Acceptable corrosion rates can be obtained at levels of 50 to 200 mg/L (as HPA). The phosphorous contribution of 25 to 150 mg/L (as PO_4) is well below what would be necessary with inorganic phosphates.

A third class of film formers is the various dibasic acids. They can be used for pH buffering and corrosion inhibition, much like phosphate. Dibasic acids work because of their limited solubility with transition metals (iron and copper) and alkaline earth cations (hardness). As the corrosion process takes place at the anode, iron ions go into solution. The dibasic anion reacts with the iron ions and precipitates at the corrosion site, stopping corrosion.

Unfortunately, dibasic acids are biodegradable. In chilled water loops this can pose a serious limitation. In particular, where there is already a supply of biologically available nitrogen (i.e., nitrite), rapid biological growth can quickly consume these nutrients in a few days.

Also, as they rely on iron ions to form the inhibitor film, losses can occur if a considerable amount of corrosion product is present in a system before adding the dibasic acid. In systems (new or old) with significant amounts of corrosion products present, loss of this type of inhibitor can be dramatic.

Substituted triazines are the final type of film former. They react selectively with iron to form an inhibitory film on the metal. Although they are widely used in oil-field applications as downhole corrosion inhibitors, they have not seen extensive use in closed loops. The hexanoic acid triazine compound is an example of this chemistry.

Buffers/pH Control

Although corrosion inhibitors are frequently separated from the buffering/pH control agents, in most cases they are intertwined. Inhibitors generally function only in certain pH ranges. For example, nitrite is typically used under alkaline conditions. Others, such as some of the dibasic acid mixtures, show best performance at neutral pH. Regardless of the inhibitor type, acid pH conditions are never acceptable.

Given the variety of metals and elastomers in closed loops, the pH range is a compromise. The primary metallurgies used in North America are mild steel and copper alloys. These metals require a pH range of 8.5 to 10.5. Aluminum, which is uncommon in North

America but is seen in Europe, prefers a neutral pH range for optimum protection.

At one time, caustic (sodium hydroxide) was commonly used to raise pH. Since caustic is not a buffer, controlling pH is difficult, and excursions are not unusual. Except for cost, there is little to recommend caustic, and the risk related to its use is high. Also rarely used, carbonate buffers are sometimes encountered where other more suitable buffering systems cannot be used. Carbonate and hydroxide may have application in nuclear plants where borate cannot be accepted. Otherwise, they have little to recommend them.

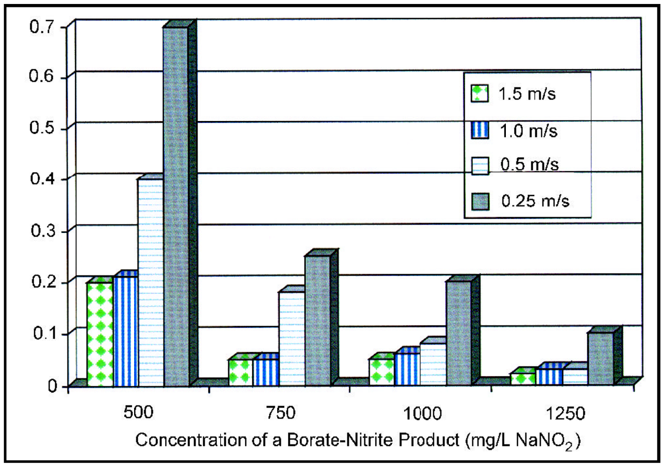

Figure 4: As the water velocity decreased, the corrosion rates on mild steel rose at all concentrations, although it was most dramatic at lower inhibitor levels.

The most widely used pH control agents are all buffers:
- Ortho phosphate,
- Borate salts, and
- Organic amines.

Ortho phosphate, typically dipotassium phosphate (or adjusted mixtures of di- and tripotassium phosphate) can be used to control the pH between 9 to 10.5. At the high levels used for corrosion control, ortho phosphate provides excellent buffering capacity. This buffering function is particularly useful in glycol containing loops, where the ortho phosphates can neutralize glycol breakdown products for extended periods of time.

Another inorganic buffering system is borate (or metaborate). Borates provide good buffering capacity and allow a slightly higher pH than phosphates. This means that less can be used to obtain the desired pH. Unlike phosphate, borate functions in the sole role of a buffer. It has effectively no impact on corrosion rates beyond that seen from pH.

Organic amines provide a number of benefits compared to inorganic buffers. Depending on the pH range desired, one can select from the commonly available amines to tailor the pH of the fluid (*Figure 1*) to the exact value required. In addition, morpholine has been shown to be a passivating agent in its own right. Another benefit of the amines is that the amount needed in the fluid is low (200 to 300 mg/L). The low concentration coupled with their low intrinsic conductivity means amines contribute less to conductivity than inorganic buffers. The lower conductivity means amines are useful in conductivity sensitive systems like cooling water loops for welders.

Yellow Metal Inhibitors

Control of copper corrosion is critical in any closed loop. While copper and its alloys are quite corrosion resistant, the impact of even low corrosion rates can be dramatic. When copper corrodes, soluble copper ions plate out onto mild steel components. When this happens, the more inert copper metal becomes a "permanent" cathode on the metal surface. At this point, the corrosion process, which had been spread over the entire steel surface, now becomes localized and continues at an accelerated rate. As this proceeds, instead of having a low general corrosion rate, high *local* corrosion rates will be seen.

Azoles are used to prevent the initial corrosion of copper alloys, as well as to inhibit copper deposits on mild steel surfaces. *Figure 2* shows the most commonly used types. MBT (mercaptobenzothiazole), a low cost, effective inhibitor, has been used for many years with good results. More and more commonly, TT (tolyltriazole) has become the inhibitor of choice due to cost considerations and its superior resistance to the corrosive effect of chloride ions.

In contrast to precipitating agents, the nitrogen atoms in the azoles bond to the copper metal via copper oxide molecules on the surface. The protective layer that is formed enhances the natural corrosion resistance of copper and copper alloys.

Monitoring

Monitoring of closed loops entails verifying that the treatment program is meeting the goals for corrosion, deposits, microbiological activity, and product/treatment level. The corrosion monitoring should also have some provision to show that localized or pitting type attack is not taking place.

Corrosion

Monitoring relies on using a model for what is happening to a system. It is meant to prevent surprises such as in *Figure 3*. Instead of having to cut out pipes to see if corrosion is taking place, a well-designed monitoring program will provide the same information about the efficacy of the water treatment program with considerably less effort.

While a physical inspection of boilers and chillers (or other related components) is the most effective way to determine overall system performance, other approaches can provide the same information on the cleanliness of the equipment.

Corrosion coupons are the most common type of monitoring, since they provide information on overall corrosion rates as well as the type of corrosion that is taking place. A coupon will give the following data:

- General/overall corrosion rate,

- Pitting corrosion rate,
- Indicators of biological attack, and
- Evidence of galvanic attack.

In a well-maintained system, the corrosion rate should be virtually nil, and there should be no sign of localized attack. In chilled water loops, it is also important to assess whether microbiologically induced corrosion (MIC) is occurring. Coupons are one of the easiest ways to look at this aspect. Most closed loops contain a variety of alloys, and yellow metals are quite common. If they are not adequately protected, the dissolved copper ions (from the corrosion process) can deposit onto steel components and cause galvanic attack. If this problem is suspected, the copper content on the surface of a steel coupon will confirm if it is an issue or not.

To be effective, corrosion coupons need to meet a number of criteria to mimic a closed system:

1. The coupons should be of similar metallurgy to the components in the system. Mild steel (typically 1010) and copper (although brass and other more specialized alloys may be appropriate) coupons should be used.
2. Exposure periods should be varied, with some as short as 30 days and some being allowed to remain in for up to a year.
3. The flow rate through the coupon rack should be close to what various sections of the loop experience. This could range from the normal flow velocities of 1.2 to 1.5 m/s (4 to 5 fps) to as low as 0.03 m/s (0.1 fps).
4. Since temperature has a large impact on corrosion rates, the coupons should see the same temperature (or as close as possible to it) as the hottest section of the system. A good location is on the supply header, shortly after the boiler. With chilled water, the return header is an ideal location.

If coupons are left in for short periods (less than 30 days), the corrosion rate will be artificially inflated. The real value of the corrosion rate is partially the level itself, but the major value is the trend over several months or years. Consistently low corrosion rates, with no localized areas of metal loss, is the goal.

If localized attack occurs, it is normally a good idea (assuming that obvious causes such as low chemical residuals are not the cause) to have the coupon checked for copper plating and MIC. Most water treatment companies provide this sort of service as part of their service program. In some cases, consultants also can arrange to have this type of testing done, though they typically use outside laboratories, which might be less experienced in what to check for.

Installing coupons to copy conditions in zones where the water velocity is low is important. It is rare to find a closed loop circuit that does not have low flow sections or is periodically stagnant. Although the high inhibitor levels used in closed systems should reduce the effect of stagnant or low flow conditions, it is necessary to ensure that the program being used meets this critical performance criteria.

Figure 4 shows the effect that reducing water velocity has on corrosion rates for a conventional borate-nitrite program. Although the corrosion rates should only be taken as relative indicator of what might happen in a system, the important point is that going from a water velocity of 1.5 m/s (5 fps) to 0.3 m/s (1 fps) allowed corrosion rates to more than triple. Higher inhibitor levels did minimize this effect, yet the general trend is still apparent. Not taking into account the effect that water velocity has on the inhibitor program has caught more than one installation by surprise.

Low-cost electrochemical measuring devices (to determine instantaneous corrosion rates) are becoming more common and accessible. Electrochemical monitoring provides rapid results (probes can generate accurate rates after only a few days) and makes it possible to trend corrosion rates not only using monthly averages but also on a day by day basis. Being able to get reliable data on corrosion rates over such short periods allows one to determine if system operation (e.g., periodic shutdowns, etc.) is affecting the corrosion protection being provided.

Although not as high tech as electrochemical monitoring methods, a simple and effective technique to follow corrosion trends is to measure iron and copper concentrations in the closed loop fluid. As system metal corrodes, it goes into the fluid. Although it is present in a precipitated form, the metal concentration in the water does serve as a good trend indicator of what is happening. While it does not tell what is causing corrosion, it does provide a quick indication of when things begin to go wrong or confirmation that the program is continuing to meet agreed upon standards.

Deposits

Deposits are rarely a concern in a closed system. The best way of monitoring deposits is to record makeup rates. If the system is operating within normal limits (makeup <10% of system volume per year) the risk of scaling is minimal. It should be noted that some treatment programs, specifically phosphate inhibitors used in some glycols, are quite sensitive to hardness in the water used. If good quality water is not used, the phosphates can react with the hardness present and form deposits.

Microbiological Activity

Microbiological monitoring is seldom needed in hot water loops that operate continuously above 140°F (60°C) or in chilled systems where the glycol concentration is above 20%. However, when these conditions are not met, bacterial monitoring should be part of the testing program, especially with readily biodegradable treatments such as nitrite. Testing can either be via plate counts/dip slides (giving results in colony forming units (CFUs) per mL) or ATP (adenosine triphosphate) assay, which gives a measure of all types of micro-organisms and provides results within minutes. The ATP test result is in ng of ATP/mL, although some companies use the less accurate and not consistent units of RLUs (relative light units: light output relative to a particular instrument and a particular batch of reagents).

Any monitoring program is only as good as the frequency with which it is carried out. Corrosion coupons and corrosion product determination (in the system fluid) are most effective at illustrating a trend rather than providing absolute values. A regular program of sampling will allow one to verify the level of protection that is being achieved and to determine if it is changing over time.

Product/Treatment Level

Monitoring the product concentration is normally a routine part of the treatment program. It can be done either by plant personnel or the chemical supplier.

The objective of the chemical testing is to confirm that the corrosion inhibitor(s) is present in an adequate amount and that the pH is buffered to the right level. In the case of glycol loops, verifying that the glycol concentration is more than 20% is critical. At levels less than this (for chilled and out of service hot loops), rapid biological degradation of either ethylene or propylene glycol to an assortment of organic acids and intermediate products, will take place.

Performance Standards

Considering what can happen if a system is not treated to a reasonable standard, closed systems must be treated to give the lowest possible corrosion rate and to control microbiological activity.

Corrosion

Using effective inhibitor packages, it is possible to obtain corrosion rates of less than 0.2 mpy on mild steel and less than 0.1 mpy on copper and copper alloys. With these corrosion rates and schedule 40 piping, a system life of more than 50 years is a realistic expectation.

While the overall, or general corrosion rate is important, a successful program must also control pitting or localized corrosion. In systems where low flows or stagnant conditions can exist for extended periods, protection from localized corrosion is equally important.

The amount of iron and copper present in the system fluid (whether water or water/glycol mixtures) should be quite low. In well maintained systems, it is common to find iron and copper concentrations at or below, 0.2 mg/L and 0.1 mg/L, respectively.

Microbiological

Microbiological activity will vary from zero in an operating hot water circuit to being present in chilled water loops treated with nitrite. In chilled water systems, it is generally agreed that $<10^3$ CFUs/mL or <0.1 ng/mL of ATP are acceptable.

The Future

At a time when the need for new, innovative approaches to treat closed loops appears to be growing, little new technology is coming to the marketplace that can match the performance of 20-year-old technologies.

As restrictions on metal-based and nitrite programs continue to grow, the demand for effective "green" alternatives will expand. Newer chemistries, such as neutralized dibasic acids, phosphonates, triazines, etc., either do not provide the level of protection of traditional programs or are not applicable to a broad range of applications.

At a minimum, treatment programs for the next millennium will need to provide:

- Low environmental impact, with good long-term biodegradability;
- Biological stability (not readily biodegradable) under use conditions;
- Mild steel and copper corrosion rates of less than 0.5 mpy and 0.1 mpy, respectively; and
- Easy testing by plant personnel.

The company that can develop and market a product with this performance profile will be well positioned to capture a low portion of this market.

References

1. Cohen, M., R. Pyke, P. Marier. 1949. *Journal of Electrochemical Society*, 96,332.
2. Cohen, M., A. Beck, and G. Mellors. 1958. *Journal of Electrochemical Society*, 105,332.
3. Lumsden, J., Z. Szklarska-Smialowska. 1978. *Corrosion*, 34(5):169.
4. Kadek, V., L. Lepin. 1972. *Proc. 5th Congress on Metallic Corrosion*, Tokyo, p. 560.
5. Conoby, J., T. Swain. 1967. *Materials Protection and Performance*, 6:55, April.
6. Hollander, O., G. Geiger, W. Ehrhardt. 1982. “A review of non-chromate inhibitors: mechanism and experimental methods.” *Corrosion/82*, paper #226, p. 7.
7. Marshall, A. 1981. *Corrosion* 37(4):214.
8. Wilcox, G.D., D.R. Babe, M.E. Warwick. 1986. “The role of molybdates in corrosion prevention.” *Corrosion Reviews* 6(3):336.
9. Roti, J., K. Saeder. “A comprehensive evaluation of molybdate based cooling water treatment technology.” Cooling Tower Institute, 1988 Annual Meeting, Paper TP-88-03.
10. Stranick, M.A., T.R. Weber. 1983. “Molybdate corrosion inhibition in waters of low oxygen content.” Amax Report, L-312-60.
11. Federal Register. 1988. “Proposed prohibition of hexavalent chromium chemicals in comfort cooling towers.” Part V, 40 CFR, Part 749.
12. Union Carbide Technical Bulletin. “Dilution of ucartherm heat transfer fluid.” UC-38, 2/94-1M.■