

**ELECTROCHEMICAL STUDIES WITH COUPLED MULTIELECTRODE ARRAY SENSORS ON CORROSION INHIBITION OF COPPER AND AFFECTED METALS IN THE PRESENCE OF AMMONIA AND OTHER CORROSIVE IONS IN ZERO LIQUID DISCHARGE COOLING WATER**

Dan Duke  
Water Conservation Technology International, Inc.  
Temecula, CA

Lietai Yang  
Corr Instruments, LLC  
San Antonio, TX

**ABSTRACT**

Studies were performed with coupled multielectrode array sensors (CMAS) to establish the corrosion inhibition performance of azoles corrosion inhibitors for copper and metals normally corroded by the presence of ammonia. The studies were conducted with water at high pH and high total dissolved solids (TDS) that result from the operation of an evaporative cooling tower system at zero liquid discharge (ZLD). The study compares the effect of tolytriazole treated versus untreated water with chemistry at pH 10, low hardness (<100 mg/L as CaCO<sub>3</sub>) and TDS of 150,000 mg/L along with the presence of silica corrosion inhibitor generated from source water.

Laboratory test results are compared with field test results in a comparably treated ZLD system where “reclaim” water which contains significant residuals of ammonia is used for makeup to a cooling system with copper tube exchangers.

**Keywords:** Electrochemical studies, copper corrosion, zinc corrosion, CMAS probes, multielectrode sensor, array sensor, corrosion sensor, ammonia, zero liquid discharge, ZLD, high pH, high TDS, low hardness, azoles inhibitor, tolytriazole, corrosion inhibition, cooling tower.

Copyright

©2008 by NACE International. Requests for permission to publish this manuscript in any form, in part or in whole must be in writing to NACE International, Copyright Division, 1440 South creek Drive, Houston, Texas 777084. The material presented and the views expressed in this paper are solely those of the author(s) and are not necessarily endorsed by the Association. Printed in the U.S.A.

## INTRODUCTION

Most end users are reluctant to try new technologies in their full scale operations fearing failure and disruptions of operations. This concern can be overcome if sufficient confidence can be gained from bench or pilot scale investigations. In pursuing the development of silica-azoles chemistry in potential ammonia containing water systems as described in this paper, the authors have demonstrated that by using the corrosion evaluation techniques described the performance at the pilot level matches and reliably predicts corrosion inhibition performance in field system operations.

Even with the research and evaluation techniques provided in advance to predict performance outcome, the end user must be motivated to accept some risks to their operation when undertaking verification of new water reuse and conservation approaches. Such motivation and commitment by the facilities management at this automotive industry leader permitted this report. Most would choose to avoid the risk of preparing for future challenges in water supply and source quality. Leadership by this facility will encourage others in the community to follow their success, and contribute to our collective future in water conservation. Use of reclaim water is one of many areas of innovation and conservation undertaken by this facility toward attainment of "Gold" Green Building Association status.

As more commercial and industrial facilities move to zero liquid discharge (ZLD) and use of reclaim or other waste water reuse sources to conserve water, they will be faced with increased corrosion from higher total dissolved solids (TDS) and ammonia that is corrosion aggressive to copper, copper alloys and other affected metals. They will also face significantly increased biological growth and fouling potentials with use of reclaim or other waste waters containing contaminants such as ammonia, phosphate and organics that enhance biological activity.

Municipal reclaim water typically contains high levels of ammonia as a result of incomplete removal of this byproduct of human waste in the treatment process. Reclaim water also contains residuals of phosphate from soaps and detergents, residual organic contaminants, as well as increased TDS residuals. Chemical treatment of cooling tower waters that contain ammonia, organics and phosphates is challenging and expensive, as it requires significant increases in the quantities of traditional inhibitors and biocides used to control corrosion and bio-fouling. Such water quality also generally requires increased blowdown water wastage to avoid scale limitations. These traditional water treatment issues have reportedly been the major limitation and resistance to increasing use of reclaim water in evaporative cooling applications.

Over the past five years, cooling tower systems have been operated at ZLD with TDS levels between 10,000 and 200,000 mg/L using potable makeup sources and the silica chemistry process discussed in this paper without scale, corrosion or biological fouling problems<sup>(1-3)</sup>. Establishing the ability to use reclaim or wastewater quality sources with comparable results using the silica chemistry process with ZLD will further expand water conservation alternatives. Therefore, establishing the viability of silica-azoles chemistry for application in ZLD / high TDS water containing ammonia becomes very relevant for the industry.

The objective of this paper is to answer the following two questions:

- Can silica-azoles chemistry prevent corrosion of copper by ammonia in high TDS waters
- Can silica-azoles chemistry prevent corrosion of multiple system metals in the presence of organics and high TDS contributed by use of "reclaim" water as makeup

## Background Information

Corrosion attack of copper by ammonia in water is well known in the water treatment industry, and presents a particular challenge to reuse of wastewater sources that contain ammonia in cooling water systems that use copper and other metal alloys which are vulnerable to ammonia. Ammonia and ammonium ion are reported to exist in equilibrium as both the ammonium ion and ammonia gas in the pH 7 to 11 range. The equilibrium shifts toward increased ammonium ion concentration as pH approaches 7 and to increased ammonia gas concentration as pH approaches 11. Ammonia gas can then be volatilized from water by heat, pH elevation and circulation over a cooling tower, typical of commercial ammonia stripper design. With cooling water pH control at greater than pH 9, total ammonia/ammonium ion residuals will be reduced to lower ranges by such tower stripping. Dilute aqueous concentrations of ammonia or ammonium ion (less than 200 mg/L as  $\text{NH}_4^+$ ) are easily measured by test procedures which convert and measure the total residual as ammonium ion.

Relative to seawater (high TDS), as reported by Tuthill <sup>(4)</sup>, the corrosion resistance of copper nickel alloys depends upon formation of a protective film. Such film formation is referred to sometimes as "passivation". Film formation is affected by pH, time, aeration, velocity, temperature, pollution and other factors. Copper will generally form either a cuprous oxide film,  $\text{Cu}_2\text{O}$ , or a cupric oxide,  $\text{CuO}$ , film depending on water chemistry conditions. Temperature also has a major influence on the rate of film formation. At higher temperatures the film forms and matures faster. At lower temperatures, the film forms and matures more slowly.

Another major factor influencing film formation is pH. Tuthill references studies that reported on film formation for UNS C70600, C71500 and C68700 copper alloys in seawater which found no film formation below pH 6. The unfiled corrosion rates were high, of the order of 35 mpy (0.89 mm/yr). At higher pH, corrosion rates for these metals were reported to be lower and normal for seawater. Tuthill reported corrosion rates for these three copper tubing alloys in seawater systems, depending on chlorination practices, varied from less than 1 mpy to 3.2 mpy (0.025 to 0.08 mm/yr). Corrosion behavior in fresh, brackish and higher salinity waters is similar to performance in seawater.

Tuthill also reports that ammonia is sometimes encountered in the seawater feed to desalination plants. In the presence of air and ammonia, aluminum brass is subject to stress corrosion cracking. Aluminum bronze is more resistant, while copper nickel alloys are highly resistant to ammonia stress corrosion cracking. Ammonia also tends to increase the general corrosion rates of copper alloys. Copper nickel alloys have been reported to be three orders of magnitude more resistant than aluminum brass.

Adkinson <sup>(5)</sup> reported that the surface activity of copper is controlled by use of azoles inhibitors such as benzotriazole (BTA), as follows: Cuprous oxide is normally a protective surface for copper, but is readily attacked by  $\text{Cl}^-$ ,  $\text{SH}^-$ ,  $\text{OH}^-$ ,  $\text{NH}_4^+$  and to a lesser extent  $\text{CO}_2$ .

BTA and other azoles can affect the properties of cuprous oxide films by stabilizing the film. The copper oxide-BTA layer interferes with the anodic and/or cathodic reactions of the corrosion process. Copper oxide-BTA films will form in an acidic or neutral solution, and the type of film formed is dependent on the pH of the BTA solution. At pH values of 3.5 to 4, thick, shag-carpet like films are formed, while at pH greater than 4, thin, compact, highly protective films are formed. Copper in NaHCO<sub>3</sub> solution (pH = 8.1) at 25° C yields a corrosion potential of +0.12 V versus the standard hydrogen electrode (SHE). As found in a Pourbaix<sup>(6)</sup> diagram for copper, the stable form of copper under these conditions is Cu<sub>2</sub>O. In fact, Adkinson found that an alkaline pretreatment of copper in NaHCO<sub>3</sub> solution prior to BTA application yields a significantly more corrosion-resistant Cu<sub>2</sub>O-BTA layer than if no pretreatment is used, as measured using potentiodynamic scans in 3000 mg/L NaCl to calculate corrosion rates.

Metikos-Hukovic<sup>(7)</sup> reported that corrosion inhibition of copper by BTA inhibitor provided rapid film formation and was increasingly effective at higher pH (pH = 10) in evaluations from pH 4 to pH 10 range. Increased BTA concentration also improves corrosion inhibition, but such improvement is time and concentration dependent at acidic or neutral pH less than 9.-

Nitrogen-containing compounds, such as benzotriazoles (BTA), are commonly used as antioxidants and corrosion inhibitors for copper and copper alloys in many environments and applications. The lone electron pairs on the nitrogen atom will coordinate with the metal substrate and will result in a direct attach in the case of cyanate esters, and a parallel attach in the case of triazines, isocyanurates, and blocked isocyanates by physical absorption. The lone electron pairs of the nitrogen atom further facilitates the coordination of the nitrogen atoms to the Cu substrates in the event any oxidation occurs to form Cu<sup>+</sup> or Cu<sup>2+</sup> ions or oxides. Such nitrogen containing inhibitors are referred to as azoles in the water treatment industry, and include the commonly applied tolytriazole (TTA), BTA, and variations of chemical structure that produce comparable inhibiting films on metal surfaces.

Further to the previously noted findings by Adkinson and Metikos-Hukovic, we have determined that application of azoles in evaporative cooling water, where pH is desirably controlled at or greater than 9, contributes to more rapid and highly protective film formation to protect copper and other affected metals from corrosion by ammonia as well as high concentrations of corrosive ions in high TDS / high pH / low hardness cooling water that results from evaporative concentration of makeup water that is pretreatment softened from potable, well or reclaimed waste water sources.

## **Silica-azoles Chemistry**

The silica corrosion inhibitor chemistry discussed in this paper was presented in previous publications<sup>(1-3)</sup>. The chemistry has proven to be exceptionally effective in inhibiting corrosion of all metals commonly used in evaporative cooling water systems. However, ammonia is not typically contained in potable or well makeup water sources generally used for cooling towers. Ammonia is particularly corrosive to copper and copper alloys, as well as other metals less typically used in cooling systems. Testing of silica inhibited water after addition of ammonia confirmed that copper is not well protected from ammonia by silica alone, and became the basis for the studies presented in this paper. Since application of silica chemistry has permitted operation at high TDS to conserve water, and scale free operation with ZLD, our objective was to evaluate the high TDS / high pH / soft water conditions used with application of silica chemistry to establish an effective supplement for inhibition of corrosion of copper by

ammonia.

Recent U.S. patents <sup>(3)</sup> disclose methods for controlling silica and silicate fouling problems while concurrently controlling the corrosion of system metallurgy in evaporative cooling systems with high concentrations of dissolved solids (high ionic strength). The corrosiveness of various source waters is generally a function of the concentration of corrosive ions (such as chloride and sulfate) and electrolytic (or ionic) strength that are concentrated in evaporative systems that cool heat transfer surfaces. Accordingly, varying source water quality will impact system corrosion, and determines the required level of protection needed from a corrosion inhibiting mechanism.

Silica chemistry can be applied to provide significantly greater corrosion protection for system metals that encounter very high concentrations of corrosive ions or electrolytic strength. Since this technology permits cooling system operation at much greater concentrations of corrosive ions (high TDS) without consequence of corrosion to system metals, significant water conservation benefit is provided for both the applicant and water resource sustainability. Field testing and laboratory studies have confirmed that silica chemistry can prevent corrosion of mild steel, copper, stainless steel, aluminum, zinc, galvanized steel and various alloys of such metals in the presence of high evaporative concentrations of corrosive ions in the source water when approaching ZLD operation <sup>(1)</sup>.

Prior traditional chemical treatment methods have not enabled pursuit of water conservation at such high TDS / ZLD concentration levels, due to ineffective corrosion protection or prohibitive cost of pretreatment and inhibitor application. The cost for pretreatment removal of multivalent metal ions (hardness) with methods such as ion exchange is much lower (typically from \$0.07 to \$0.15 per 1000 gallons makeup) than the cost of using additional makeup water required for blow down wastage, or use of cooling tower blowdown recycle water recovery methods.

However, silica chemistry alone is not effective in eliminating corrosive attack of copper by ammonia, as is true with traditional corrosion inhibitors that do not include additional specific copper inhibitors. No historical inhibitor performance data existed for application of azoles chemistry used for copper corrosion inhibition in ZLD cooling system water where tower chemistry operates with a combination of high pH (9 to 10 pH), high TDS (10,000 to 150,000 mg/L TDS) and low total hardness (< 100 mg/L) in the cooling tower water chemistry.

Specifics of inhibitor mechanisms and film formation chemistry are not addressed in this discussion. For those who may wish to investigate further, a number of references from prior reports are provided <sup>(8-12)</sup>. It is believed that establishing and controlling saturated soluble silica residuals in equilibrium with amorphous silica promotes formation of a non porous silica surface barrier on all polyvalent metal surfaces. The references noted above support the probable silica polymerization and surface chemistry behavior (film formation) of related silica applications believed to function in this method of silica corrosion inhibition. The mechanisms by which azoles inhibit metal surfaces are well described by many prior publications and some referenced in this paper, although not at the water chemistry conditions evaluated by these studies. However, these studies demonstrate a higher level of effectiveness and efficiency for copper inhibition with azoles when applied in combination with the silica inhibition chemistry method control conditions.

## EXPERIMENTAL PROCEDURES

### Laboratory Studies

The study was conducted with cooling water taken from a system that has operated with zero liquid discharge for two years while treated with the silica inhibitor method. Analysis of the study water sample (Table I) determined the key chemical parameters were approximately 150,000 TDS, pH 10, total hardness of 100 mg/L as CaCO<sub>3</sub> and 1250 mg/L silica (soluble SiO<sub>2</sub>). Non inhibited control testing was conducted with simulated ZLD water (15% wt sodium chloride, or approximately 150,000 TDS solution) with adjustment to pH 10. Temperature of test waters were controlled at room temperature and aerated.

**Coupled Multielectrode Array Sensor Tests.** Coupled multielectrode array sensors (CMAS)<sup>(12)</sup> were used to measure the maximum localized corrosion rates of copper (CDA 110-UNS C11000), aluminum (Type 1100, UNS A91100), and pure zinc. Baseline testing was conducted with and without ammonia in both non TTA inhibited ZLD silica sample (15% TDS) and pH 10 adjusted uninhibited sodium chloride salt water (15% TDS) control. Azoles inhibitor (TTA) was applied in the silica-inhibited ZLD solution in the performance evaluation testing prior to addition of ammonia. Ammonia was added at dosages from 125 to 375 mg/L to establish sufficient concentration to result in corrosive impact to affected metals.

In a CMAS probe, there are multiple miniature electrodes made of materials identical to the component of interest. Statistically, some of the electrodes have the properties that are close to the anodic sites and others have the properties that are close to the cathodic sites of the corroding metal. The resulting electrical currents are measured. The maximum localized corrosion rate is calculated using the current from the most anodic electrode in the array<sup>(13)</sup>. The multielectrode array sensor probes were made of 1-mm diameter wires of these metals and each has 16 electrodes. During the study, these probes were immersed in the test solutions and connected to a nanoCorr A-50<sup>\*</sup> multielectrode corrosion analyzer.

**Verification Test with Metal Loss Method.** To confirm the corrosion rate measured with the CMAS probe, copper 110 specimens of known surface area (3 inch long by 0.5 inch wide) were immersed in a glass container filled with 200 ml the silica inhibited test solution in the presence of ammonia with and without the addition of azoles. The glass container was capped to prevent loss of dissolved gasses. The test solution was measured for copper residual after 48 hours, using a Hach Colorimeter and test Method 8506 to evaluate the metal loss. This step also provided time for a silica inhibition film to form on the copper coupon. Ammonium hydroxide was measured by ASTM D 1426-98, Ammonia Nitrogen in water, Test Method A. ALPHA Standard Methods, 18th ed., pp 4-78, Method 4500-NH<sub>3</sub> C (1992).

## RESULTS AND DISCUSSIONS

### Laboratory Results from Coupled Multielectrode Array Sensors

The effect of ammonia on the measured maximum localized corrosion rates for copper, zinc and aluminum in silica-treated tower water without the presence of TTA is shown in Figure I.

---

\* Trade name of Corr Instruments, LLC, San Antonio, Texas, USA

Figure II shows the effect of pH and ammonia on the maximum localized corrosion rates for copper and zinc in a pure sodium chloride salt solution (15% NaCl) without the presence of TTA. Figure III shows the effects of ammonia on the maximum localized corrosion rates for copper, zinc and aluminum in the silica-treated tower water with the presence of TTA inhibitor. The effects of ammonia on the different metals are discussed as follows:

**Copper.** The maximum localized corrosion rate for copper in the uninhibited pure sodium chloride salt solution (non TTA treated) was 2.0 to 3.0 mpy (0.05 to 0.075 mm/yr) in the presence of ammonia in Figure II, and 1.0 to 2.0 mpy (0.025 to 0.05 mm/yr) in the silica-treated ZLD tower water (no TTA) in the presence of ammonia in Figure I. The maximum localized corrosion rate for copper was approximately 0.5 mpy (0.013 mm/yr) in both non TTA inhibited test solutions prior to ammonia addition, which reflects the corrosive effect of high TDS (150,000 mg/L) salts for copper. In contrast, Figure III shows the exceptionally inhibitive effect of the TTA in the silica-treated ZLD tower water for localized corrosion of copper in the presence of ammonia, with virtually no localized corrosion (approximately 0.01 mpy (0.254  $\mu\text{m}/\text{yr}$ )). The electrodes after the tests with and without the presence of TTA were visually examined and in both cases, the electrode surfaces were shiny. This is expected because the corrosion rate even without the presence of TTA [1 to 3 mil (0.025 to 0.075)] would not produce significant metal loss during the short test period.

The maximum localized corrosion rate of copper increased from 0.5 mpy (0.012 mm/yr) to about 1 mpy (0.025 mm/yr) when the pH of the pure sodium chloride solution was changed from 8.15 to 10.75 in Figure II. However, this increase appeared to be temporary and the pH started to decrease shortly after the initial increase.

**Zinc.** The maximum localized corrosion rate in the presence of ammonia was 80 mpy (2 mm/yr) for zinc in the uninhibited pH 10 pure salt solution (non TTA Treated) in Figure II, and 0.05 to 0.10 mpy (1.25 to 2.5  $\mu\text{m}/\text{yr}$ ) in the silica-treated ZLD tower water (non TTA treated) in Figure I, indicating that the corrosion of zinc was well inhibited by silica. Prior to the addition of ammonia, the maximum localized corrosion rate for zinc was approximately 30 to 40 mpy (0.75 to 1 mm/yr) at pH 8.15 in the uninhibited pure salt solution (non TTA treated) in Figure II, reflecting the corrosive effect of high TDS (150,000 mg/L) salts and high alkalinity (pH) on zinc. Zinc was also well inhibited by silica in the silica-treated ZLD tower water (non TTA Treated) prior to the ammonia addition in Figure I. The maximum localized corrosion rate for zinc in the TTA and silica treated ZLD tower water in the presence of ammonia varied from 0.10 to 0.30 mpy (2.5 to 7.5  $\mu\text{m}/\text{yr}$ ) in Figure III. This corrosion rate is not significantly different from the corrosion rate obtained without TTA in the silica-treated ZLD tower water, thus the CMAS test results do not indicate an additional inhibitive effect on zinc by TTA in the presence of both silica and ammonia.

**Aluminum.** Both Figures I and III show that aluminum was unaffected by the presence of ammonia, and is exceptionally well inhibited by silica at corrosion rates in the 0.01 to 0.02 mpy (0.25 to 0.5  $\mu\text{m}/\text{yr}$ ) range in the silica-treated ZLD tower water. TTA provides no further corrosion inhibitive effect.

The control studies with simulated uninhibited 150,000 TDS (15% sodium chloride) as shown in Figure II showed that the maximum localized corrosion rates were from 30 to 80 mpy (0.75 to 2 mm/yr) for zinc and 0.5 to 3.0 mpy (0.013 to 0.075 mm/yr) for copper in the combined presence of high TDS and / or ammonia. These tests were conducted at room temperature to

avert volatilizing ammonia at higher temperature and the high pH used to simulate the ZLD water chemistry conditions. The study was intentionally designed for exposure of metals to abnormally high levels of ammonia. Corrosion rates for both zinc and copper would be expected to increase significantly with higher operating temperatures, as has been noted in prior CMAS studies<sup>(5)</sup> on copper corrosion in particular. Considerable historical data and experience with copper corrosion in the presence of ammonia exists for both low TDS as well as high TDS (seawater) water chemistry. Some examples are cited in the discussion of historical field corrosion data for copper under field studies.

### **Laboratory Results from Metal Loss Studies**

The inhibiting effect of TTA on copper in high TDS water was confirmed by separate laboratory testing and chemical analysis by exposing copper metal in silica-treated zero liquid discharge (ZLD) tower water samples, with and without TTA in the presence of ammonia. The ZLD water sample was from a cooling tower system operating with water chemistry residuals of 83,000 mg/L TDS, pH 10.1, 70 mg/L total hardness (as CaCO<sub>3</sub>), 490 mg/L soluble silica (as SiO<sub>2</sub>), and 0.7 mg/L copper. Table II shows the changes of the copper concentrations in the ZLD tower water sample before and after the 48 hours at respective test conditions. Soluble copper concentration increased from 0.7 to 40 mg/L as copper in the uninhibited test solution. There was no increase in soluble copper in the TTA inhibited test solution.

The corrosion rate was calculated, assuming all the copper increase in the solution was due to the corrosion of the copper specimen. The calculated corrosion rate in Table II was 2.5 mpy (0.064 mm/yr) without the addition of TTA, and essentially zero (below the detection limit) with the addition of TTA, indicating that TTA is an excellent inhibitor for copper in the silica-treated ZLD tower water. The corrosion rate obtained from the metal loss method (2.5 mpy) without the addition of TTA is close to the maximum localized corrosion rate measured using the CMAS probe in Figure I at comparable chemistry conditions. Because Figure II shows the maximum localized corrosion rate, the closeness between the maximum localized corrosion rate and the general corrosion rate (the rate from the metal loss method) indicates that the corrosion of copper in the presence of ammonia in the silica-treated ZLD tower water is mainly general corrosion. This is consistent with the results from the field studies.

### **Field Studies**

Analytical tests were performed on samples from a cooling tower system serving central chiller and adsorption machines at a corporate automotive facility using softened reclaim water (California Title 22) as makeup for a ZLD / silica inhibited treatment approach. The system was started up with ZLD-silica treatment with softened potable water to establish the expected performance with comparable applications in the Southern California area, and comparable excellent corrosion inhibition results were quickly attained. An existing side stream (5% of circulation) sand filter for the cooling tower system water continued with normal operation, with no notable change in backwash frequency. The facility makeup water use volume reduction was approximately 25% with ZLD operation. The overall makeup water use cost reduction was approximately 53% of the previous chemical treatment operation due to the combination of volume use reduction and lower cost rate for reclaim water (30% less than potable water cost). Traditional chemical treatment of reclaim water was projected to increase chemical program cost by 500% over potable water chemical treatment.



Monthly and annual average historical reclaim water quality parameters were provided by the West Basin Municipal Water District for the water supplied with specified California Title 22 water standards. Based on the water quality information provided, pretreatment multimedia filtration was designed in addition to the pretreatment softening systems to meet the peak operating load evaporative makeup demand for the cooling towers. Pretreatment filtration was required due to an average of 3 mg/L total suspended solids (TSS) in the reclaim water. TSS would foul the ion exchange softening process and also potentially foul heat transfer surfaces in the cooling system at higher concentrations attained with ZLD operation. The pretreatment equipment produced quality was thus designed to facilitate conversion of source water silica to a general corrosion inhibitor, which combined with supplemental addition of TTA (azoles) corrosion inhibition chemistry, would demonstrate efficacy in inhibiting corrosion of copper by ammonia contained in the reclaim water.

Samples of filtered and softened reclaim makeup water and the treated ZLD cooling tower system water are compared in Table III for chemical concentration (COC) of makeup water chemistry. Corrosion rate studies were conducted using linear polarization probes with copper and carbon steel tips, with results shown in Table IV. Testing was also conducted using weight loss on test coupon specimens via ASTM Standards G4-01 "Standard Guide for Conducting Corrosion Tests in Field Applications" and G1-03 "Standard Practice for Preparing, Cleaning, and Evaluating Corrosion Test Specimens". Results from coupon weight loss for copper and steel are also shown in Table IV.

## Field Results

Water Analyses. The analyses of cooling tower and reclaim makeup water chemistries illustrated in Table III show the effectiveness of the method in maintaining solubility of the principle ions (sodium, chloride, alkalinity, sulfate, TDS) in the softened makeup water, and higher levels of soluble silica in the cooling tower water. All the soluble silica in the makeup does not concentrate in the tower water since the majority of the silica is polymerized to polysilicates which are not detected by the soluble silica test (acid molybdate procedure). Some of the excess silica may be precipitated as non-adherent amorphous silica material due to adsorption on dust and solids scrubbed from the air by the cooling tower, which accumulate with normally experienced buildup in the tower basin if not removed by side stream filtration. System heat exchange surfaces inspected in two chillers were free of silica or other deposits.

The test results show the presence of TTA fed to the tower water (high residual from small quantity fed only once per month, due to absence of blowdown losses). Depletion of the TTA residual occurs over time due to adsorption on air scrubbed suspended solids and molecular breakdown. The test results also show that makeup ammonia residuals (34 mg/L) do not cycle in the tower water, and are controlled at less than 1.0 mg/L by the tower chemistry process that converts ammonium ion to the soluble ammonia gas due to the resulting concentrated makeup carbonate alkalinity and elevated pH. The soluble gas is stripped from the water as it is circulated over the cooling tower for heat rejection. The other chemistry of importance is the total phosphate residual of 0.6 mg/L as  $\text{PO}_4$  in the reclaim soft makeup versus 16 mg/L in the tower water, which indicates that  $\text{Ca PO}_4$  solubility is maintained at the high pH (9.8) due to the combination of low calcium residual controlled in the tower water and the increased solubility effect of high concentrations of high solubility ions (uncommon ions) on the lower solubility polyvalent metal salts at high TDS concentrations. Ortho phosphate residuals approaching 100 mg/L have been maintained in other ZLD systems operating at pH 10 with calcium levels

at 70 mg/L as CaCO<sub>3</sub> as illustrated in Table I. The lower concentrations of polyvalent metals in the filtered tower water samples in Table I also indicate that polyvalent metal ions or salts are likely adsorbed on stable colloids of silica in the tower water that were removed by the filtration step prior to analysis.

**Biological Plate Counts.** Dip stick biological count cultures were used to evaluate biological organism control, and were counted after 24 and 48 hour intervals following inoculation and incubation at tower bulk water temperature. During a one week period, water chemistry conditions were below desired control ranges due to water losses that occurred during installation of two new cooling tower cells. Subsequently, a rapid biological bloom occurred in the cooling tower system while using the nutrient rich reclaim makeup water, and dip stick results were measured at 10<sup>6</sup> cfu. After restoring desired tower water control chemistry (>10,000 mg/L TDS and > 9.6 pH), dip stick cultures have shown no biological count (10<sup>0</sup> cfu) after 48 hour incubation. System heat transfer efficiencies were maintained within expected and historical approach temperatures. Inspection of two chiller bundles showed no scaling, but slight biological fouling following the noted temporary loss of control chemistry.

**Corrosion Rate Measurements.** Data in Table IV illustrate the effectiveness of the method in inhibiting corrosion of mild steel and copper as determined by both linear polarization and coupon weight loss measurements. Excellent general corrosion rates were obtained for copper, and no pitting was observed on copper surfaces. While both carbon steel corrosion rates were low, the coupon showed slight differential cell corrosion under the coupon mount. The carbon steel rates were slightly higher than normally experienced with silica inhibitor chemistry, primarily due to less than optimum silica residuals during the test period. Equipment and exchanger tube surface inspections have confirmed excellent corrosion protection. Comparable corrosion rates for mild steel in this water quality with previous traditional chemical treatment methods were optimally in the range of 2 to 4 mpy for carbon steel.

**Historical Field Corrosion Data.** Copper and copper alloy corrosion rate data from several sources identify both ammonia and high TDS contribute to significant corrosion of copper. The data referenced in Table V shows copper corrosion of 14 mpy in the presence of 0.8% ammonia at 104° F, presumably in relative low TDS water. The relatively higher corrosion rates given for copper and copper alloys in this study would be expected at the elevated temperature and ammonia concentrations.

High TDS and high alkalinity have been established as a major contributor to corrosion of aluminum and zinc metals, as both metals are subject to excessive corrosion as pH increases above 9.0, particularly with high TDS / high sodium carbonate alkalinity concentrations in the water. This vulnerability of aluminum and zinc to corrosion at high pH / high TDS is reflected in the CMAS study data previously discussed. Since ZLD operation of cooling towers produce high concentrations of TDS, sodium carbonate alkalinity and pH above 9.0, these contributing factors to corrosion of these metals in the presence of ammonia need to be evaluated for collective impact on inhibition effectiveness as zinc and aluminum may be alloyed with copper in various metal structures that comes into contact with water in cooling tower systems, such as the 70:30 copper-zinc alloy corrosion data presented in Table VI. The CMAS data in this study confirms prior corrosion inhibition studies that show silica provides excellent inhibition of aluminum and zinc in high pH / high TDS water, and the presence of ammonia has no additional impact on the ability of silica alone to inhibit their corrosion. So the primary need

was to establish an effective supplemental inhibitor for copper in the presence of ammonia to inhibit corrosion of copper. Additional studies with alloys of copper, particularly under stressed conditions will be required to predict inhibition effectiveness, and control of stress related corrosion mechanisms, for the less commonly used applications of alloys of copper in some cooling tower systems.

**Galvanized Coupon Study.** Field studies with galvanized steel surfaces in ZLD / high TDS / low hardness / silica cooling water has shown inhibitive effects on galvanized coated steel test coupons by the addition of TTA. This may reflect different corrosion behavior for galvanized surface materials, which are primarily composed of zinc, but are not equivalent to the pure zinc metal used in the CMAS study. The results from field testing were provided by the following study in a ZLD-silica treated system operating at 50,000 TDS.

The first exposed galvanized coated carbon steel test coupon #283 was installed for 60 days exposure to the ZLD cooling system water. The exposed galvanized surface (coupon #283) experienced localized corrosion (pitting), as compared to the unexposed #282 control coupon. Removal of the galvanized coating (acid striped) shows the exposed #283 coupon experienced localized corrosion (pitting) that extended through the galvanized coating, with penetration to the carbon steel subsurface (see Figure IV).

The second exposed galvanized coated carbon steel coupon #234 was installed for 60 days after addition of 100 mg/L of tolytriazole (as TTA), as measured by Hach test procedure 730, to the same ZLD cooling system water. The galvanized surface of #234 test coupon did not experience localized corrosion (pitting) with TTA treated ZLD / high pH / high TDS / low hardness cooling water (see Figure V).

It is also well known in prior water treatment art that galvanized coated steel metal surfaces contacting circulating cooling water should only be exposed to pH maintained in the 6.0 to 8.0 range in the cooling water during start up conditioning to passivate the galvanized surface from white rust and corrosion, and the cooling water chemistry control should not be allowed to exceed pH 9.0 during routine cooling tower operation as reported by Reganni<sup>(15)</sup>. The manufacturers of cooling towers using galvanized surface materials specify control within such water chemistry pH control parameters to warranty the equipment. Even with use of environmentally acceptable prior art corrosion inhibitors, including azoles inhibitors, galvanized surfaces were corroded at pH outside this range.

This study demonstrates that galvanized surfaces can be protected from general and localized corrosion at pH above 9 in evaporative cooling water with addition of azoles at sufficient concentration when applied in combination with amorphous silica inhibitor methods recently being applied to protect carbon steel and other metals at high TDS and high pH water chemistry conditions resulting from reduced blow down or ZLD water conservation programs. Observation of galvanized coating surfaces treated only with the silica inhibitor method chemistry indicated significantly improved general (cathodic) corrosion inhibition, but still experienced localized (anodic) corrosion typical of the sacrificial multi-metal galvanized coating. Azoles are reported to function by forming inhibiting films at anodic corrosion sites to protect metal oxide films, but may also form inhibiting films in synergy with concurrently applied inhibitor films such as those formed by amorphous silica inhibitor. It is believed that the synergy of this combination of operating chemistry inhibits both anodic and cathodic corrosion in the presence of high TDS, high pH and low hardness cooling water. Such supplemental

treatment with azoles is very cost efficient due to very low loss of the azoles with ZLD-silica treatment operation.

## **SUMMARY & CONCLUSIONS**

The effect of silica-azoles (TTA) treatment on the corrosion of copper, zinc and aluminum in zero discharge water solutions water containing high dissolved solids and ammonia were evaluated with coupled multielectrode array sensor probes (CMAS) and weight loss method in the laboratory. Field data was also obtained from a cooling tower using ammonia containing (reclaim) makeup water and compared to the experimental study data to verify predicted corrosion inhibition performance.

General corrosion inhibition performance was excellent for copper, aluminum, and zinc with the combination of silica inhibitor and TTA chemistry in the presence of ammonia in the laboratory evaluation, and the field test results with this inhibitor chemistry verified the inhibitor protection predicted by laboratory test results. The CMAS measurements indicate that silica inhibitor rapidly reduced localized corrosion rates for aluminum and zinc, and the corrosion of copper was very effectively controlled in the presence of ammonia by the addition of supplemental TTA inhibitor. The corrosion rate for copper that was determined using quantitative copper residuals from laboratory test solutions based on metal surface area weight loss also confirmed corrosion rates measured with the CMAS method and indicates that general corrosion was the major mode of attack on copper in the solution containing ammonia.

No studies were conducted with alloys of copper or metals under physically stressed conditions that would determine that related stress corrosion would be controlled by the inhibitor chemistry evaluated. Further studies need to be conducted in this area with appropriate stressed metal test evaluation methods. Separate field studies in a ZLD treated system demonstrated that use of azoles with silica chemistry provide additional localized corrosion protection of galvanized metal surfaces.

The field application using reclaim water verified that excellent biological and fouling control was provided by attainment of naturally biostatic chemistry as has demonstrated during the previous four years of field applications with ZLD-silica chemistry in various cooling tower systems using potable makeup water sources. Effective biostatic control of bio-growth and bio-film deposition thus permits effective metal surface contact and protection with the inhibitor chemistries, and minimizes potential for under deposit corrosion attack.

## **ACKNOWLEDGEMENTS**

The authors would like to express their appreciation for the support of this automotive facility and management in undertaking use of reclaim water and application of this innovative water conservation technology for cooling tower treatment. We also appreciate the water quality information and input provided by West Basin Municipal Water District during this project implementation.

## REFERENCES

1. Duke, D. & Yang, L., Laboratory and Field Studies of Localized and General Corrosion Inhibiting Behaviors of Silica in Zero Liquid Discharge (High TDS Cooling Water) Using Real Time Corrosion Monitoring Techniques, NACE paper # 07626, (2007).
2. Duke, D. & Reed, J., "Zero Liquid Discharge (ZLD) Cooling Tower Treatment at CSI", AIST 2007.
3. Duke, D. et al, U.S. Patents 6,929,749; 6,940,193; 6,998,092; and 7,122,148.
4. Tuthill et al. in *Experience with Copper Alloy Tubing, Waterboxes and Piping in MSF Desalination Plants*, IDA World Congress on Desalination and Water Reuse, Volume I, Sessions 1 to 3, October 1997, Madrid, Spain.
5. Adkinson et al, *Cathodic Delamination of Methyl Methacrylate-Based Dry Film Polymers on Copper*, IBM Jour. Res. Develop., Vol. 29, No. 1, January 1985, p.29.
6. *Atlas of Electrochemical Equilibria in Aqueous Solutions*, 2<sup>nd</sup> Ed., National Association of Corrosion Engineers, Houston, TX, 1974.
7. Metikos-Hukovic et al, *Copper Corrosion At Various pH Values with and without Inhibitor*, Journal of Applied Electrochemistry, 30: 617-624, 2000.
8. Iler, R K, *The Chemistry of Silica*, 1979 Wiley, pp. 4-6, 10-15, 22-23, 30-31, 40-43, 46-51, 54-55, 74-75, 82-89, 92-93, 116-117, 124-145, 160-163, 174-177, 188-189, 194-197, 204-205, 212-215, 218-219, 312-317, 324-325, 354-361, 366-369, 374-377, 554-559.
9. Incopini, G A, Kinetics of Silica Oligomerization and Nanocolloid Formation as a Function of pH and Ionic Strength at 25° C, Penn State U., Dept of Geosciences, pub. *Geochimica Et Cosmochimica ACTA*, Vol. 69, No. 2, pp. 293-303 (2005).
10. Barr, T, U. Wisconsin-Milwaukee, Modification and Characterization of Mineralization Surface Corrosion Protection, ([www.elisha.com/docs/CorrosionProtection.pdf](http://www.elisha.com/docs/CorrosionProtection.pdf), Jan 06 dl).
11. Mauritz, K, Sol Gel Chemistry, U. Southern Mississippi, School of Polymers, ([www.psrc.usm.edu/mauritz/solgel.html](http://www.psrc.usm.edu/mauritz/solgel.html), Jan 2006 dl).
12. Stumm, W, Formation of Polysilicates as Determined by Coagulation Effects, *Environmental Science and Technology*, Vol.1, 221-227, 1967.
13. Yang, L. and N. Sridhar, "Coupled Multielectrode Array Systems and Sensors for Real-Time Corrosion Monitoring - A Review", CORROSION/2006, paper no. 06681 (Houston, TX: NACE, 2006).
14. Sun, X. and L. Yang, "Real-Time Monitoring of Localized and General Corrosion Rates in Simulated Marine Environments Using Coupled Multielectrode Array Sensors", CORROSION/2006, paper no. 06284 (Houston, TX: NACE, 2006).
15. Reggiani, *White Rust: an Industry Update and Guide*, Association of Water Technologies, 2002, p. 6 Table1.

Table I - ZLD Cooling Tower

ZLD Tower / Soft Makeup Water COC (Concentration of Chemistry) Ratios				
Sample / Tests	Tower	Tower/ Filtered	Soft MU	COC
TDS, mg/L (NaCl Myron L 6P)	153,000	153,000	255	600
pH	10.05	10.05	7.58	NA
Copper, mg/L Cu	0.8	0.26	0.0015	NA
Iron, mg/L Fe	21	ND	ND	
Zinc, mg/L Zn	4.0	ND	ND	
Silica, mg/L SiO <sub>2</sub>	1250	1250	30	42
Calcium, mg/L CaCO <sub>3</sub>	68	17	<0.1	
Magnesium, mg/L CaCO <sub>3</sub>	29	14	<0.1	
Phosphate, mg/L PO <sub>4</sub>	92	-	0.15	613
Nitrate, mg/L NO <sub>3</sub>	2715	2715	4.5	603
Sodium, mg/L Na	152,000	151,000	250	608
Sulfate, mg/L SO <sub>4</sub>	10,750	10,750	18	597
Chloride, mg/L NaCl	23,475	23,475	38	618
Tot. Alkalinity, mg/L CaCO <sub>3</sub>	72,700	72,700	120	606

Table II – Copper Inhibition by TTA in Ammonia

Copper / TTA / Ammonia Corrosion Study Results				
	NH <sub>4</sub> <sup>+</sup> , mg/L	TTA, mg/L	Cu, mg/L	CR, mpy
Sample # 1	0	0	0.7	2.5
Beginning	300	0	0.7	
After 48 hours	300	0	40	
Sample # 2	0	0	0.7	0.0
Beginning	300	200	0.7	
After 48 hours	300	200	0.7	

Table III – ZLD Cooling Tower with Reclaim Water Makeup

ZLD Tower / Soft Reclaim Makeup Water COC (Concentration of Chemistry) Ratios			
Sample / Tests	Tower	Soft MU	COC
TDS, mg/L (NaCl Myron L 6P)	30,000	1100	27
Ph	9.8	7.1	NA
Silica, mg/L SiO <sub>2</sub>	350	24	15
Calcium, mg/L CaCO <sub>3</sub>	13	0.2	NA
Magnesium, mg/L CaCO <sub>3</sub>	6	0.1	NA
Sulfate, mg/L SO <sub>4</sub>	3300	127	26
Chloride, mg/L NaCl	5800	214	27
Tot. Alkalinity, mg/L CaCO <sub>3</sub>	5300	192	28
Ammonia, mg/L NH <sub>4</sub>	0.5	34	NA
Total Phosphate, mg/L PO <sub>4</sub>	16	0.6	27
TTA, mg/L as tolytriazole	15	NA	NA

Table IV - Cooling Tower (Reclaim Makeup) Corrosion Test Data

Linear Polarization (LP) and Coupon Weight Loss (CWL) Measurements		
Specimen Type	Mild Steel (1008)	Copper (110)
Test location	Tower Return Loop	Tower Return Loop
LP Corrosion Rate (mpy)	< 0.2	< 0.1
CWL Corrosion Rate (mpy)	0.22	< 0.007

Table V - Corrosion Rates of Several Copper Alloys in 0.8% Ammonia at 104° F (40° C)

Alloy	Corrosion rate		
	mdd	mpy	mm/y
Copper	85	14	0.36
Cartridge Brass (70:30 Cu-Zn) 260	49	7	0.2
Gun Metal (88:10:2 Cu-Sn-Zn) 905	30	5	0.1
Copper-manganese alloy (95:5 Cu-Mn)	9	2	0.05

Source: After J.A Radley, J.S. Stanley and G.E. Moss, Corrosion Technology 6:229:1959

Figure I - ZLD / Silica treated Tower Water (without TTA)  
Ammonia impact on Copper, Zinc and Aluminum Corrosion

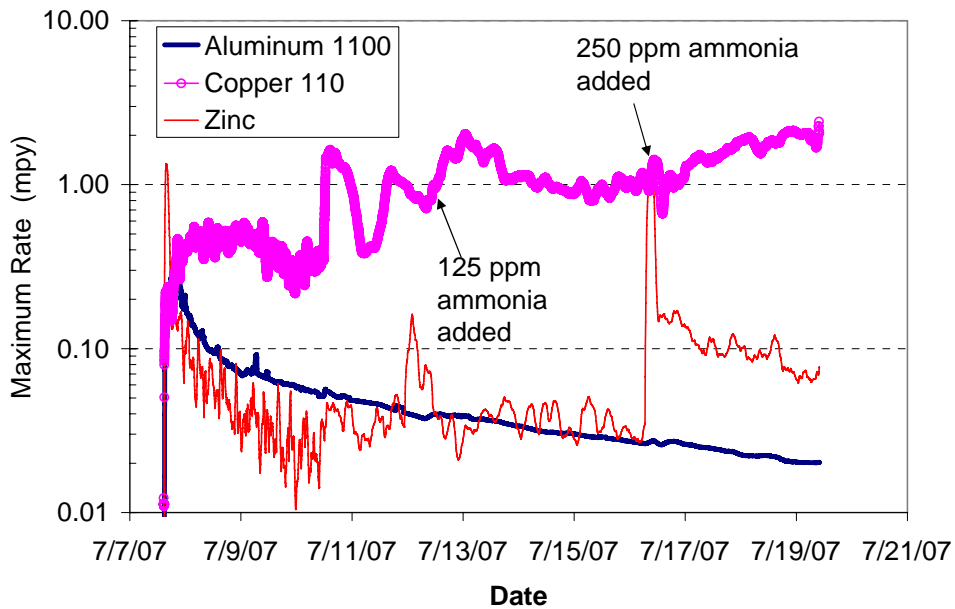


Figure II - 15% NaCl solution with pH adjusted, no Inhibitors  
Ammonia Effect on Corrosion of Copper and Zinc

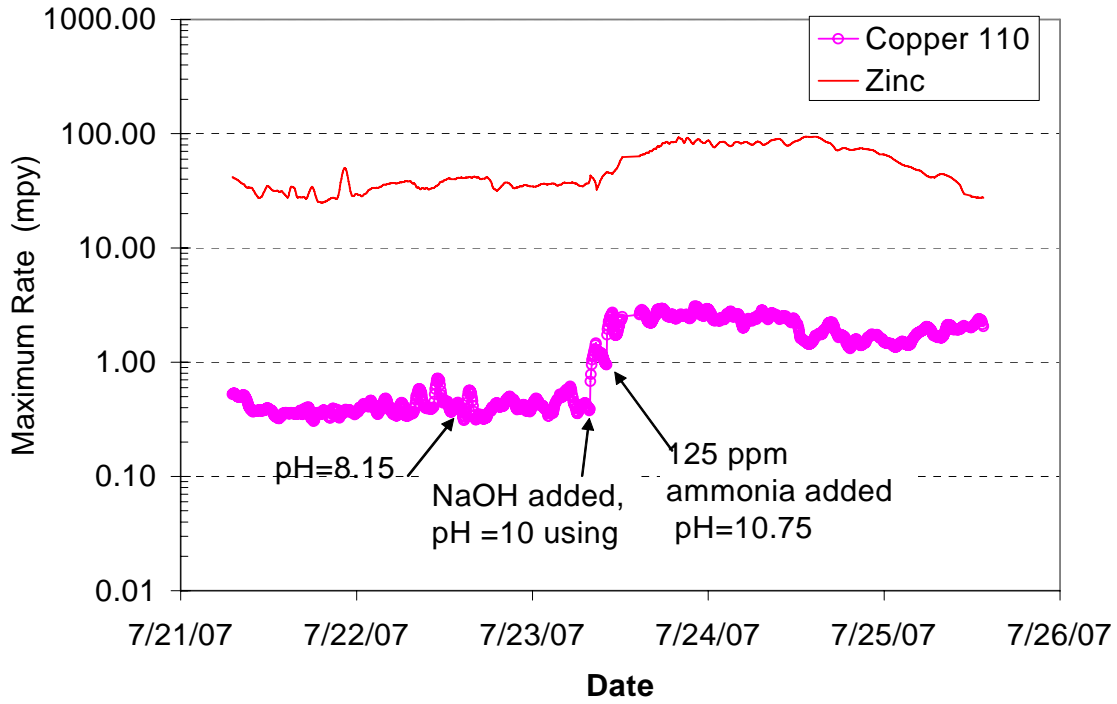


Figure III - ZLD / Silica treated Tower Water, with TTA Inhibitor Supplement  
Ammonia impact on Copper, Zinc and Aluminum Corrosion

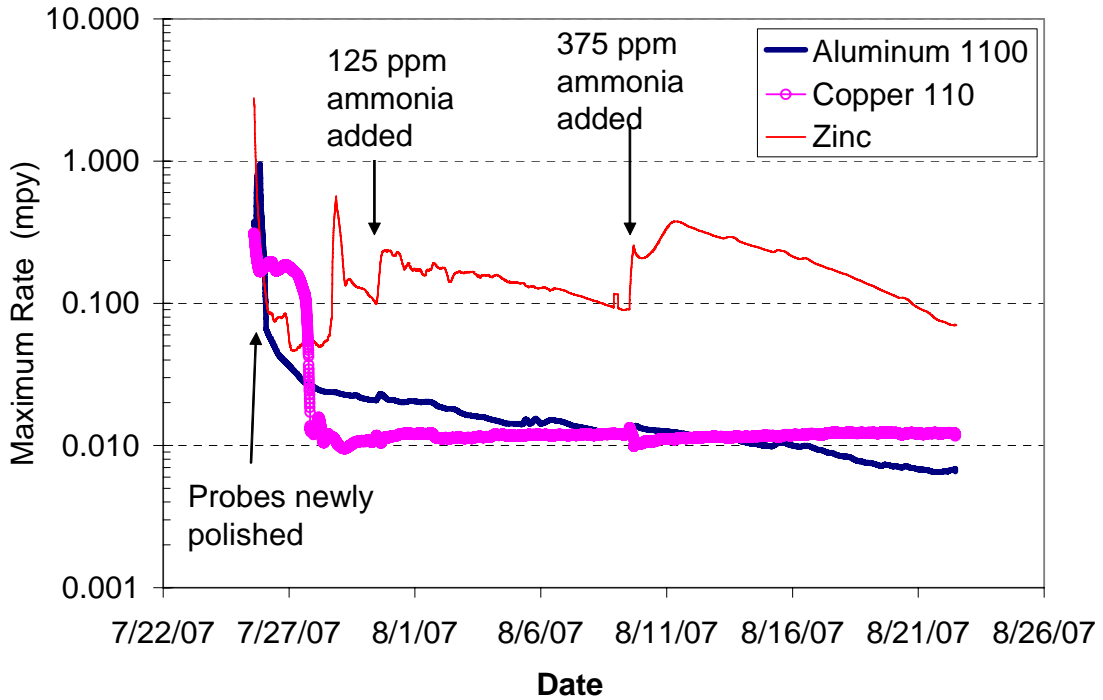




Figure IV – Galvanized coupon #283 exposed to ZLD Tower water for 60 days and #282 unexposed before and after acid strip of galvanized coating. (Note: mm/yr= mpy/39.4)



Figure V - Galvanized Coupon # 234 exposed 60 days in ZLD Tower Water Treated with TTA Supplement to Silica Inhibitor

