

Corrosion Control When Using Secondary Treated Municipal Wastewater as Alternative Makeup Water for Cooling Tower Systems

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ABSTRACT: Secondary treated municipal wastewater is a promising alternative to fresh water as power plant cooling water system makeup water, especially in arid regions. Laboratory and field testing was conducted in this study to evaluate the corrosiveness of secondary treated municipal wastewater for various metals and metal alloys in cooling systems. Different corrosion control strategies were evaluated based on varied chemical treatment. Orthophosphate, which is abundant in secondary treated municipal wastewater, contributed to more than 80% precipitative removal of phosphorous-based corrosion inhibitors. Tolyltriazole worked effectively to reduce corrosion of copper (greater than 95% inhibition effectiveness). The corrosion rate of mild steel in the presence of free chlorine 1 mg/L (as Cl₂) was approximately 50% higher than in the presence of monochloramine 1 mg/L (as Cl₂), indicating that monochloramine is a less corrosive biocide than free chlorine. The scaling layers observed on the metal alloys contributed to corrosion inhibition, which could be seen by comparing the mild steel 21-day average corrosion rate with the last 5-day average corrosion rate, the latter being approximately 50% lower than the former. *Water Environ. Res.*, **82**, 2346 (2010).

KEYWORDS: Corrosion, cooling, municipal wastewater, power plant, mild steel, copper, corrosion inhibitors, tolyltriazole, water reuse.

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Introduction

Secondary treated municipal wastewater (MWW) is of increasing interest as an alternative source of makeup water for thermoelectric power plant recirculating cooling water systems. In the U.S., 17 power plants reported employing treated municipal wastewater as makeup in 1986 (Breitstein and Tucker, 1986), while a more recent survey identified 47 power plants using treated municipal wastewater in recirculating cooling water systems (Veil, 2007). Most of the 47 plants are in southwestern regions and Florida, corresponding to the regions susceptible to

water supply constraints. Another analysis has shown that secondary treated municipal wastewater represents a widely available alternative cooling water source for existing and future power plants in terms of quantity and proximity to the ultimate use location (Chien et al., 2008).

When MWW is used in recirculating cooling water systems, control of corrosion, scaling, and biological fouling becomes more challenging due to the degraded quality of the water. For example, MWW usually has higher concentrations of organic matter, hardness, orthophosphate, ammonia, and total dissolved solids compared to freshwater sources (Williams, 1982; Weinberger, 1966). Organic matter, phosphate, and ammonia increase the growth of biomass; high hardness and phosphate increase scaling potential; ammonia is highly corrosive to copper, and total dissolved solids generally increase the corrosiveness of water to various metals by increasing the aqueous conductance (Breitstein and Tucker, 1986; Selby et al., 1996; Goldstein, 1981). Thus, when MWW is to be used for cooling, water quality requirements are more difficult to fulfill, and extraordinary corrosion, scaling and biological fouling control programs are often required (EPRI, 2003).

Orthophosphate and ammonia are the constituents of particular interest in MWW since the former is protective and the latter is corrosive to mild steel and copper alloys (Jones, 1996; Uhlig and Reive 1985). Ammonia is corrosive because it can form soluble complexes with copper (Strmčnik et al., 2009) and iron (Uhlig and Revie, 1985). Orthophosphate behaves as a weak anodic inhibitor and can facilitate the formation of iron oxides or participate in protective film formation (McCoy, 1974; Saha and Kurmaih, 1986; Drogowska et al., 1992; Borrás et al., 2000; Giacomelli et al., 2006; Benzakour and Derja, 1993). Despite its corrosion inhibition ability, orthophosphate in MWW containing high calcium and alkalinity can be removed by the formation of calcium orthophosphate scales (Goldstein et al., 1981).

Higher microbial concentrations in MWW increase the potential for microbiologically influenced corrosion (Schumerth, 2006). The use of biocide mitigates microbiologically influenced mild steel corrosion (Gayosso et al., 2005; Ramesh et al., 2003). However, free chlorine residual is aggressive to copper (Harrison and Kennedy, 1986), reacts readily with other metallic materials (Nalepa et al., 1999; Jones, 1996; Tuthill et al., 1998), and increases the corrosion rate of carbon steel and cast iron

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significantly at concentrations higher than 0.5 ppm as Cl_2 (Boffardi, 1992). In addition, high doses of chlorine increase the corrosion rate of mild steel (Nalepa et al., 1999). It has been determined that using monochloramine instead of free chlorine can reduce metal and metal alloy corrosion in drinking water distribution systems (MacQuarrie et al., 1997). However, the influence of monochloramine on metal and metal alloy corrosion in recirculating cooling systems using MWW has not been evaluated.

The use of corrosion inhibitors is the most widely employed approach to control corrosion in recirculating cooling water systems (Frayne, 1999). Corrosion inhibitors usually form barrier layers on the surface of a metal and thus decrease the corrosion rate. Barrier forming inhibitors are categorized into three types: adsorbed layer formers, oxidizing inhibitors (passivators), and conversion layer formers (Dean et al., 1981). Briefly, adsorbed layer formers function by adsorbing to the metal surface; oxidizing inhibitors function by shifting the metal's electrochemical potential to a region where the metal oxide or hydroxide is stable (passivating); and conversion layer formers function by forming a low solubility scale deposit layer on the metal surface (Dean et al., 1981). Among the commonly used corrosion inhibitors, phosphorous-based chemicals and tolyltriazole were tested in this research based on a review of the cooling water practice literature (McCoy, 1974; Frayne 1999; Jones, 1996; Harston, 2004) and by consulting cooling water control practitioners.

Phosphorous-based inhibitors, such as polyphosphates, are the most common corrosion inhibitors used in cooling water systems (Frayne, 1999) and water utilities (McNeill and Edwards, 2002). Polyphosphates are identified as cathodic corrosion inhibitors (Saha and Kurmaih, 1986). Polyphosphate compounds in water gradually hydrolyze to orthophosphate (Frayne, 1999), which is an anodic inhibitor (Saha and Kurmaih, 1986). However, orthophosphate scaling potential increases when the aqueous solution has high hardness (Goldstein et al., 1981). The feasibility of employing phosphorous-based inhibitors in cooling water systems using secondary treated municipal wastewater with high hardness and alkalinity has not been well documented.

Tolyltriazole (TTA) is a corrosion inhibitor specifically targeted for use with copper alloys. Its NH group can adsorb onto the metal surface thus forming a barrier layer (Hollander and May, 1985). Copper corrosion inhibition by TTA can be reduced by free chlorine residual (Breske, 1983; Lu et al., 1994; Harrison and Kennedy, 1986), which is often maintained in cooling systems to prevent microbial growth and biofouling. Alternatively, monochloramine has lower oxidizing power, but its influence on copper corrosion inhibition by TTA has not been studied.

The paper addresses the following aspects of corrosion potential and control in cooling systems that use secondary treated municipal wastewater as makeup water: 1) evaluate the influence of ammonia and orthophosphate, typically present in secondary treated municipal wastewater, on metal and metal alloy corrosion, 2) evaluate the effects of phosphorous-based inhibitors, TTA, free chlorine, and monochloramine additives on corrosion of specific metals and metal alloys, and 3) test the optimal chemical corrosion control strategies identified from bench-scale experiments in pilot-scale cooling systems operated with secondary treated municipal wastewater in the field.

Methodology

Secondary treated municipal wastewater characterization and synthetic wastewater preparation. The quality of MWW varies with location and time. A representative composition of MWW was determined (Table 2) by averaging the qualities of four municipal wastewater effluents (Tsai, 2006; EPRI, 2003). The generalized water quality was replicated by a synthetic municipal wastewater at four cycles of concentrations (SMW CoC4) for bench-scale experiments (Table 2). Cycles of concentration (CoC) is the concentration factor for the water in evaporative cooling systems, e.g., CoC 4 implies that the recirculating cooling water has four times the total dissolved solids concentration compared to the makeup water.

Actual MWW from the Franklin Township Municipal Sanitary Authority (Murrysville, PA) was used for testing in a bench-scale water recirculating system and three pilot-scale cooling towers in the field. The characteristics of the actual wastewater (FTMW) sampled on September 3, 2008, are shown in Table 3. Water samples were collected in a 1-L polyethylene container and then transferred to appropriate polyethylene or glass sample containers provided by a commercial laboratory, TestAmerica (Pittsburgh, PA). Appropriate preservatives were added to the sample bottles prior to the sampling event by TestAmerica. Analyses were conducted using appropriate standard methods. The scaling tendency of FTMW was expressed as the Langelier Saturation Index (LSI) and is shown in Table 3. A positive LSI indicates the supersaturation of calcite, while a negative LSI the undersaturation of calcite. The LSI of FTMW was 0.52, indicating that FTMW possessed a positive calcite scaling potential. The detailed calculation procedure for LSI given by EPRI (2003) was employed.

Part of the FTMW was concentrated in the laboratory by heated evaporation (35–40°C) to reach CoC 4 as determined by 75% water volume reduction for the bench-scale experiments.

Metal alloy pre-exposure and post-exposure treatment. Metals and metal alloys chosen for study were mild steel (UNS G10180), aluminum (UNS A91100), copper (UNS C10100), and cupronickel (UNS C70600). They are commonly used in cooling water systems (Herro and Port, 1993). The specimens tested were cylinder-shaped with a diameter of 0.953 cm and a length of 1.27 cm (Metal Samples Company, Munford, AL). The particular geometry was selected so that the specimens could be used directly for electrochemical measurements.

Prior to exposure in bench-scale or pilot-scale tests, the metal and metal alloy specimens were wet polished with SiC paper to a 600 grit surface finish, dried, weighed to 0.1 mg, degreased with acetone, rinsed in distilled water, and then inserted in the bench-scale water recirculating system or the pilot-scale cooling towers.

During exposure in the bench-scale water recirculating system, polarization resistance, R_p , of the metal and metal alloy specimens was semi-continuously monitored. Specimens were removed at the end of the third day, cleaned using acids by following ASTM G1 (ASTM, 2005), and then reweighed to 0.1 mg for determining weight loss, WL , during exposure.

In pilot-scale testing, the weight loss method was used and the post-exposure treatment of the metal and metal alloy specimens was the same as for the bench-scale experiments. For each tower, five mild steel specimens were removed from the recirculating water at intervals over the three week test period. Aluminum, copper, and cupronickel specimens were removed at the end of field testing.

Table 1—Corrosion criteria for commonly used metal alloys in cooling tower systems.

Metal	Corrosion rate (mm/yr)	Classification
Mild steel piping	< 0.0254	Excellent
	> 0.0254 to 0.0762	Good
	> 0.0762 to 0.127	Fair
	> 0.127 to 0.254	Poor
	> 0.254	Unacceptable
Mild steel heat exchanger tubing	< 0.0051	Excellent
	> 0.0051 to 0.0127	Good
	> 0.0127 to 0.0254	Fair
	> 0.0254 to 0.0381	Poor
	> 0.0381	Unacceptable
Copper and copper alloys	< 0.0025	Excellent
	> 0.0025 to 0.0051	Good
	> 0.0051 to 0.0076	Fair
	> 0.0076 to 0.0127	Poor
	> 0.0127	Unacceptable
Galvanized steel	< 0.051	Excellent
	> 0.051 to 0.102	Good
	> 0.102 to 0.203	Fair
	> 0.203 to 0.254	Poor
	> 0.254	Unacceptable
Stainless steel	< 0.0025	Acceptable
	> 0.0025	Unacceptable

Source: P. Puckorius. "Cooling water system corrosion guidelines," *Process Cooling*, July 1, 2003 (Available at http://ewr/pubs/IEP_Power_Plant_Water_R&D_Final_1.pdf, accessed: 10/17/2008)

Corrosion inhibitors. The corrosion inhibitors tested in this study included tetra-potassium pyrophosphate (TKPP), sodium polyphosphate glassy (SHMP), 2-phosphonobutane-1, 2, 4-tricarboxylic acid, (PBTC), and tolyltriazole (TTA). TKPP, SHMP, PBTC, and TTA (The National Colloid Company, Steubenville, OH) are commonly used corrosion inhibitors in cooling water systems.

Table 2—General water quality of secondary treated municipal wastewater and the water quality of synthetic secondary treated municipal wastewater (SMW CoC4) used in this study. The SMW CoC4 was prepared to simulate four-time concentrated secondary treated municipal wastewater in cooling water systems. Units are in mg/L except for pH.

Analyses	General secondary effluent	SMW CoC4
pH	8.3	8.6
Ca	76	304.6
Na	77	309.1
K	6.8	27.3
Mg	43.5	170.0
NH ₃ -N	25	100.0
Cl	276	1104.9
SO ₄	68	272.7
PO ₄	6.5	20.0
Total Alkalinity (as CaCO ₃)	336	1367

Table 3—Characteristics of secondary treated municipal wastewater from Franklin Township Municipal Sanitary Authority (sampled on September 3, 2008). Units are in mg/L except for pH and the Langelier Saturation Index (LSI).

Analyses	Result (unfiltered)	Reporting limit
Al	0.2	0.2
Ca	41.5	5.0
Cu	0.0282	0.025
Fe	0.504	0.1
K	16.3	5
Mg	10.7	5
Mn	0.317	0.015
Na	94.2	5
SiO ₂	8.54	1.07
Zn	0.0741	0.02
pH	7.1	
NH ₃ -N	21.0 ^(a)	0.50
Bicarbonate Alkalinity	177 ^(a)	5.0
BOD	31.9	2.0
Cl	106	10
NO ₃ -N	3.6	0.05
SO ₄	86.0	1.0
Total P	4.5	0.50
Total Alkalinity	177 ^(a)	5.0
TOC	27.0	1.0
LSI	0.52 ^(b)	

^(a) Method blank contamination. The associated method blank contains the target analyte at a reportable level.

^(b) calculated using the procedure given in EPRI (2003)

In addition to corrosion inhibitors, polymaleic acid (PMA, The National Colloid Company, Steubenville, OH) was used in the pilot-scale testing for scaling control evaluation.

Bench-scale recirculating water system configuration. A bench-scale water recirculating system was designed and constructed for the testing of metal and metal alloy specimens exposed to temperature, flow velocity, and the water quality similar to those in an actual recirculating cooling water system. The bench-scale water recirculating system consisted of a centrifugal pump, a water bath on a hotplate to control the water temperature, and a 1.91 cm nominal diameter PVC pipe rack to hold the metal and metal alloy specimens (Figure 1a). The pipe rack consisted of several tee sections onto which alloy specimen holders were mounted.

Corrosion measurements were performed using the combination of gravimetric weight loss and electrochemical polarization resistance measurements to determine average and instantaneous corrosion rates (Hsieh et al., 2010a). For electrochemical measurement in the bench-scale water recirculating system, the pipe rack was equipped to accommodate a reference electrode (RE) and a counter electrode (CE). Each specimen holder was made of an end-cap plug containing a threaded stainless steel rod with a metal or metal alloy attached. The specimen, RE, and CE were connected to a potentiostat for electrochemical corrosion analysis (Figure 1b). After exposure, each specimen was removed for gravimetric corrosion analysis.

Electrochemical polarization resistance measurement. Electrochemical polarization resistance (R_p) of metal and metal alloy

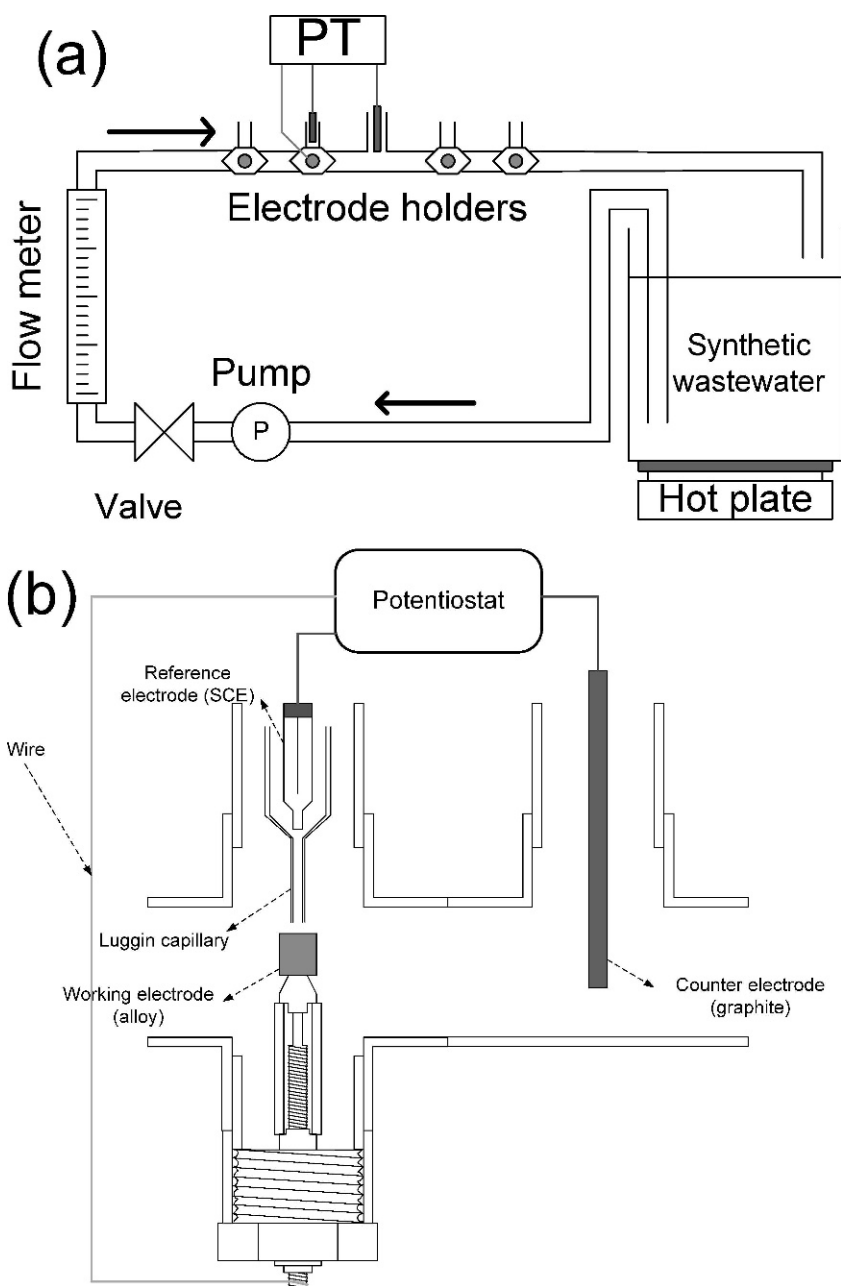


Figure 1—Schematics of (a) bench-scale water recirculating system (b) detail of mild steel specimen holder and ports for counter electrode and reference electrode equipped in bench-scale water recirculating system.

specimens in the bench-scale water recirculating system was measured with a PGSTAT100 potentiostat (ECO CHEMIE, the Netherlands). A three electrode system was employed with the alloy specimen as the working electrode, graphite as the CE, and a saturated calomel electrode as the RE in a Luggin capillary probe. Each polarization scan was performed from -30 mV to $+30$ mV relative to the corrosion potential at a scan rate of 0.3 mV/s.

Corrosion experimental matrix for bench-scale experiments with SMW CoC4. Preliminary studies revealed that the water quality parameters distinguishing MWW from freshwater with respect to corrosion are ammonia and orthophosphate. Polyphosphate and TTA were also found to be widely applied as corrosion inhibitors in cooling water systems. Combining these constituents

with some commonly used scaling and biomass inhibitors, an experimental matrix was designed to study the influence of the following parameters: ammonia, orthophosphate, free chlorine, monochloramine, TKPP, TTA, and PBTC.

The experimental matrix for corrosion and scaling analysis of alloys in contact with SMW is shown in Table 4. The matrix was designed to investigate a) the influence of orthophosphate and ammonia on corrosion, b) the effect of inhibitors on corrosion, c) the necessity to remove orthophosphate and/or ammonia from the raw wastewater, d) the effect of biocide on corrosion, and e) the necessity of adding each inhibitor for corrosion control. The temperature of the SMW was maintained at $40 \pm 1^\circ\text{C}$. The flow rate was controlled at 0.189 L/s, (3 gpm) yielding a flow velocity

Table 4—The experimental matrix for bench-scale corrosion study with synthetic municipal wastewater (SMW CoC4). Flow velocity 0.6 m/s, temperature 40 ± 1°C, and no pH adjustment (pH ~ 8.6 ± 0.15).

Synthetic wastewater composition tested	Objectives of experiments with different wastewater compositions				
	Influence of PO ₄ and NH ₄ in raw water	Efficacy of inhibitors	Necessity to remove PO ₄ and/or NH ₄ in raw water	Effect of chlorine on corrosion	Necessity of each ingredient in Mix1
CoC4	X	X			
CoC4(noNH)	X				
CoC4(noPO)	X				
CoC4_Mix(0.5x)		X			
CoC4_Mix		X	X	X	
CoC4(noPO)_Mix			X		X
CoC4(noNH)_Mix			X	X	
CoC4(noNH)_Mix_FC1				X	
CoC4_Mix1_MCA1				X	
CoC4(noPO)_Mix(noTTA)					X
CoC4(noPO)_Mix(noTKPP)					X
CoC4(noPO)_Mix(noPBTC)					X

CoC: cycles of concentration (the quality of SMW CoC4 is provided in Table 2). noPO: no orthophosphate. noNH: no ammonia. Mix: PBTC (2-phosphonobutane-1,2,4-tricarboxylic Acid) 10 mg/L, TTA (tolyltriazole) 4 mg/L, TKPP (tetra-potassium pyrophosphate K₂P₂O₇) 10 mg/L as PO₄. Mix(0.5x): half concentration of Mix. FC1 and MCA1: intermittently maintain 1 ppm total Cl₂ twice per day. FC represents free chlorine and MCA represents monochloramine.

of around 0.6 m/s in the 1.91 cm diameter pipe. The pH of SMW at equilibrium was 8.8 ± 0.1.

For corrosion analysis, in each experiment, mild steel, aluminum, copper, and cupronickel specimens were exposed to SMW CoC4 in the bench-scale water recirculating system for 3 days. The instantaneous corrosion rate was measured semi-continuously by electrochemical polarization resistance, and the weight loss of each specimen was determined immediately after the 3-day exposure. The average corrosion rate was then calculated from the weight loss. In cases where the weight loss was not detectable, the average corrosion rate was determined through the electrochemical polarization resistance method.

Corrosion analysis of actual wastewater in bench-scale water recirculating system. Raw FTMW (FTMW CoC1) and FTMW CoC4 were tested in the bench-scale water recirculating system with different chemical treatments to investigate the effectiveness of inhibitors with FTMW CoC4 and to verify the representativeness of the results from experiments with SMW CoC4. The FTMW and chemical treatment conditions included: 1) CoC 1, no chemical addition; 2) CoC 4, no chemical treatment; 3) CoC 4, PBTC 10 mg/L, TTA 4 mg/L, and TKPP 10 mg/L as PO₄; 4) CoC 4, PBTC 10 mg/L, TTA 4 mg/L, and TKPP 10 mg/L as PO₄, and free chlorine 0.5–1 mg/L as Cl₂.

Pilot-scale cooling tower configuration. Three pilot-scale cooling towers were constructed to test the optimal chemical control methods identified from bench-scale experiments. A schematic of the cooling tower is shown in Figure 2. The towers were transported to the Franklin Township Municipal Sanitary Authority for side-by-side evaluation of different corrosion/scaling/biofouling control programs. The three towers were operated with following conditions: 1) CoC 4; 2) flow rate 0.189 L/s (3 gpm) (passing through a 1.91 cm nominal diameter PVC pipe rack); 3) recirculating water temperature of 40.6°C (105°F) delivered to the cooling tower and 35°C (95°F) in the collection basin.

The side-stream coupon rack was used to evaluate the corrosion of eight metal specimens by the gravimetric weight loss method.

Corrosion experimental matrix for pilot-scale testing with actual wastewater. The experimental matrix for pilot-scale testing was based on the results of bench-scale testing. TKPP, PBTC, TTA, and monochloramine were chosen to study their influence on corrosion.

The three pilot-scale cooling towers were operated side-by-side for 21 days after CoC 4 had been reached. Two of the three towers were operated for another 21-day run to complete the intended chemical treatment program. Thus, in total the matrix included five different chemical treatment strategies as shown in Table 5. In the pilot-scale testing, corrosion inhibitors TKPP and PBTC concentrations were monitored by following APHA/AWWA/WEF Standard Method 4500-P (Eaton et al., 2005), TTA concentration was monitored by HACH® Method 8079 (HACH Company, 2008). Other water chemistry parameters (monochloramine, anions, alkalinity, pH, and conductivity) and cooling tower operational parameters (recirculating water flow rate, air flow velocity, temperature, makeup water flow rate, and blowdown water flow rate) were also monitored regularly. Monochloramine was measured with a Chlorine Pocket Photometer (HF Scientific Inc., FL), and anions were measured by ion chromatography (DIONEX, Sunnyvale, CA).

Results and Discussion

Bench-scale water recirculating system with SMW: corrosion and precipitation analysis. The average corrosion rate and corrosion inhibition effectiveness (percentage compared to the case where no inhibitors were added and no removal of ammonia and orthophosphate was performed) of each metal or metal alloy is shown in Table 6, which also shows the corrosion inhibition effectiveness (percentage) when compared to the case of no inhibitors and no removal of ammonia and orthophosphate. Also, the occurrence of pitting corrosion observed visually is indicated. The precipitation potential was qualitatively recorded after visual

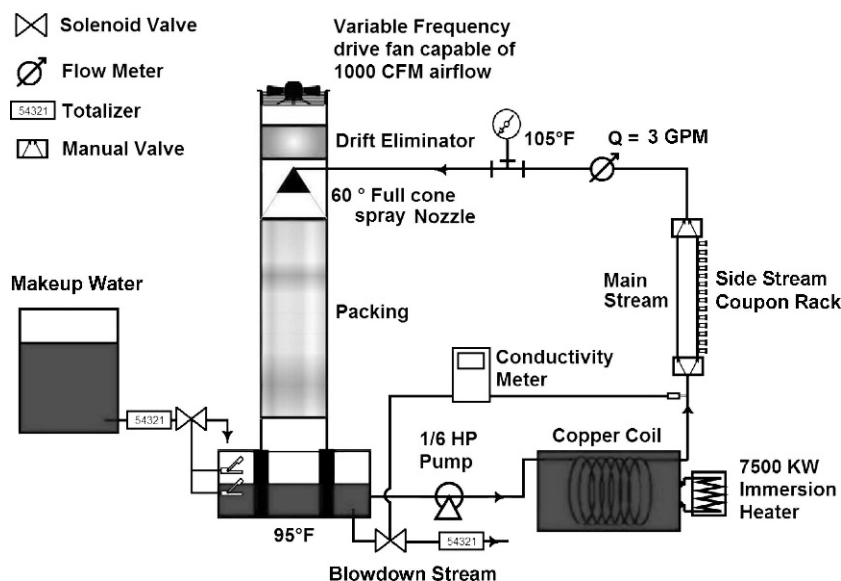


Figure 2—Schematic of pilot-scale cooling tower. The coupon rack has a similar design as Figure 1(b) except that there are no ports for counter and reference electrodes.

observation of the water turbidity. These average corrosion rates were derived from semi-continuous electrochemical measurements. Due to space limits the detailed electrochemical measurements are not included here but can be found in Appendix C of Hsieh (2009).

The results summarized in Table 6 revealed the following:

- 1) Influence of ammonia and phosphate: The presence of ammonia in SMW CoC4 exacerbated the corrosion of mild steel, aluminum, and copper. On the other hand, the presence of phosphate inhibited the corrosion of all metal and metal alloys tested except aluminum.
- 2) Influence of inhibitor mixture: The addition of TKPP (5–10 mg/L as PO_4), TTA (2–4 mg/L), and PBTC (5–10 mg/L) decreased the corrosion rate of mild steel, aluminum, and copper. The inhibition effectiveness reached was greater than 90% compared to the control with no inhibitor.
- 3) Necessity of ammonia and phosphate removal in the presence of inhibitor mixture: When TKPP 10 mg/L (as PO_4), TTA 4 mg/L, and PBTC 10 mg/L were present, the removal of

phosphate further enhanced the corrosion inhibition for all metal alloys tested, likely due to the absence of scaling. The removal of ammonia, which can form soluble complexes with copper, reduced copper corrosion.

- 4) Influence of free chlorine and monochloramine in the presence of inhibitor mixture: Copper and cupronickel were vulnerable to free chlorine of 1 mg/L (as Cl_2) but the corrosion rates were still within 0.0051 mm/yr when 4 mg/L of TTA was present. Mild steel corrosion was also exacerbated by the addition of free chlorine. In contrast, copper and cupronickel were not as sensitive to chloramine. The aggressiveness of monochloramine to mild steel was also less than free chlorine.
- 5) Influence of each ingredient in the inhibitor mixture: When TTA was not added, copper showed an extremely high corrosion rate, indicating that TTA is a very effective inhibitor to lessen the aggressiveness of ammonia for copper. When TKPP was removed, mild steel corrosion rate increased more than 10 times. The removal of PBTC did not reduce the corrosion inhibition of mild steel, copper, and cupronickel.

Table 5—The experimental matrix of field testing with pilot-scale cooling towers with secondary treated municipal wastewater at Franklin Township Municipal Sanitary Authority, with inhibitor chemicals and target doses shown. In parenthesis are the monitored results from field testing. Samples for analysis were all filtered with 0.45 μm membrane.

Chemical	Unit	Chemical concentrations				
		Tower A1	Tower B1	Tower C1	Tower A2	Tower B2
TTA	mg/L	2 (2.0 \pm 0.9)	1 (1.0 \pm 0.8)	2 (1.8 \pm 1.0)	2 (1.8 \pm 1.0)	0
TKPP	mg/L as PO_4	10 (0.6 \pm 0.4)	0	10 (0.6 \pm 0.4)	0	0
PBTC	mg/L	5 (0.8 \pm 0.3)	0	10 (0.9 \pm 0.7)	0	0
PMA	mg/L	10 (4.3 \pm 1.3)	0	20 (9.7 \pm 2.1)	10 (4.5 \pm 1.3)	0
MCA	mg/L as Cl_2	1–2 (1.0 \pm 0.7)	1–2 (1.2 \pm 0.9)	1–2 (1.5 \pm 0.8)	2–3 (3.6 \pm 2.2)	2–3 (3.2 \pm 1.3)

TTA: tolyltriazole; TKPP: tetra-potassium pyrophosphate; PBTC: 2-phosphonobutane-1,2,4-tricarboxylic acid; PMA: polymaleic acid; MCA: monochloramine

Table 6—Average corrosion rates of metals and metal alloys tested and corrosion inhibition effectiveness of different treatment programs after 3 days of metal contact with synthetic municipal wastewater at CoC 4.

	Average corrosion rate, mm/yr (Corrosion inhibition effectiveness, %)			
	Mild steel	Aluminum	Copper	Cupronickel
Control: CoC4	0.390 (—)	2.03 (P) (—)	0.021 (—)	0.0025 (—)
Influence of NH ₃ /PO ₄				
CoC4(noNH)	0.074 (81.0%)	0.320 (84.2%)	~ 0.0069 ^c (67.7%)	0.0051 (–104.0%)
CoC4(noPO)	1.15 (–195.1%)	2.06 (P) (–1.1%)	0.197 (–829.3%)	0.085 (–3298.0%)
Influence inhibitors mixture				
CoC4_Mix(0.5x)	0.0305 (92.2%)	0.120 (94.1%)	0.00097 (95.5%)	0.0031 (–22.2%)
CoC4_Mix	0.0122 (N) (96.9%)	0.160 (92.1%)	0.00048 (97.7%)	0.00074 (70.7%)
Necessity of NH ₃ /PO ₄ removal				
CoC4(noPO)_Mix	0.0051 (N) (98.7%)	0.0104 (99.5%)	0.00028 (98.7%)	0.00028 (88.9%)
CoC4(noNH)_Mix	0.0262 (N) (93.3%)	0.171 (91.6%)	0.0001 (99.5%)	0.001 (59.6%)
Influence of free Cl ₂ and chloramine				
CoC4(noNH)_Mix_FC1	0.0833 (78.7%)	0.222 (89.1%)	< 0.001 ^c (P) (> 95.1%)	< 0.00196 ^b (> 22.2%)
CoC4_Mix_MCA1	0.0551 (85.9%)	0.373 (81.6%)	0.00048 (97.7%)	0.00175 (30.3%)
Influence of ingredients in Mix1				
CoC4(noPO)_Mix(noTTA)	0.0653 (83.3%)	NA	0.208 (–882.4%)	0.00193 (23.2%)
CoC4(noPO)_Mix(noTKPP)	0.0676 (82.7%)	0.539 (P) (73.5%)	0.00038 (98.2%)	0.00135 (46.5%)
CoC4(noPO)_Mix(noPBTC)	0.0109 (N) (97.2%)	0.0757 (P) (96.3%)	0.00031 (98.6%)	0.00086 (65.7%)

^a not measured.

^b Estimated value; electrode only immersed for 40 hours.

^c Intermittent free chlorine sudden increase made corrosion rate not stable. **P**: Pitting. **N**: For mild steel, non-corroded surface except threaded side. **Mix**: PBTC 10 mg/L, TTA 4 mg/L, TKPP 10 mg/L as PO₄. **noPO**: no orthophosphate. **noNH**: no ammonia. Shaded: satisfactory results: no pitting, mild steel < 0.051 mm/yr and “N”, aluminum < 0.051 mm/yr or estimated to decrease below 0.051 mm/yr, copper < 0.0051 mm/yr, cupronickel < 0.0051 mm/yr. **Bold**: Inhibition reached 95% and no pitting, or instantaneous corrosion rate of aluminum is predicted to drop below 0.051 mm/yr.

Visual observation showed that TKPP and PBTC inhibited precipitation in the absence of orthophosphate but not in the presence of it. The result is in agreement with batch reactor tests, which showed that PBTC, TKPP, and SHMP were co-removed with orthophosphate in synthetic water having pH, alkalinity, and hardness similar to MWW (Hsieh, 2009).

Overall, the presence of the mixture of inhibitors generally reduced the corrosion rates of all metals and metal alloys tested but the precipitation potential remained. In the cases in which orthophosphate was removed from the wastewater and TKPP, PBTC, and TTA were present, precipitation was inhibited and corrosion was retarded. Thus, corrosion inhibition was more effective when precipitation was controlled. TKPP or PBTC could inhibit precipitation only in the absence of orthophosphate. Orthophosphate caused the precipitation of TKPP and PBTC. In the SMW, ammonia was corrosive to all metals and metal alloys and. Monochloramine biocide had lower corrosivity compared to free chlorine.

The largest challenge of using MWW (when ammonia and orthophosphate not removed) in cooling systems would be scaling regardless to the use of phosphorous-based inhibitors. Protection of mild steel from corrosion may occur from orthophosphate already present in the wastewater. Copper corrosion protection could be provided by TTA. Cupronickel would have the best corrosion resistance in this type of water and might not need any corrosion inhibitor.

Bench-scale water recirculating system with FTMW: corrosion analysis. The results in Table 7 show that FTMW

CoC4 had higher corrosivity to mild steel than FTMW CoC1 and also caused pitting corrosion of aluminum. FTMW CoC1 and FTMW CoC4 were both not very corrosive to copper and cupronickel. With the addition of the mixture of inhibitors, the corrosion rates of metals and metal alloys all decreased. The addition of free chlorine in the presence of the inhibitor mixture (FTMW CoC4_Mix1_FC) caused mild steel and copper corrosion rates to increase but the rates were still very low. Free chlorine also caused pitting of aluminum. Pitting corrosion for aluminum is common in waters with high chloride concentration (Uhlig and Revie, 1985), and the presence of aggressive species, such as free chlorine, might cause more severe pitting corrosion by breaking the passivating layer of aluminum oxide.

Overall, the mixture of the inhibitors effectively inhibited the corrosivity of FTMW CoC4. However, free chlorine biocide was aggressive to most alloys except cupronickel. The corrosion results with the FTMW generally agreed with the results obtained with SMW using the bench-scale system.

The results of bench-scale experiments with SMW CoC4 and FTMW CoC4 indicated that in secondary treated municipal wastewater 1) TTA is a very effective copper corrosion inhibitor, 2) phosphorus-based inhibitors (TKPP, PBTC, or SHMP) can mitigate metal and metal alloy corrosion but can also be co-removed via precipitation with orthophosphate present in the wastewater, 3) monochloramine biocide is less corrosive than free chlorine biocide, and 4) cupronickel is a satisfactory corrosion resistant metal alloy even in the absence of any inhibitors. These

Table 7—Corrosion rates after 7 days of metal contact with secondary treated municipal wastewater from Franklin Township Municipal Sanitary Authority with bench-scale recirculating system.

	7-day average corrosion rate, mm/yr			
	Mild steel	Aluminum	Copper	Cupronickel
FTMW CoC1	0.0569	0.0676	0.0058	0.0056
FTMW CoC4	0.3782	0.052 (P)	0.002	0.0043
FTMW CoC4_Mix	0.0091	ND	ND	ND
FTMW CoC4_Mix_FC	0.0292	0.01168 (P)	0.00584	ND

MPY: mils per year. FTMW: Franklin Township secondary treated municipal wastewater. CoC#: # cycles of concentration. Mix: PBTC 10 mg/L, TTA 4 mg/L, TKPP 10 mg/L as PO₄. FC: free chlorine 0.5–1 mg/L as Cl₂. P: pitting corrosion. ND: not detectable (the lower detection limit for copper and cupronickel was 0.000432 mm/yr)

results were used for developing the pilot-scale experimental matrix (Table 5).

Pilot-scale experiments. The corrosion results obtained in the pilot-scale experiments (Table 5) are shown in Table 8 and Figure 3. Table 8 shows the average corrosion rates of metals and metal alloys and Figure 3 shows the average corrosion depth of mild steel with time during the 21-day field testing with FTMW CoC4.

The concentrations of corrosion inhibitors (TTA, TKPP, and PBTC) monitored during the pilot-scale experiments are shown in Table 5. TTA was well maintained in the towers, but more than 90% of TKPP and 80% of PBTC added were not detected as they apparently precipitated in the system. Similarly, most orthophosphate from the makeup wastewater (11.5 ± 1.8 mg/L as PO₄) was not detected due to precipitation. The concentrations of orthophosphate (mg/L as PO₄) in towers were expected to be four times of these in the makeup water but were only 4.1 ± 1.0 in Tower A1, 5.9 ± 1.1 in Tower B1, 5.2 ± 0.6 in Tower C1, 8.1 ± 3.3 in Tower A2, and 7.5 ± 2.7 in Tower B2. The results are in agreement with the results from bench-scale tests in the laboratory: i) phosphorous-based inhibitors can not be maintained in solution, and ii) orthophosphate gives additional scaling potential in cooling tower systems using MWW as makeup water.

Copper and cupronickel showed very good corrosion resistance both in the absence and presence of corrosion inhibitors (Table 8). Higher monochloramine made corrosion rates of copper and cupronickel higher but still fit the general criteria of “good performance”. It was initially expected that ammonia would be a major concern for copper in the concentrated MWW in cooling

water systems. However, dissolved ammonia as monitored in the cooling tower systems was less than 1 mg/L as N. Thus, more than 98% of ammonia had been removed from the system probably through volatilization. This might explain that copper and cupronickel still had low corrosion rates in the absence of TTA.

The average corrosion rates for aluminum were not acceptable (Table 8) and pitting corrosion occurred in the absence of inhibitor and with higher monochloramine biocide dose. Although the average corrosion rates for aluminum were low in the presence of inhibitors and low monochloramine dose, pitting corrosion still occurred. Thus, pitting corrosion is likely the main concern for aluminum and makes aluminum an inappropriate material in cooling tower systems using MWW as makeup water.

The 21-day average corrosion rates of mild steel were generally classified as “fair” except in the case where none of inhibitors were present (Tower B2), where the classification was “poor”. Also, higher monochloramine biocide concentration resulted in higher 21-day average corrosion rates of mild steel. However, the average corrosion rates of mild steel in the last 5 day (days 16–21) were approximately 50% lower than the relative 21-day average and could be classified as “fair”. Also, for the last 5-day average corrosion rates, no significant difference was observed among the towers. Figure 3 shows that the average corrosion depth of mild steel in Tower A2 (which had higher monochloramine than A1, B1, and C1, and only had TTA as corrosion inhibitor) and in Tower B2 (which had higher monochloramine and no inhibitor) were higher initially but then were similar to other observed rates. It was observed that the mild steel specimens in all towers after 21 day exposure were covered by a thick layer of scales even in the

Table 8—Average corrosion rates of metal alloys contacted with secondary treated wastewater at CoC 4 in cooling tower for three weeks and their category according to general corrosion criteria for cooling systems.

Metal alloys	Average corrosion rate, mm/yr, and category ^(a)				
	Tower A1	Tower B1	Tower C1	Tower A2	Tower B2
Mild steel (21-day avg.)	0.0851 (fair)	0.0892 (fair)	0.0833 (fair)	0.121 (fair)	0.209 (poor)
Mild steel (last 5 days avg.)	0.0505 (good)	0.0094 (excellent)	0.0823 (good)	0.0622 (good)	0.0892 (fair)
Aluminum (21-day avg.)	0.058, pitting (unacceptable)	0.0442, pitting (unacceptable)	0.0300, pitting (unacceptable)	0.174, pitting (unacceptable)	0.348, pitting (unacceptable)
Copper (21-day avg.)	ND (excellent)	ND (excellent)	0.0008 (excellent)	0.0028 (good)	0.002 (excellent)
Cupronickel (21-day avg.)	ND (excellent)	0.0008 (excellent)	ND (excellent)	0.0013 (excellent)	0.001 (excellent)

^(a) Corrosion rate category is based on corrosion criteria shown in Table 1

ND: non-detectable (the lower detection limit for copper and cupronickel was 0.000432 mm/yr)

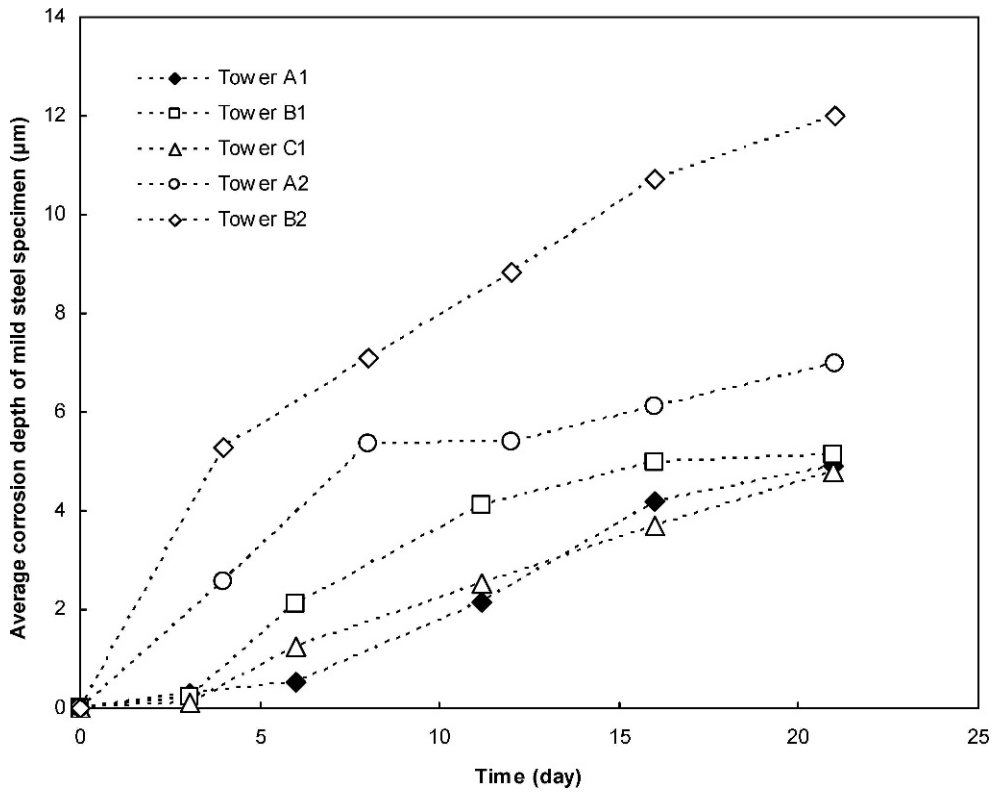


Figure 3—Average corrosion depth of mild steel specimens with time in pilot-scale cooling tower field testing with the Franklin Township Municipal wastewater at CoC 4.

presence of PMA (Figure 4). The addition of PMA could only mitigate scaling about 20–30% (Li et al., 2010). Thus, it was evident that the growth of the scaling layer gradually inhibited the corrosion of mild steel specimens in all towers. The aggressiveness of monochloramine and protection of TTA and TKPP became negligible. In order to avoid the complementary inhibition effect of scaling, a related study on the TTA corrosion protection on copper

in a cooling system using secondary treated municipal wastewater in the absence of scaling was conducted (Hsieh et al., 2010b)

Conclusions

The corrosion control of metals and metal alloys in cooling tower systems using secondary treated municipal wastewater was evaluated in this study. It was determined that commonly used phosphorous-based corrosion inhibitors were largely co-removed by precipitation with orthophosphate present in the wastewater. This precipitative co-removal was observed in bench-scale and pilot-scale experiments. TTA showed very effective corrosion inhibition for copper and copper alloys in the bench-scale experiments. Ammonia from the wastewater was largely removed from pilot-scale cooling tower systems through volatilization, and was not a concern for corrosion control in the pilot-scale testing. Monochloramine biocide was less corrosive than free chlorine biocide. Phosphorous-based inhibitors cannot be kept freely dissolved to provide good corrosion protection and are not suitable for cooling systems using secondary treated municipal wastewater as makeup water. However, corrosion in cooling water systems may not be a concern since the wastewater has high scaling potential and the scaling layer can provide a certain degree of protection to metal alloys.

Overall, for corrosion control of metals and metal alloys contacted with CoC 4 municipal wastewater in cooling systems, 1) TTA can be employed for copper and copper alloy corrosion inhibition, 2) monochloramine biocide can be used to replace free chlorine biocide, and 3) phosphorous-based corrosion inhibitors

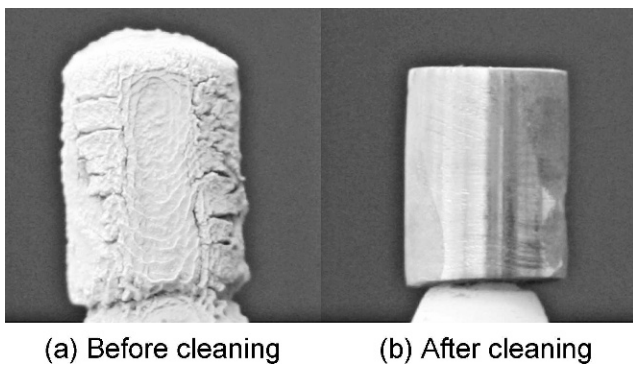


Figure 4—Mild steel specimen withdrawn from pilot-scale cooling tower system (Tower B2) after 21 days running with secondary treated municipal wastewater from Franklin Township Municipal Sanitary Authority. (a) Dried mild steel specimen before surface cleaning. (b) Mild steel specimen after acid surface cleaning.

are not appropriate to be used due to their precipitation with orthophosphate.

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