

# EFFECTIVE USE OF RECYCLED WATER IN COOLING TOWERS WITH NEW GREEN TECHNOLOGY

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## Abstract

Use of recycled water in cooling towers presents a unique challenge with conflicting goals and characteristics. Ideally, cooling towers evaporate water resulting in two to six cycles of concentration of minerals before a significant portion (17-50%) of the water must typically be discharged to waste treatment plants. The cycles of concentration (COC) varies based on the concentration of minerals which cause scale and corrosion of metals.

Recycled water has the added negative characteristic of higher nutrient levels that sustain bacteria growth. As the cycles of concentration increase, the cooling tower becomes an incubator for bacterial growth that creates biofilms. Recycled waters usually have higher mineral content that limits cycles of concentration. This has resulted in other recycled water users having to operate at low concentrations, excess blow down and high chemical biocide use to limit biofouling.

Use of recycled water therefore results in fewer cycles of concentration, two to four times the chemical treatment cost, more discharge volume (increasing quantities of BOD and COD discharged to sewers), lower cooling efficiency due to biofilm, and more operational cost to clean and maintain the cooling system.

A new “green” technology, that uses simple filtration and ion-exchange (softened) pretreatment of recycled cooling tower makeup water, was been implemented at a US automotive corporate headquarters. This unique treatment process addresses all of the issues inherent in all cooling tower make-up water systems to enhance efficiency, reduce discharge to the sewer system, dramatically reduce corrosion, and reduce overall water usage by enabling cycles of concentration to increase to 50 or greater! This site was ideal for a study of this process as they used potable water with this treatment approach prior to converting to recycled water.

The filtering and softening treatment permit the recycled water to be used at dramatically increased TDS levels. As cycles increase several benefits are derived:

- Silica, naturally present in the water, converts to a corrosion inhibitor eliminating the need for chemical corrosion inhibitors,
- High TDS (study system reached 60,000 TDS) and pH levels prevents bacteriological growth and eliminates the need for toxic biocides to prevent biogrowth,
- Without scale or biogrowth, energy efficiency of the cooling system is increased and cleaning costs are reduced,
- Less water is used with dramatic increase in cycles (discharge reduced by 95% or more),
- Nitrification treatment of recycled water is no longer required, and

- And most importantly, the technology provides an economical process to expand recycled water use in cooling towers that can provide a major water-energy sustainability impact in California.

## **Introduction**

Use of recycled water can replace 100% of fresh water use in towers, and displace energy cost of \$272 / AF<sup>(1)</sup> consumed to purify and transport fresh water. West Basin Municipal Water District (West Basin) has been a leader in use of recycled water in cooling towers, providing nitrification pretreatment for several large refinery towers. Typical treatment includes nitrification of tertiary disinfected recycled water which is later treated with various chemicals by the user to mitigate corrosion and biogrowth.

Since nitrification is not cost effective for smaller cooling towers, some sites have opted to use tertiary disinfected recycled water without the nitrification process. While this approach saves money compared to potable water or nitrified recycled water, increased biogrowth and corrosion potential have required substantial increases in chemical use and operation at lower COC's. Some sites have also encountered higher maintenance costs and reduced efficiency which more than offset water savings.

These set-backs had the potential to greatly limit the application of tertiary disinfected recycled water for small to medium sized cooling towers until the implementation of a unique treatment process in the central plant of a US automotive corporate facility in 2007. This new "green" technology uses simple filtration and high efficiency softening (HES) of recycled makeup water for cooling towers. The unique treatment process addresses all of the issues inherent in all cooling tower water systems to enhance efficiency, reduce discharge to the sewer system, dramatically reduce corrosion and scale, mitigate biological fouling, and reduce overall water usage by enabling operation of towers at greater than 50 cycles of concentration.

## **Background**

As commercial and industrial facilities convert to use of municipal recycled or other waste water reuse sources to conserve water, they will potentially face increased corrosion from higher total dissolved solids (TDS) and ammonia that is corrosion aggressive to copper, copper alloys and other metals. They also face significantly increased biological growth and fouling potentials from recycled waters that contain ammonia, phosphate and organics that support biological activity.

Municipal recycled water typically contains high levels of ammonia as a result of incomplete removal of this byproduct of human waste in the treatment process. Recycled 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 tower water wastage to avoid scale limitations. These traditional water treatment issues have reportedly been the major limitation and resistance to increasing use of recycled water in evaporative cooling applications.

Over the past five years, a new technology has permitted cooling towers to operate at zero blow down (ZBD), and maintain TDS levels between 10,000 and 150,000 mg/L without hardness or silica scales. The patented treatment process discussed in this paper mitigates scale, corrosion or biological

fouling problems<sup>(4-6)</sup>. Establishing this process as an effective and economical approach to facilitate use of recycled and other wastewater sources, by mitigating traditional treatment limitations, will further expand water conservation alternatives. Establishing the viability of silica-azoles chemistry for application in ZBD tower systems using recycled water (typically containing high TDS, ammonia, organics, and phosphates) becomes very relevant for the industry.

Corrosive attack of copper by ammonia in water is well known in the water treatment industry, and presents a particular challenge for reuse of wastewater sources that contain ammonia in cooling tower systems. Many of these systems use copper and copper alloys which are vulnerable to ammonia. Ammonia in water 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. Thus, ammonia gas can be volatilized from water by pH elevation, heat and circulation over a cooling tower, typical of commercial ammonia stripper design. ZBD chemistry naturally controls tower water at greater than pH 9, and causes ammonia/ammonium ion residuals to be reduced to lower ranges by such tower stripping.

Increasing azoles concentration improves copper corrosion inhibition, but such improvement is time and concentration dependent at acidic or neutral pH (less than 9). These 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. Studies by Water Conservation Technology International (WCTI) have determined that application of azoles in cooling towers, with control of pH between 9 to 10 in high TDS and low hardness water, contributes to more rapid and highly protective film formation to protect copper and copper alloys from corrosion by ammonia. This high TDS and low hardness chemistry results from evaporative concentration of natural makeup water minerals, following HES softening of potable, surface or recycled waste water sources used for makeup to cooling towers treated with the patented methods<sup>(2,6)</sup> described in this paper.

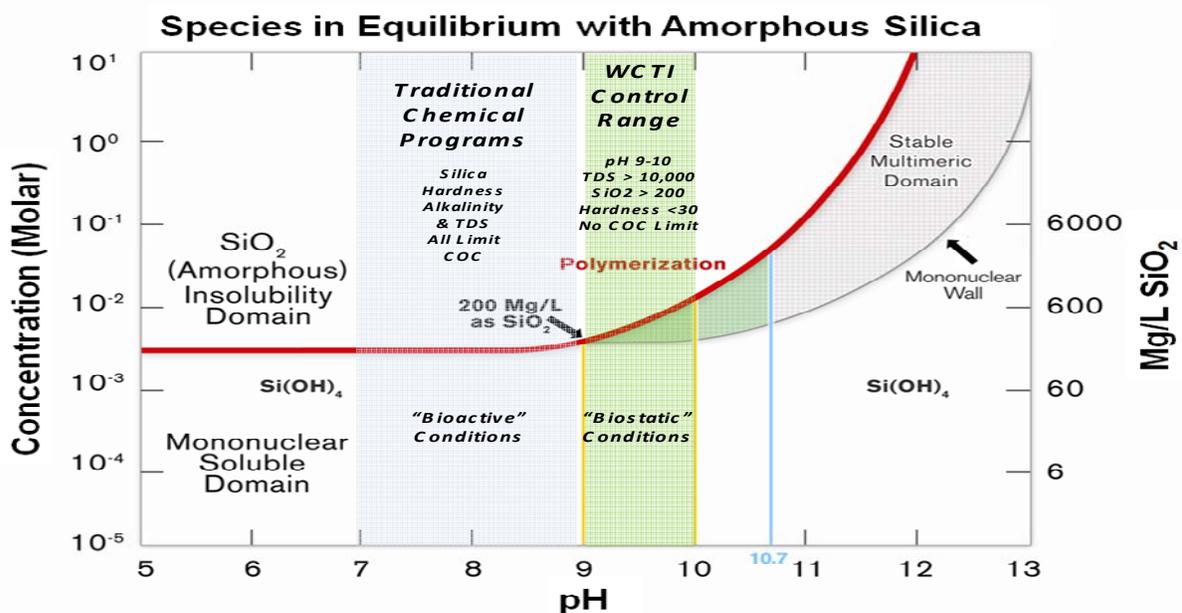
## **Silica-azoles Chemistry**

The silica corrosion inhibitor chemistry discussed in this paper has been described in previous publications<sup>(4-6)</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 fresh water sources generally used for cooling towers. Ammonia is particularly corrosive to copper and copper alloys commonly used in cooling systems. Tests performed with silica inhibited tower 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 at zero-blow-down (ZBD), 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>(6)</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. 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. Since this technology permits cooling systems to operate at much greater concentrations of corrosive ions (high TDS) without corrosion of system metals, significant water conservation benefit is provided for both the tower operator and sustainability of water resources. 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 exposed to high evaporative concentrations of corrosive ions contained in water with ZBD operation<sup>(4)</sup>. Figure 1 illustrates the application ranges of silica chemistry with the patented methods, and shows the contrast to the application ranges and limitations with traditional chemical treatment.



**Figure 1 – Silica Concentration / pH Dependent Relationship.**

Silica chemistry alone is not effective in inhibiting corrosive attack of copper by ammonia, as is also true for traditional treatment chemicals without use of specific copper inhibitors. Prior inhibitor performance data did not exist for application of azoles chemistry for copper corrosion inhibition in ZBD cooling systems where tower chemistry was controlled with a combination of high pH (9 to 10 pH), high TDS (10,000 to 150,000 mg/L TDS) and low total hardness (< 30 mg/L).

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 provide more in depth discussion<sup>(2-6)</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 film on metal surfaces. The silica polymer film thickness is self limiting, and does not inhibit heat transfer. The mechanisms by which azoles inhibit metal surfaces are well described by many prior publications referenced in this paper, although not at the water chemistry conditions evaluated in these studies. These studies demonstrate a higher level of effectiveness and efficiency for copper inhibition with azoles when applied in combination with the silica inhibition chemistry and control methods.

## **ZBD Reduction of Water Use / Energy Use / Discharge Issues**

Traditional chemical treatment methods do not permit operation at ZBD (high COC) concentration levels due to ineffective corrosion and scale protection. Traditional chemical treatment methods also require either significant tower water blow down, or use of cooling tower water blow down or pre-treatment (RO, IX, evaporators) water recovery technologies which impose prohibitively expensive capital, energy and operating costs <sup>(7)</sup>.

Typical cost for removal of hardness from makeup water with HES softening is generally much lower (between \$0.07 to \$0.15 per 1000 gallons) than the cost to replace blow down from the tower with increased makeup water (typically \$2.00 to \$10.00 per 1000 gallons water and sewer cost). This water use and cost efficiency provides exceptional savings incentive to tower operators to conserve water, particularly with elimination of corrosion, scale and bio-fouling issues that are mitigated with use of this treatment method.

ZBD tower operation and HES softening technology also provide excellent opportunity to reduce the TDS loading from tower discharge to sewers and recycled water systems. Proprietary HES design reduces salt use by 30 to 50% and exceeds the California salt use efficiency standard, while providing exceptionally low hardness water required to facilitate ZBD operation and water use reduction. The quantity (pounds per day) of TDS (salts) discharged by HES pre-treatment are significantly less than the TDS quantity typically discharged by operation of cooling towers at low COC where TDS in the makeup water are concentrated and discharged with blow down from the tower.

Further, the HES reduced waste discharge volume (typically 1% of tower water use) provides volume economy for segregation of high TDS waste for disposal through brine lines, hauling, evaporation ponds or other disposal options. Reduced cooling tower discharge volume and cost efficient segregation of high TDS waste for disposal provides opportunity to reduce this major source of steadily increasing TDS levels in sewers and recycled water operations. Some industrial and municipal facilities are currently utilizing the waste reduction efficiency of this chemistry to minimize cooling tower TDS discharge and reduce hydraulic loads on limited processing facilities by implementing high TDS segregation and disposal infrastructure. Table 1 below illustrates reduced TDS loading to sewer with the ZBD / HES process using typical Los Angeles CA water quality, and potential “zero” TDS loading with utilization of brine line or haul options.

| <b>Table 1 – TDS Discharge to Sewer with 1000 Ton Tower Load (13,140,000 GPY) Evaporation</b> |           |              |                  |                         |                                    |
|---|-----------|--------------|------------------|-------------------------|------------------------------------|
|   | MU<br>TDS | Tower<br>COC | Discharge<br>TDS | Discharge<br>Gal / Year | Discharge to Sewer<br># / Year TDS |
| Tower BD (Chemicals & low COC)  | 730       | 2.5          | 1,825            | 8,239,000               | 125,604                            |
| ZBD / HES Tower Operation   | 730       | 75           | 54,750           | 0                       | 0                                  |
| HES Waste   | -         | -            | 22,700           | 181,028                 | 33,146                             |
| Basin Clean (once / year)   |           |              | 54,750           | 10,000                  | 4,566                              |
| Brine Line or Haul  | -         | -            | -                | 191,028                 | 0                                  |

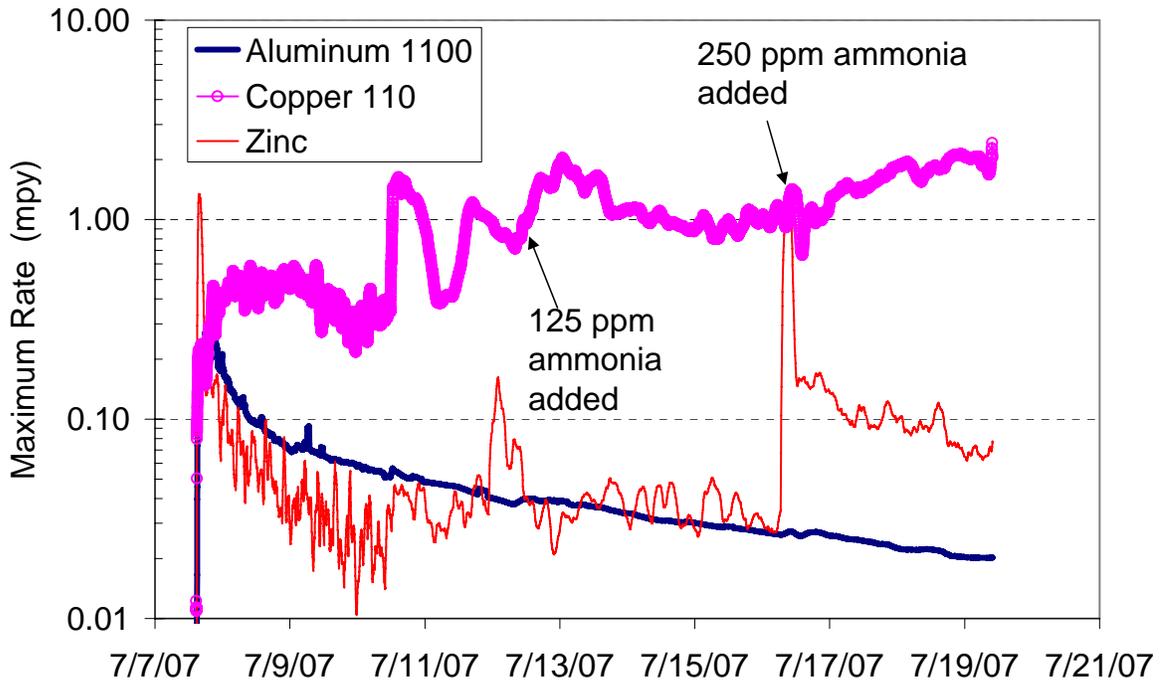
This chemistry has also demonstrated it is effective in removing existing scale and silica deposits to restore heat transfer and energy efficiency, without use of acid, chemicals or corrosive consequences. Table 2 below summarizes the benefits derived with conversion of a tower system severely limited by

high silica source water that caused high water wastage, mineral scales, biological fouling and significantly increased energy consumption.

| <b>Performance Measurements</b> | <b>Chemical Treatment</b>  | <b>WCTI</b>                |
|---------------------------------|----------------------------|----------------------------|
| Tower Makeup Discharge          | 70%                        | 1%                         |
| Tower Fill / Exchanger          | Visible Scale / Deposits   | Removed / Clean Surfaces   |
| Average Planktonic Count        | $10^4 - 10^5$ CFU/ml       | $10^0$ CFU/ml              |
| Average Sessile Count           | $10^6$ CFU/cm <sup>2</sup> | $10^1$ CFU/cm <sup>2</sup> |
| Average Biocide Usage           | 2.0 – 2.5 gpd              | 0.05 gpd                   |
| Exchanger Amperage Loading      | 34                         | 25                         |

### Lab Study Results Using Coupled Multielectrode Array Sensors (CMAS) (1)

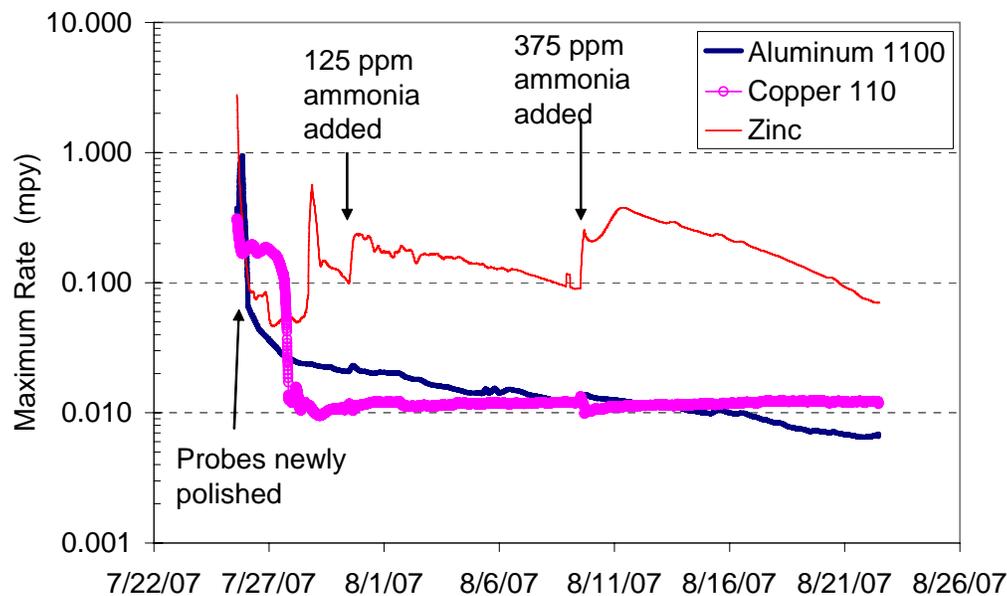
The laboratory study was intentionally designed for exposure of the tested metals to very high levels of ammonia, and conducted at room temperature to avoid volatilization of ammonia. Corrosion rates for zinc and copper would be expected to increase significantly with higher operating temperatures, as has determined in prior CMAS studies (4, 7). The effect of ammonia on the maximum localized corrosion rates for copper, zinc and aluminum in silica-treated tower water (without TTA) is shown in Figure 2, showing that ammonia primarily increases the corrosion of copper, and had no significant affect (other than short term re-stabilization) on the silica inhibited aluminum and zinc.



**Figure 2 – Effect of Ammonia on Metal Corrosion in Silica Treated Tower Water (without TTA)**

(1) Trade name of Corr Instruments, LLC, San Antonio, Texas, USA

Ammonia no longer has any significant corrosive impact on copper when TTA inhibitor is added to the silica-treated tower water as shown in Figure 3. The combination of silica-azoles inhibitors protects the most commonly used metals in cooling systems. A more detailed discussion of the results of this study for each metal follows below.



**Figure 3 – Effect of Ammonia on Metal Corrosion in Silica Treated Tower Water, with TTA**

**Copper**

The maximum localized corrosion rate for copper in the presence of ammonia was 1.0 to 2.0 mpy in the silica-treated ZBD tower water, without TTA (Figure 2). The maximum localized corrosion rate for copper was approximately 0.5 mpy (0.013 mm/yr) in non TTA inhibited test solutions prior to ammonia addition, which reflects the corrosive effect of high TDS (150,000 mg/L) salts on copper<sup>(4,5,7)</sup>. Figure 3 shows the exceptional inhibition of copper by TTA in the silica-treated ZBD tower water in the presence of ammonia, with virtually no localized corrosion (approximately 0.01 mpy).

**Zinc**

The maximum localized corrosion rate for zinc is 30-40 mpy in uninhibited pure salt solution at pH 8, without presence of ammonia, reflecting the corrosive effect of high TDS (150,000 mg/L) or salt solution<sup>(3,4,7)</sup>. The localized rate for zinc was 0.05 to 0.10 mpy in the silica-treated ZBD tower water (without TTA) in Figure 2, indicating that the corrosion was well inhibited by silica. The maximum localized corrosion rate for zinc in the TTA and silica treated ZBD tower water in the presence of ammonia varied from 0.10 to 0.30 mpy in Figure 3, which is not significantly different from the corrosion rate obtained without use of TTA in the silica-treated ZBD tower water. This indicates no further corrosion inhibition benefit with use of TTA when silica is present.

**Aluminum**

Both Figures I and II 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 range in the silica-treated ZBD tower water. TTA provides no further corrosion inhibition benefit when silica is present. TTA may be beneficial for inhibiting aluminum and zinc when silica residuals are not present, such as during transition from low COC operation with chemicals to ZBD.

### Historical Corrosion Data

Copper and copper alloy corrosion rates from several sources indicate that both ammonia and high TDS contribute to significant increase in corrosion of copper. The data referenced in Table 3 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 due to the elevated temperature and ammonia concentrations.

| 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*

High TDS and high alkalinity (high pH) 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 concentrations in the water. This vulnerability of aluminum and zinc to corrosion at high pH and TDS in uninhibited water is discussed in prior referenced CMAS study papers <sup>(3, 4, 8)</sup>. ZLD operation of cooling towers will produce high concentrations of TDS and sodium carbonate alkalinity (9 to 10 pH). The CMAS data in this study confirms prior studies that show silica provides excellent inhibition of aluminum and zinc in such high pH / high TDS water, and the presence of ammonia has no additional impact on the ability of silica to inhibit their corrosion. This study confirmed that the primary need was to establish an effective supplemental copper inhibitor to aid silica chemistry when ammonia is present.

### **Cooling Tower System Study Results**

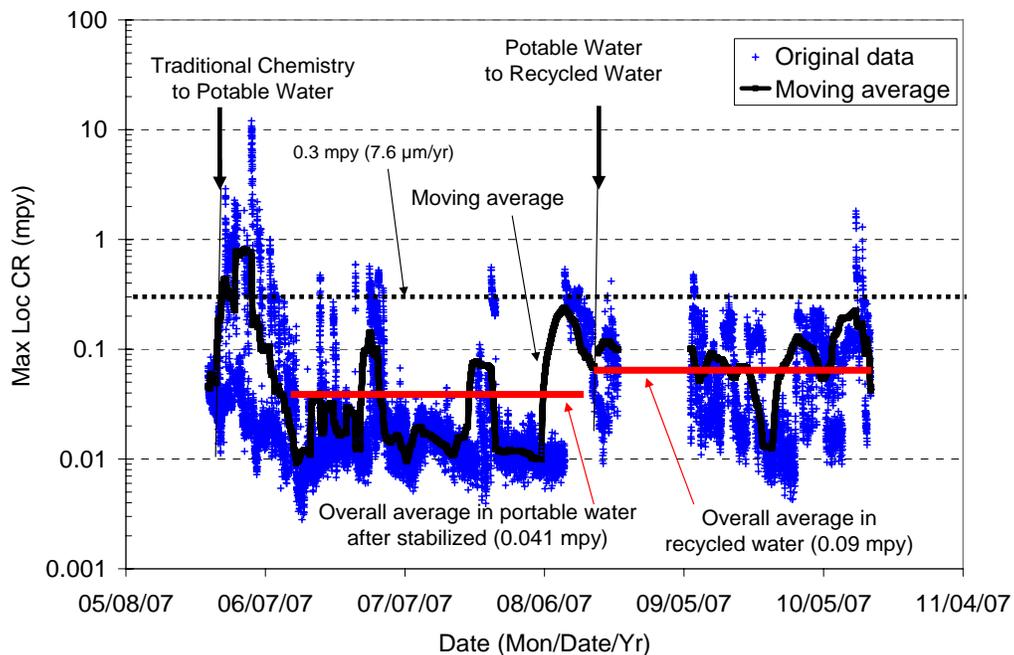
Analytical tests were performed on samples from the makeup and five cooling tower system serving the central chiller and adsorption machines at this automotive corporate facility. The system was started with HES softened potable water to establish expected performance with comparable applications in the Southern California area, and excellent corrosion inhibition results were quickly attained. Recycled makeup water was used after implementing multimedia filtration and HES softened recycled water (California Title 22) for the ZLD / silica / azoles inhibited treatment. 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 water use cost reduction was approximately 53% less than with prior traditional chemical treatment operation, due to the combination of reduced water use and lower cost for reclaim water. Recycled water use and discharge reduction has replaced 25 million gallons per year of potable water use. Continued use of traditional chemical treatment with reclaim water was projected to increase prior chemical treatment cost by 400%.

WCTI used the annual recycled water quality profile from West Basin recycled water to design multimedia filtration and HES softening systems to treat the makeup water at peak operating load 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 will foul ion exchange softening processes, and also foul heat transfer surfaces in the cooling system. The softening process must produce very low hardness water to facilitate

ZBD operation (high COC), the conversion of source water silica to a general corrosion inhibitor, and sufficient TDS and pH for natural biostatic tower chemistry.

Samples of filtered and softened recycled makeup water and the treated ZLD cooling tower system water are compared in Table 4 for chemistry concentration (COC) and mass balance of source water ions. Corrosion rate studies were conducted using linear polarization probes with copper and carbon steel tips, and weight loss on test coupon specimens per ASTM Standard methods. An on-line real time study of copper corrosion using CMAS technology was conducted for several months to determine the impact of ammonia during the transition from potable to recycled water, with results shown in Figure 4. Discussion of study results follows these figures.

| <b>Table 4 – ZLD Cooling Tower with Reclaim Water Makeup</b>                         |        |         |     |
|--|--------|---------|-----|
| <b>ZLD Tower / Soft Reclaim Makeup Water COC (Concentration of Chemistry) Ratios</b> |        |         |     |
| 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  |



**Figure 4 - Real Time CMAS Copper Study, during Change from Potable to Recycled Water.**

## Discussion of Tower Study Results

### Water Analyses

The analyses of cooling tower and reclaim makeup water chemistries in Table 4 show that this method maintains solubility of the principle ions (sodium, chloride, alkalinity, sulfate, TDS) in softened makeup water, and permits higher levels of soluble silica in the cooling tower water. All soluble silica in the makeup does not cycle up in the tower water since the majority is polymerized to stable amorphous multimeric silica particles which are not detected by the soluble silica test (acid molybdate procedure). Some excess silica may be precipitated as non-adherent amorphous silica in the basin with adsorption on dust and solids scrubbed from the air by the cooling tower. Dirt accumulation in the tower basin is comparable to traditional chemical treatment, if not removed by side stream filtration. System heat exchange surfaces inspected in all chillers and absorbers were free of scale, silica or other deposits.

The test results show the TTA fed to the tower water (only small quantity fed once per month, since ZBD eliminates loss to sewer). TTA residuals slowly deplete over time due to adsorption on air scrubbed suspended solids and 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 natural ZBD tower chemistry that converts ammonium ion to the soluble ammonia gas through concentration of makeup alkalinity that increases pH. The soluble gas is stripped from the water as it is circulated over the cooling tower for heat rejection. The other recycled chemistry of importance is the total phosphate residual of 0.6 mg/L as  $\text{PO}_4$  in the soft makeup compared to 16 mg/L in the tower water, which indicates that  $\text{PO}_4$  solubility is maintained at the high pH (9.8) with low calcium residual and increased solubility effect of high TDS (uncommon ion effect). 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  $\text{CaCO}_3$  <sup>(5)</sup>.

### 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  $10^6$  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 ( $10^0$  cfu) after 48 hour incubation. System heat transfer efficiencies were maintained within expected and historical approach temperatures. Inspection of chiller and absorber bundles showed no scaling, corrosion or biological fouling.

### Corrosion Rate Measurements

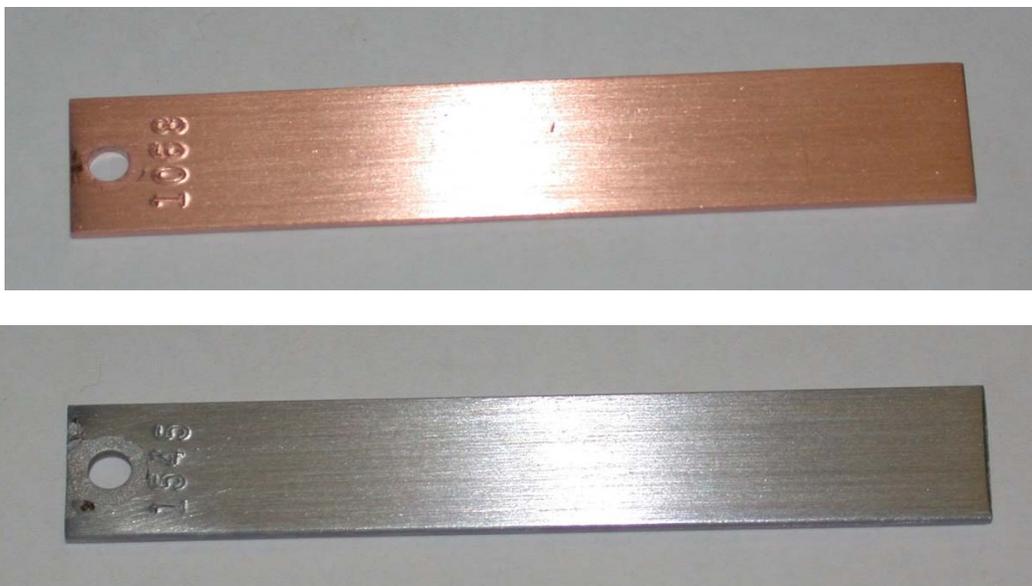
The change from potable water makeup to ammonia laden recycled water makeup increased the copper corrosion rate from approximately 0.041 mpy in overall average to 0.09 mpy in overall average (Figure 4) during the CMAS real time monitoring study. Some increase in copper corrosion would be expected with the ammonia content of recycled water, but the corrosion rates are so low that that traditional monitoring method accuracy would not even detect the change.

Data in Table 5 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 carbon steel corrosion rates were very low, the coupon showed slight differential cell corrosion

under the coupon mount. The carbon steel rate was slightly higher than normally experienced with silica inhibitor chemistry, 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. To provide perspective on the effectiveness of copper corrosion protection in the tower water, the facility had to replace existing brass makeup valves with stainless valves within a year due to the impact of the ammonia present in the untreated recycled makeup water. Copper lines used to supply reclaim water to bathroom applications also failed in less than two years. PVC or stainless piping is recommended for transport of recycled water to applications.

| <b>Table 5 - Cooling Tower (Reclaim Makeup) Corrosion Test Data</b> |                   |                   |
|---|-------------------|-------------------|
| Linear Polarization (LP) and Coupon Weight Loss Measurements        |                   |                   |
| Specimen Type   | Mild Steel (1008) | Copper (110)      |
| Test location   | Tower Return Loop | Tower Return Loop |
| LP Corrosion Rate (mpy)   | < 0.2             | < 0.1             |
| Coupon Corrosion Rate (mpy)   | 0.426             | < 0.016           |



**Figure 5 – Copper & Steel Test Coupons, 99 days exposure.**

### **Summary & Conclusions**

The effect of silica-azoles (TTA) treatment for inhibiting corrosion of copper, zinc and aluminum in zero blow-down, high TDS, soft tower water containing ammonia was evaluated with coupled multielectrode array sensor (CMAS) probes in the laboratory. Field corrosion data was obtained from a cooling tower using recycled makeup water which contained high levels of ammonia, and results compared to the laboratory study data to verify predicted corrosion inhibition performance.

Corrosion inhibition performance was excellent for copper, aluminum, and zinc with the combination of silica and TTA inhibitors while exposed to ammonia in both laboratory studies and tower study test results. CMAS measurements indicate that silica inhibitor reduced localized corrosion

rates for aluminum and zinc, while corrosion of copper was very effectively controlled in the presence of ammonia by the addition of supplemental TTA inhibitor. Tower system corrosion studies confirmed the laboratory predicted results.

The study of cooling towers using recycled water verified that excellent biological and fouling control was provided through attainment of natural biostatic chemistry as demonstrated over five years with ZLD-silica chemistry in various cooling tower systems using potable water. Effective biostatic mitigation of bio-growth and bio-film deposition permits efficient heat transfer, clean metal surface contact for inhibitor protection and minimizes potential for under deposit corrosion attack.

This technology eliminates the scale, corrosion and biofouling performance limitations associated with use of recycled water treated with traditional chemical approaches. It provides opportunity to replace potable water with recycled water, conserve energy, reduce discharge volumes, reduce sewer TDS loadings, and eliminate use of toxic and persistent chemicals discharged to sewers. It provides these benefits much more cost effectively than current treatment approaches that waste water and chemicals with low COC operation. It provides an opportunity to use natural green chemistry and water reuse that will promote sustainable water ecosystems and energy resources.

## References

1. California Sustainability Alliance, May 2008, The Role of Recycled Water in Energy Efficiency and Reduction of Greenhouse Gases.
2. Duke, et al, US Patent Application US0080264870, Cooling Water Corrosion Inhibition Method.
3. Duke, D. & Yang, L., Paper 08372, 2008, Electrochemical Studies with Coupled Multielectrode Array Sensors on Corrosion Inhibition of Copper and Affected Metals in the Presence of Ammonia in Zero Liquid Discharge Cooling Water, CORROSION 2008, NACE paper # 08372.
4. Duke, D. & Yang, L., 2007, 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, CORROSION 2007, NACE paper # 07626.
5. Duke, D. & Reed, J., 2007, Zero Liquid Discharge (ZLD) Cooling Tower Treatment at CSI, AIST.
6. Duke, et al, US Patents 6,929,749; 6,940,193; 6,998,092; and 7,122,148.
7. Duke, D., 2007, ZLD: New Silica Based Inhibitor Chemistry Permits Cost Effective Water Conservation for HVAC and Industrial Cooling Towers, IWC Report 07-11.
8. X. Sun and L. Yang, 2006, Real-Time Monitoring of Localized and General Corrosion Rates in Simulated Marine Environments Using Coupled Multi-electrode Array Sensors, CORROSION 2006, NACE paper # 06284.