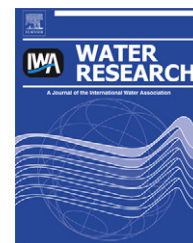


Available at www.sciencedirect.comjournal homepage: www.elsevier.com/locate/watres

Control of mineral scale deposition in cooling systems using secondary-treated municipal wastewater

Heng Li^a, Ming-Kai Hsieh^b, Shih-Hsiang Chien^a, Jason D. Monnell^a, David A. Dzombak^b, Radisav D. Vidic^{a,*}

^a Department of Civil and Environmental Engineering, University of Pittsburgh, Pittsburgh, PA 15261, United States

^b Department of Civil and Environmental Engineering, Carnegie Mellon University, Pittsburgh, PA 15213, United States

ARTICLE INFO

Article history:

Received 10 June 2010

Received in revised form

19 August 2010

Accepted 30 August 2010

Available online 9 September 2010

Keywords:

Scaling

Mineral deposition

Precipitation

Cooling water

Municipal wastewater

Antiscaling

ABSTRACT

Secondary-treated municipal wastewater (MWW) is a promising alternative to freshwater as power plant cooling system makeup water, especially in arid regions. A prominent challenge for the successful use of MWW for cooling is potentially severe mineral deposition (scaling) on pipe surfaces. In this study, theoretical, laboratory, and field work was conducted to evaluate the mineral deposition potential of MWW and its deposition control strategies under conditions relevant to power plant cooling systems. Polymaleic acid (PMA) was found to effectively reduce scale formation when the makeup water was concentrated four times in a recirculating cooling system. It was the most effective deposition inhibitor of those studied when applied at 10 mg/L dosing level in a synthetic MWW. However, the deposition inhibition by PMA was compromised by free chlorine added for biogrowth control. Ammonia present in the wastewater suppressed the reaction of the free chlorine with PMA through the formation of chloramines. Monochloramine, an alternative to free chlorine, was found to be less reactive with PMA than free chlorine. In pilot tests, scaling control was more challenging due to the occurrence of biofouling even with effective control of suspended bacteria. Phosphorous-based corrosion inhibitors are not appropriate due to their significant loss through precipitation reactions with calcium. Chemical equilibrium modeling helped with interpretation of mineral precipitation behavior but must be used with caution for recirculating cooling systems, especially with use of MWW, where kinetic limitations and complex water chemistries often prevail.

© 2010 Elsevier Ltd. All rights reserved.

1. Introduction

With increasing shortages of freshwater, wastewater is now being recognized as a significant source of water for non-potable uses (Miller, 2006; Metcalf & Eddy, 2007). Among different types of wastewater, secondary-treated municipal wastewater (MWW) is of increasing interest, primarily because it holds promise as a viable alternative source of cooling water in terms of quantity and geographical proximity

to existing and future power plants in the US (Vidic and Dzombak, 2009). A number of power plants already use MWW as makeup water in their recirculating cooling water systems (Ehrhardt et al., 1986; EPRI, 2008). The majority of these power plants are in regions of the US most susceptible to freshwater constraints, i.e., the southwest and Florida. These power plants typically use MWW only as a fraction of the total makeup water needed or only after significant additional treatment to obtain better water quality.

* Corresponding author. Tel.: +1 412 624 9870; fax: +1 412 624 0135.

E-mail address: vidic@pitt.edu (R.D. Vidic).

0043-1354/\$ – see front matter © 2010 Elsevier Ltd. All rights reserved.

doi:10.1016/j.watres.2010.08.052

The primary challenges with MWW reuse for cooling arise from its low quality. Secondary-treated MWW usually contains appreciable amounts of hardness, phosphate, ammonia, dissolved solids, and organic matter compared to the amounts in freshwater (Weinberger et al., 1966; Williams and Middlebrooks, 1982). In recirculating cooling systems, the water constituents become concentrated many times (typically 4–8 times) because of the evaporative loss of water. The elevated concentrations and high water temperature can cause severe mineral deposition (scaling) problems, along with the problems of corrosion and biofouling. Because of these challenges, intensive chemical control programs are usually implemented (EPRI, 2003). Neither the mineral deposition characteristics of MWW under cooling system conditions nor the feasibility of controlling deposit formation through chemical addition when using MWW as the sole source of makeup water in a recirculating cooling system have been studied.

Presently, three types of deposit inhibition chemicals—antiscalants—are widely used to prevent mineral deposition on pipe and heat exchanger surfaces in cooling systems: carboxylic polymers, such as polyacrylic acid (PAA), polyacrylamide, and polymaleic acid (PMA); phosphonates; and polyphosphates. Polymeric antiscalants often incorporate functional groups in addition to carboxylate such as sulfonate or benzenesulfonate (Shakkthivel and Vasudevan, 2006; Du et al., 2009).

Multiple antiscaling mechanisms working together contribute to the effectiveness of the antiscaling chemicals. First, the precipitation propensity of minerals is mitigated through complexation with antiscalant molecules to increase the operational solubility of cationic species, primarily Ca and Mg, the most common potential scale forming species in water (Eriksson et al., 2007). Second, the antiscalants can interact with newly formed mineral nuclei to disrupt the crystallization process, thereby hindering the growth of the precipitating particles (Frayne, 1999; Shakkthivel and Vasudevan, 2006). Antiscalants for which this mechanism is dominant are commonly referred to as threshold inhibitors. Third, antiscalant molecules can stabilize the mineral particulates through electrostatic and/or steric interactions to keep them dispersed in the aqueous suspension, rendering them less prone to sedimentation or deposition (Eriksson et al., 2007). A fourth mechanism of scale inhibition involves adsorption of antiscalants onto pipe surfaces to prevent mineral deposition onto the surfaces. For example, phosphorous-bearing groups exhibit strong interactions with surfaces of metals and metal oxides (Nowack, 2003). Based on the similar mechanism of surface adsorption, some phosphonates and polyphosphates are used as corrosion inhibitors as well because a surface layer of these molecules retards surface redox reactions (Kielemoes et al., 2000). However, many of the phosphorous-based compounds, particularly the polyphosphates, suffer from hydrolysis reactions that produce orthophosphate (Snoeyink and Jenkins, 1980), potentially exacerbating phosphate scaling when the water contains significant hardness. The effectiveness and fate of phosphorous-based inhibitors when applied in cooling systems using MWW have not been well studied.

Numerous polymer antiscalants with varied molecular weight, structural features, and effectiveness in different

waters are available commercially. PMA was selected in this study as a model polymer antiscalant based on a literature survey and consultation with practitioners in cooling system design and operation. PMA is believed to act as both a colloid dispersant and a crystal distorter, particularly for Ca-containing precipitates, the potentially dominant scale formers in MWW (Christophersen, 2007; Metcalf & Eddy, 2007; EPRI, 2008; Scandola, 2008; Beardwood, 2009). Besides PMA, representative antiscalants containing phosphonates or polyphosphates, including 2-phosphonobutane-1,2,4-tricarboxylic acid (PBTC) and tetrapotassium pyrophosphate (TKPP), were also tested for their effectiveness in MWW.

The influence of orthophosphate and ammonia present in MWW on scaling control is of particular interest because phosphate can precipitate with di- and trivalent cations while ammonia is a strong complexing agent for copper and iron, both of which are common pipe/heat exchanger materials in cooling systems (Stumm and Morgan, 1996). Another concern with the use of MWW for cooling lies in the need to control biogrowth. The use of chlorine as a biocide may potentially compromise the effectiveness of organic antiscalants because free chlorine, a strong oxidant, is aggressive toward many aqueous organic compounds and pipe materials. For example, studies show that large doses of chlorine significantly increase mild steel corrosion (Nalepa et al., 1999), which leads to iron dissolution and precipitation on the pipe. Ammonia, on the other hand, can combine with free chlorine to form chloramines, which poses less risk for metal alloy corrosion (Zhang et al., 2008). The influence of chloramines on scaling control in cooling systems that use MWW has not been investigated.

Quantitative analytical methods for studying mineral scaling in cooling systems are not readily available in the literature. There is a general lack of well-documented methods suitable for in situ measurements of mineral deposition kinetics. Most established techniques pertaining to mineral scaling phenomena confine themselves to means of static observations and analysis only after solid scales have formed and been collected. For example, ASTM standard methods D 1245-84, D 2331-80, D 933-84, D 934-80, and D 887-82 only deal with the procedures of removing water-formed deposits from sample tubes by specified mechanical or chemical means, and with qualitative identification of deposits by spectroscopy-based analysis. Very limited effort has been devoted to the study of mineral scaling kinetics in terms of how scales form, at what rate(s) they form, and the mechanisms and conditions influencing their formation in waters of varying quality.

The objectives of this study were to investigate the effects of orthophosphate and ammonia on the performance of scaling control by PMA in cooling systems using MWW, and to test the feasibility of biocontrol by chlorine and corrosion control by phosphorous-bearing chemicals without interfering with scale inhibition under recirculating cooling conditions. Equilibrium calculations were performed to evaluate the mineral deposition potential of MWW under a range of cooling water conditions. Laboratory studies were conducted to determine effective deposition control strategies under conditions relevant to industrial cooling systems, i.e., elevated temperature, circulating flow, and concentrated water constituents. In addition, pilot-scale cooling tower tests

were conducted to study the effectiveness of the model polymer antiscalant, PMA, and the potential applicability and implications of an integrated chemical regimen for the successful control of scaling, corrosion, and biofouling in using treated MWW for cooling.

2. Materials and methods

2.1. Secondary-treated municipal wastewater

A secondary-treated municipal wastewater effluent (i.e., biological trickling filter followed by secondary clarification) was collected for use in bench-scale experiments. The effluent was collected at the Franklin Township Municipal Sanitary Authority (FTMSA) wastewater treatment plant located in Murrysville, PA. Polyethylene (PE) containers (1 L bottles or 5-gallon jars) were used for temporary storage of the MWW before experiments. Typical storage time was less than 24 h, otherwise the water was refrigerated.

To characterize the water quality, both filtered (0.45 μm) and unfiltered water samples were transferred to different PE containers that were prepared with the addition of appropriate acid preservatives. Metal concentrations were determined by inductively coupled plasma mass spectroscopy (ICP-MS) at a commercial lab (Test America, Pittsburgh, PA). Other parameters were determined either in our laboratory or at the commercial lab, using appropriate standard test procedures (Li, 2010). The concentrations of calcium and magnesium, the two principal cationic species, were measured by Atomic Absorption Spectroscopy (AAS). The water quality data are provided in Table 1. As indicated in Table 1, the wastewater represents well the typical secondary-treated municipal effluent (Metcalf & Eddy, 2007).

For bench-scale experiments, the wastewater effluent sample was concentrated in the laboratory by evaporation at 40 °C to reach 4 cycles of concentration (CoC 4) as determined by 75% volume reduction, prior to use in a bench-scale water recirculating system (Fig. 1). However, it was discovered from preliminary tests that pre-concentrating the MWW resulted in a loss of mineral content due to precipitation that took place during the concentration step. This premature precipitation made the concentrated water less representative of MWW at CoC 4. As such, a synthetic municipal wastewater was prepared that truly represented CoC 4 in terms of its mineral content (i.e., four times more concentrated than the MWW) for detailed investigation in the bench-scale studies. The synthetic MWW (CoC 4) was made using DI water (resistivity > 18 M Ω cm) with the addition of desired chemical constituents (reagent grade or better). The chemical recipe of the synthetic MWW (CoC 4) is provided in Table 2. The composition of the synthetic MWW was chosen to represent the typical secondary-treated municipal effluent (Metcalf & Eddy, 2007).

2.2. Antiscalants and other chemicals

PMA and PBTC, both in 50% active content, were provided by Kroff Chemical Company (Pittsburgh, PA). TKPP (48% active content) was provided by Crown Solutions/Veolia Water

Table 1 – Chemical composition of the secondary-treated municipal wastewater (MWW) from Franklin Township Municipal Sanitary Authority, Murrysville, PA.

Analyte	Unit	Result		Detection limit
		(unfiltered)	(filtered)	
Al	mg/L	0.2	–	0.2
Ca	mg/L	42	41	5
Cu	mg/L	0.028	–	0.025
Fe	mg/L	0.5	0.37	0.1
K	mg/L	16.3	NA ^a	5
Mg	mg/L	10.7	10	5
Mn	mg/L	0.32	–	0.015
Na	mg/L	94	NA	5
SiO ₂	mg/L	8.54	NA	1.07
Zn	mg/L	0.07	NA	0.02
pH		7.1	7.2	
NH ₃	mg N/L	21.0	NA	0.5
NO ₃	mg N/L	3.6	NA	0.1
HCO ₃ Alkalinity	mg CaCO ₃ /L	177	NA	5
Total Alkalinity	mg CaCO ₃ /L	177	NA	5
BOD	mg/L	32	NA	
Cl	mg/L	106	NA	10
SO ₄	mg/L	86	NA	1
Total P	mg P/L	4.5	NA	0.5
TOC	mg/L	27	NA	1
TDS	mg/L	661	NA	10
TSS	mg/L	NA	41	5
Conductance	mS/cm	1.03	1.02	0.01
Turbidity	NTU	16.7	NA	1

a NA: Not Analyzed.

(Vandalia, OH). Free chlorine was used as concentrated sodium hypochlorite (NaOCl) solution (5%). Monochloramine was pre-formed by mixing NaOCl and ammonium chloride (NH₄Cl) at 4:1 Cl₂:NH₃ mass ratio and was used immediately (Kirmeyer et al., 1993).

PMA concentrations were determined colorimetrically at 505 nm using a commercial test kit (MCI analytical test procedure, Masters Company, Wood Dale, IL). The concentrations of PBTC and TKPP were monitored by following Standard Method 4500-P (American Public Health Association et al., 2005). Free chlorine and monochloramine were measured with a chlorine photometer (HF Scientific Inc., FL).

2.3. Scaling study in bench tests

A customized bench-scale water recirculating system was equipped with removable stainless steel (SS316) circular disc specimens to provide surfaces for scaling/deposition in the recirculating water (Fig. 1). Mineral mass deposited on the SS surfaces (5.61 cm² per disc) was determined to track the scaling process with varied water chemistries and scaling control strategies. Water temperature and flow velocity were 40 °C (105 °F) and 0.6 m/s, respectively, to reflect actual conditions of industrial cooling systems. In a typical test, the recirculating water was exposed to air so that the alkalinity may approach equilibrium with CO₂(g), as is the case with actual cooling system operation. Before use, the SS specimens were cleaned by ultrasonic wash for 5 min in an acetone/ethanol solution (1:1 v/v ratio), rinsed with DI water and air-dried in a laminar

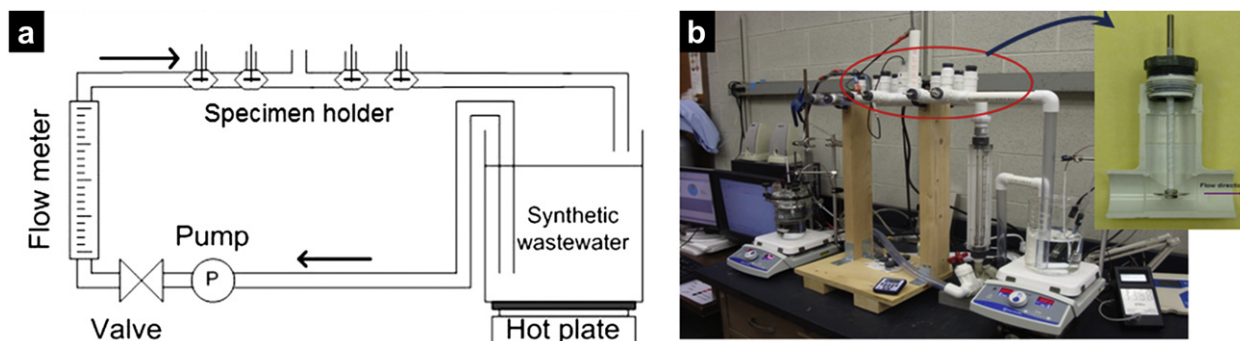


Fig. 1 – Customized bench-scale water recirculation system for examining mineral deposition. (a) Schematic flow chart. (b) Picture of the experimental setup with a pipe flow section showing the circular metal disc used to collect mineral deposits.

flow hood. At predetermined time intervals during an experiment, the SS specimens were taken out of the recirculating water through the sampling ports. The water remaining on the disc surface was carefully removed by paper tissue without disturbing the solid deposits on the surface. The discs were then air-dried for at least 48 h and the mass of each disc was measured using an analytical balance (Mettler AE163, detection limit 0.01 mg). Final weighing was performed only after a constant mass was achieved (mass measurement variation < 0.05 mg/h). Three measurements were taken for each specimen and the average value was reported as the mineral mass on the disc.

After weighing, the morphology of the scale samples was inspected using Scanning Electron Microscopy (SEM, Philips XL30, FEI Co., Hillsboro, OR), and the scale elemental compositions were determined by Energy Dispersive X-ray Spectroscopy (EDS, EDAX Inc., Mahwah, NJ). Samples were not sputtered with Au or Pd prior to the SEM/EDS analyses. These examinations were useful to identify the scale characteristics and facilitated the selection of effective scaling control approaches. For example, the identification of the mineral deposits by SEM/EDS provided evidence for the selection of the appropriate antiscaling chemicals to inhibit the formation of the specific minerals identified in the scales.

After each experiment, the recirculating system was cleaned by running HCl solution (pH 2–3) for about 1 h,

followed by a DI water rinse times, with 0.5 h of water recirculation each time.

2.4. Pilot-scale cooling tower tests

Pilot-scale cooling towers were constructed and operated with secondary-treated MWW (Fig. 2) to test the optimal chemical treatment regimen that was identified from the bench-scale experiments. The pipe section for scale collection on disc specimens had a similar design as used in the bench-scale tests. For simultaneous evaluation of different scaling control programs, three towers were operated side by side at the wastewater treatment plant of the Franklin Township Municipal Sanitary Authority (Murrysville, PA). Chemical control of biofouling and corrosion was also implemented. All three towers were operated at CoC 4, using a flow velocity of 0.6 m/s. The temperature of water entering the tower was 40 °C (105 °F) and leaving the tower was 35 °C (95 °F).

The loading rate of each tower was 123 L/min/m² (the cross-sectional area of the tower was 0.093 m²). The tower fill was fabricated from rigid, corrugated PVC sheets and had a surface area of 147.8 m²/m³ (Brentwood Industries, Reading, PA). The volume of each tower fill was 0.085 m³, or 1' W × 1' L × 3' D. Under steady state operations at CoC 4, 120–160 L of MWW makeup water was added daily to each tower.

The cooling towers were tested for two consecutive 21-day periods. The first run was a full operation with all three towers and the second run used two towers. The primary purpose for the second run was to test the biocontrol by pre-formed monochloramine instead of free chlorine (Chien et al., submitted for publication). Between the two tests, the towers were cleaned with an acetic-acid solution and treated with free chlorine as a biocide. Detailed information on tower operations was recorded, including the water temperature profile at different locations, the airflow rate inside the cooling tower, the conductivity of circulating water, the flowrates of makeup water, recirculating water, and blowdown stream, as well as the ambient conditions (weather, air temperature, relative humidity, etc.). The rates of solid deposition on stainless steel disc specimens were measured during both runs. In addition, the corrosion of selected metal alloys and the bioactivity in the towers were monitored by a coupon weight loss method (Hsieh et al., in press) and by

Table 2 – Chemical composition of synthetic MWW (simulating CoC 4) used for MINEQL+ modeling calculations and bench-scale experiments.

Cation	Concentration		Anion	Concentration	
	mM	mg/L		mM	mg/L
Ca ²⁺	7.60	305	SO ₄ ²⁻	2.84	273
Mg ²⁺	7.16	174	HCO ₃ ⁻	13.44	820
Na ⁺	26.88	618	Cl ⁻	31.13	1105
K ⁺	0.70	27	PO ₄ ³⁻	0.21	20
NH ₄ ⁺ (as N)	7.01	98			

The initial level of TDS of the water, before any precipitation takes place, is 3455 mg/L.

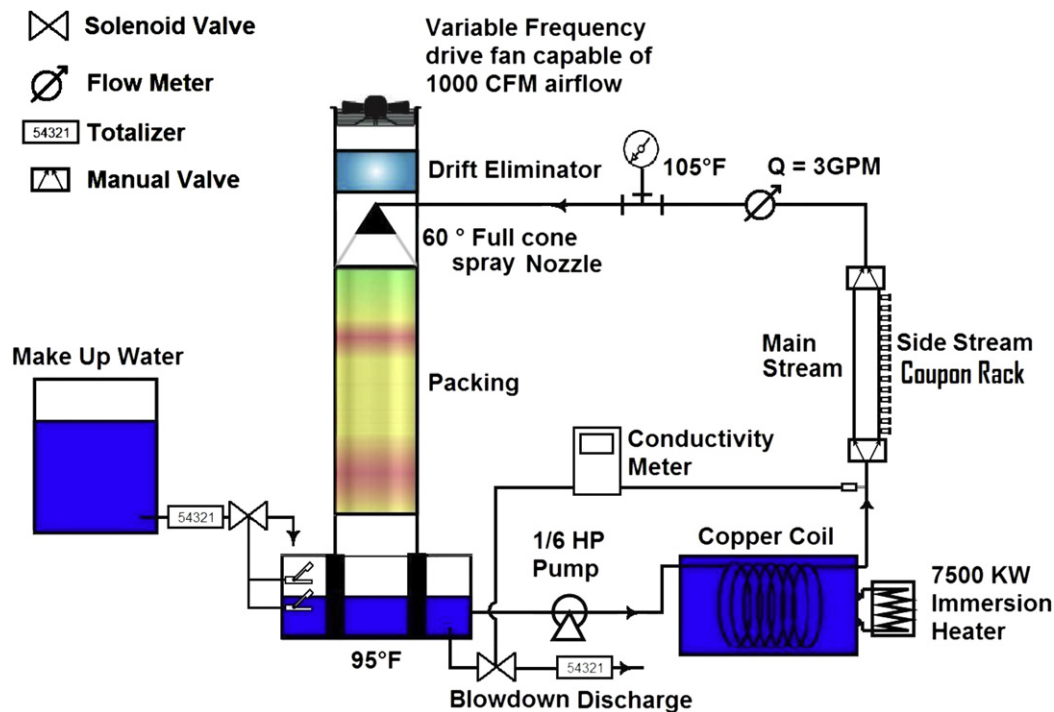


Fig. 2 – Schematic of pilot-scale cooling tower. The disc coupon rack had a similar design as in the bench-scale recirculation system (Fig. 1).

heterotrophic planktonic/sessile bacteria counts (Chien et al., submitted for publication), respectively. A planktonic heterotrophic bacteria plate count was performed following the spread plate count method. Plate count agar was used as the culture medium and the plates were incubated for at least 48 h at 35 °C.

2.5. MINEQL modeling

Chemical equilibrium modeling using MINEQL+ (Schecher and McAvoy, 1992, 1999) version 4.6 was performed to estimate the mineral precipitation potential of the secondary-treated MWW, the chemical composition of solid precipitates, and their relative abundance. System parameters specified for the modeling included temperature of 40 °C and a closed system with respect to carbonate equilibria.

3. Results and discussion

3.1. Bench-scale recirculating experiments with synthetic MWW (CoC 4)

The use of a synthetic municipal wastewater allowed the representation of the recirculating cooling conditions in which secondary-treated MWW as the sole makeup water was concentrated to CoC 4. A series of experiments was conducted to test the effectiveness of the antiscalants PMA and PBTC at CoC 4 and to evaluate the impact of chlorine-based biocides, ammonia, and phosphate on the performance of the antiscalants. In cooling systems using freshwater, typical doses of

antiscalants are 5–10 mg/L, depending on the specific water quality (Christophersen, 2007; Scandolari, 2008). In this study using MWW, higher doses were used considering the impaired water quality.

3.1.1. Effect of antiscalants addition

Without antiscalants addition, the mineral deposits collected on a disc specimen at CoC 4 during the recirculation of the synthetic MWW were, on average, more than 2 mg (Fig. 3). As a comparison, the deposits collected at CoC 1 were between 0 and 0.2 mg (data not shown in figure). The antiscalant PBTC dosed at 10 mg/L suppressed deposition to about 0.2 mg, which was more effective than when dosed at 5 mg/L (Fig. 3), suggesting that the MWW concentrated to CoC 4 demands higher doses of antiscalants for scaling control, as compared with typical values used for freshwater (Christophersen, 2007; Scandolari, 2008). PMA dosed at 10 mg/L inhibited scaling nearly completely, demonstrating its superior antiscaling effect in the synthetic MWW (CoC 4). Based on data in Fig. 3, the initial scaling rate (within the first 12 h or so) of MWW with 10 mg/L of PMA addition was estimated to be near zero while the initial scaling rate with 10 mg/L of PBTC was 0.025 mg/h. The overall average scaling rate with 10 mg/L of PMA was calculated to be 0.0018 mg/h and that with 10 mg/L of PBTC was 0.0085 mg/h.

It appeared that scaling occurred within about 12 h beyond which no significant amount of additional scale formed. In these bench-scale tests, supersaturated synthetic MWW representing CoC 4 was subjected to recirculating in a water loop where external heat was provided to raise the water temperature to 40 °C. Mineral precipitation and deposition (scaling)

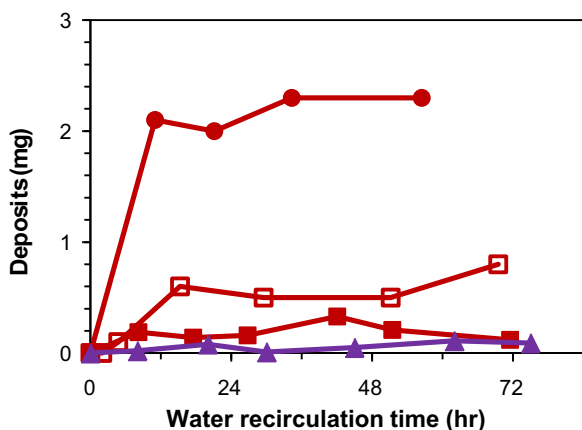


Fig. 3 – Scaling behavior of a synthetic municipal wastewater (CoC 4) in bench-scale tests with inhibitors at different dosing (40 °C): No inhibitors (●), 5 mg/L of PBTC (□), 10 mg/L of PBTC (■), 10 mg/L of PMA (▲).

took place until the supersaturation level was substantially decreased. Because no additional CoC 4 water was added to the system during mass gain data acquisition, no continued scaling was observed after about 12 h.

3.1.2. Influence of ammonia and phosphate

As can be seen in Fig. 4, the removal of ammonia, which was present as 100 mg N/L in the other tests, resulted in significant scale formation compared with the case in which the addition of antiscalants substantially reduced scaling in the presence of ammonia. Conversely, the removal of orthophosphate (as 20 mg PO₄/L) did not exhibit a profound impact on scaling control by PBTC, which implies that the addition of the antiscalant (10 mg/L) was sufficient to reduce phosphate mineral scale formation. The beneficial role of ammonia for scaling inhibition was due to both complexation reactions between ammonia and calcium (confirmed by chemical equilibrium

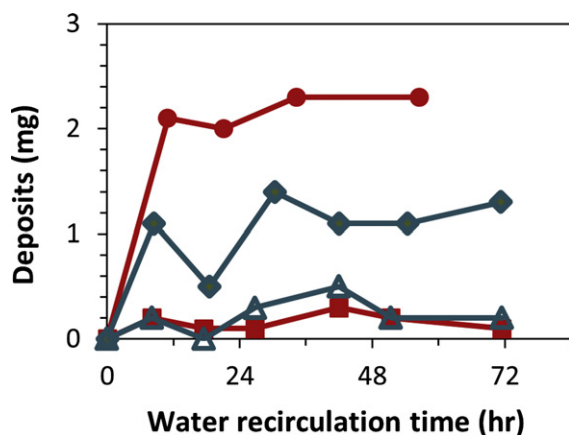


Fig. 4 – Influence of ammonia and phosphate on scaling control in bench tests with a synthetic MWW at CoC 4 (40 °C). No inhibitors (●), 10 mg/L of PBTC (■), 10 mg/L of PBTC, no ammonia (◆), 10 mg/L of PBTC, no phosphate (▲).

modeling) and ammonia adsorption onto mineral surfaces to disrupt particle growth (Gehrke et al., 2005). Also, given the predominance of ammonium ions in the experimental pH range (pH 7.5–8) where the water recirculating system operated, some complexation between NH₄⁺ and carbonate species could also occur to further decrease the precipitation potential of carbonate minerals.

3.1.3. Interference of chlorine biocides

As shown in Fig. 5, the addition of chlorine biocides for bio-growth control negatively impacted scaling inhibition by either PBTC or PMA. In the absence of the biocides, PBTC substantially inhibited scale formation while PMA nearly completely inhibited scaling. However, the addition of free chlorine caused a significant decrease in the antiscaling efficiency as both antiscalants were significantly impaired by the oxidizing biocides. It is noteworthy that free chlorine was more detrimental than monochloramine to compromise the antiscaling effects of PBTC and PMA, even for the case with elevated dosing of 20 mg/L of PMA (Fig. 6).

The interaction between PMA and free chlorine is explained by the data shown in Fig. 6. In the absence of free chlorine, the PMA concentration remained stable during the entire period of experiment (6 days). After 3 days of interaction with free chlorine, PMA started to deplete for both doses tested. Furthermore, during the experiment with 20 mg/L of PMA addition, total chlorine demand was much greater than in the experiment with 10 mg/L of PMA. To maintain a constant level of chlorine in solution, i.e., 1 mg/L, a total of 26 mg/L of chlorine was added over the 6 days of the experiment. In comparison, only 6 mg/L of chlorine was needed to maintain the 1 mg/L concentration level over the same period of experiment with 10 mg/L of PMA addition. This explains, at least in part, the sharp decrease in PMA after day 3. PMA was substantially consumed by chlorine, especially after 3 days, and consequently, the scaling inhibition efficiency was greatly reduced, as evidenced by the appreciable increase in the mineral mass deposited on test coupons after 3 days. A number of studies have used PMA as a model compound of natural organic matter (NOM) owing to its resemblance of the chemical and structural characteristics of natural humic and fulvic acids (Anderson and Russell, 1976; Hess and Chin, 1996; Wang et al., 1997). It is hence not surprising to observe the destruction of PMA by free chlorine, given the extensively-studied formation pathways of disinfection by products (DBPs) from NOM and chlorine biocides (Li et al., 2000; Kitis et al., 2001; Hassan et al., 2006; Roccaro et al., 2008; Chowdhury et al., 2009; Johnstone and Miller, 2009). Separate batch tests of PBTC in the presence of chlorine additives showed stability of PBTC up to 150 h. As such, deposit data beyond 72 h were not collected in Fig. 5.

3.2. Pilot-scale study with secondary-treated MWW

3.2.1. Changes of water chemistry due to scaling

Table 3 shows the chemical treatment program for simultaneous control of scaling, corrosion, and biofouling in pilot-scale cooling towers. The program included the addition of PMA and PBTC as scaling inhibitors, TKPP and Tolyltriazole (TTA) as corrosion inhibitors, and free chlorine (the first run) or

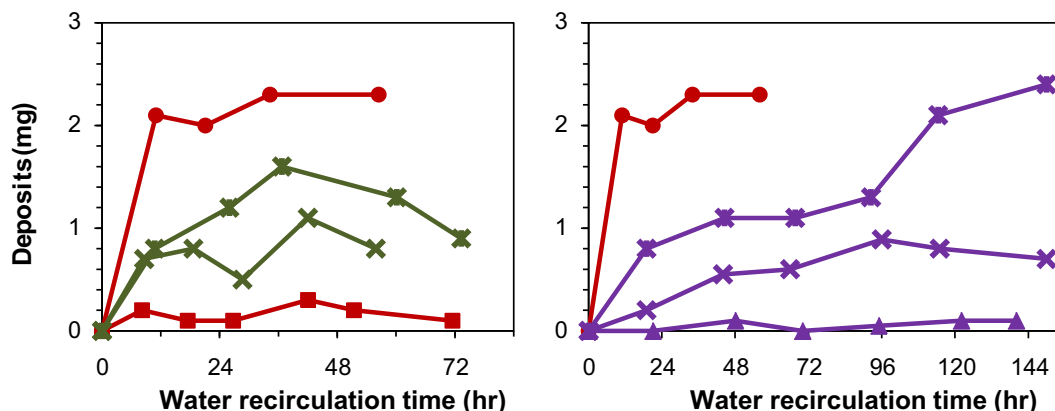


Fig. 5 – Interference of chlorine-based biocides on scaling control in bench tests with a synthetic MWW at CoC 4 (40 °C). Left: No inhibitors, no biocides (●), 10 mg/L of PBTC, no biocides (■), 10 mg/L of PBTC, 1 mg/L of free chlorine (*), 10 mg/L of PBTC, 1 mg/L of monochloramine (×). Right: No inhibitors, no biocides (●), 10 mg/L of PMA, no biocides (▲), 10 mg/L of PMA, 1 mg/L of free chlorine (*), 10 mg/L of PMA, 1 mg/L of monochloramine (×).

monochloramine (the second run) as biocides. The results of the pilot-scale studies provided evidence for the effectiveness of PMA, PBTC, and TKPP in preventing scaling from the MWW at larger scale.

Water samples, obtained from the recirculating loop of each cooling tower operated at steady state, were analyzed for key constituents and chemical parameters (Tables 4 and 5). Before reaching the steady state of CoC 4, a sharp increase of water pH from 7.2 of the makeup water (secondary effluent) to 8.3 was observed in each tower, primarily due to an aeration effect of the cooling towers that liberated CO₂ from the water. It is well known that effluent from the secondary clarifier in a wastewater treatment plant is commonly over saturated with CO₂ yielded by the continuing aerobic biodegradation of residual organic carbon (Sperandio and Paul, 1997; Ficara and Rozzi, 2004; Weissenbacher et al., 2007; Zhang et al., 2009). We analyzed the pH behavior of the cooling towers through measurements and modeling. Detailed description about the pH changes will be reported separately. After reaching CoC 4, the alkalinity in the recirculating water was generally 2–4

times higher than in the makeup water, further raising the pH to 8.5–9. The concentration factor of 2–4 for alkalinity was lower than the volume-based CoC because part of the alkalinity was lost to the precipitation of carbonate solids.

Concentrations of chloride in the cooling water were typically 6–7 times higher than in the makeup water. This ratio is higher than the expected ratio based on the water volume reduction (i.e., CoC 4–5). The extra chloride of some 350 mg/L (estimation based on Table 5) in the recirculating water came from the addition of chlorine biocides (either free chlorine for the first run or monochloramine for the second run).

Concentrations of sulfate in the cooling water were generally 4–5 times higher than in the makeup water, which corresponded well to the volume-based CoC because there was no additional sink or source for sulfate, and as such, sulfate behaved as a conservative species.

Total phosphate concentrations in the tower water were much lower than that in the makeup water—nearly 90% of the phosphate precipitated out of water due to its low solubility in the presence of high calcium (100 mg/L, or 2.5 mM) under the

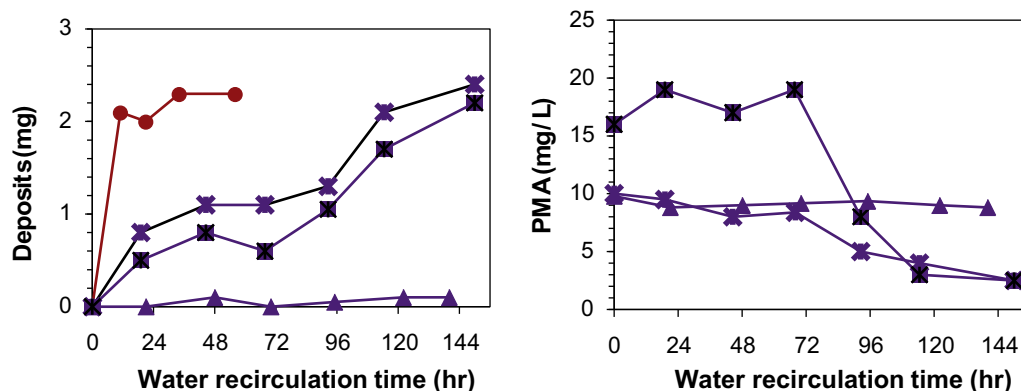


Fig. 6 – Interference of chlorine biocides with PMA on scaling control in bench tests with a synthetic MWW at CoC 4 (40 °C). Left: Scaling behavior. Right: Depletion of PMA concentration in the aqueous solution. No inhibitors, no biocides (●), 10 mg/L of PMA, no biocides (▲), 10 mg/L of PMA, 1 mg/L of free chlorine (*), 20 mg/L of PMA, 1 mg/L of free chlorine (*).

Table 3 – Chemical treatment program (target concentration) for pilot-scale cooling tower tests with secondary-treated MWW at Franklin Township, PA (unit: mg/L).

Chemical addition		First Run			Second Run	
		Tower A	Tower B	Tower C	Tower A	Tower B
		Corrosion Control	TTA	1	2	2
Scaling Control	TKPP	0	10	10	0	0
Biocontrol	PMA	0	10	20	0	10
	PBTC	0	5	10	0	0
	Free Cl ₂	1.5	1.5	1.5	0	0
	MCA	0	0	0	3	3

TTA: Tolyltriazole; TKPP: tetrapotassium pyrophosphate; PMA: polymaleic acid; PBTC: 2-phosphonobutane-1,2,4-tricarboxylic acid; MCA: monochloramine.

cooling tower conditions investigated. For example, TKPP, a polyphosphate, was added primarily as a corrosion inhibitor (10 mg/L as PO₄). However, the measured TKPP concentration in the recirculating water was less than 1 mg/L—most of it precipitated and became unavailable for corrosion control. Therefore, the feasibility of using phosphate-based corrosion inhibitors such as TKPP in secondary-treated municipal wastewater is questionable because it may only add to more challenges for scaling control.

Tower A, which received no PMA or PBTC for scaling inhibition, precipitated the greatest amount of calcium. The amount of calcium in the recirculating water accounted for 60–70% of the amount fed with the makeup water, i.e., 30–40% of the calcium precipitated. The degree of calcium removal by precipitation will be discussed in more detail.

Similar to sulfate, magnesium was 4–5 times more concentrated in the cooling water than in the makeup water, suggesting that magnesium precipitation was minimal. This was confirmed by the EDS analysis, which revealed nearly undetectable amount of magnesium in the collected solids.

PMA was added to Towers B and C for scaling control during the first run. The concentrations and fate of PMA were monitored periodically. The target levels of PMA in Towers B and C were 10 mg/L and 20 mg/L, respectively (daily addition was based on the volume of blowdown water). Detected PMA in Tower A, however, was 7 mg/L on average, suggesting that about 30% of the PMA was removed with precipitated mineral solids and settled out of the liquid phase, or was degraded by chlorine. Furthermore, free PMA (the filterable fraction) accounted for about 60% of total aqueous PMA. The rest (40%) was most likely associated with suspended solids. Studies have shown that anionic polyelectrolytes such as PMA tend to adsorb onto mineral particles and prevent solids settling by providing an electrostatic and/or steric stabilization mechanism (Wang et al., 1997; Shakkthivel et al., 2005; Eriksson et al., 2007; Sonnenberg et al., 2007).

3.2.2. Mass deposition measurement

Fig. 7 shows the accumulated scale solids deposited on stainless steel disc specimens in the three cooling towers with different dosing strategies. Tower A, as a control tower, received no antiscaling chemicals. In Tower B, the addition of 10 mg/L of PMA and 5 mg/L of PBTC resulted in the least scaling among the three towers. However, when the dosing of PMA and PBTC was doubled in Tower C, expected better scaling inhibition was not observed and actually the scales accumulated as much as those in the control tower without antiscaling treatment (Tower A). It appeared that overdosing had occurred. Given the small increment between the two dosings, the ionic strength of the cooling water was not increased significantly, and as such, compression of the electrical double layer of suspended particles was unlikely to be important in destabilizing them in Tower C. It is more likely, however, that interparticle bridging due to the double dosing of PMA might cause particle destabilization and subsequent deposition (scaling), an effect similar to enhanced coagulation by polymers.

The main difference between bench-scale experiments (Figs. 3–6) and pilot-scale cooling towers (Fig. 7) was the

Table 4 – Concentrations of cationic species and PMA in makeup water (secondary effluent) and recirculating water (CoC 4–5) in field testing with pilot-scale cooling towers (unit: mg/L).

Species		Raw water	First Run			Second Run	
			Tower A	Tower B	Tower C	Tower A	Tower B
Ca	Total	35.2 ± 1.5	97 ± 7	112 ± 8	111 ± 10	105 ± 3	113 ± 7
	Filterable	34.5 ± 1.1	91 ± 7	100 ± 9	102 ± 11	98 ± 4	103 ± 6
Mg	Total	10 ± 1	47 ± 8	58 ± 5	57 ± 5	46 ± 3	43 ± 3
	Filterable	10 ± 1	45 ± 8	55 ± 4	54 ± 5	44 ± 3	42 ± 3
Fe	Total	0.37 ± 0.11	0.59 ± 0.23	0.81 ± 0.25	0.68 ± 0.25	0.74 ± 0.24	0.86 ± 0.28
	Filterable	0.12 ± 0.03	0.06 ± 0.02	0.05 ± 0.04	0.07 ± 0.03	0.06 ± 0.03	0.08 ± 0.05
Cu	Total	0.06 ± 0.03	0.12 ± 0.03	0.13 ± 0.03	0.13 ± 0.04	0.28 ± 0.14	0.22 ± 0.09
	Filterable	0.06 ± 0.03	0.10 ± 0.03	0.10 ± 0.03	0.11 ± 0.04	0.23 ± 0.11	0.18 ± 0.09
PMA	Total	–	–	6.8 ± 1.9	14.6 ± 2.6	–	6.9 ± 1.6
	Filterable	–	–	4.3 ± 1.3	9.7 ± 2.1	–	4.5 ± 1.3

Data are mean values ± 1 sd. Sample size for raw water $n = 7$. Samples for recirculating water in the cooling towers were from day 4 to day 24 during the tower operation (sample size for tower A: 10, tower B: 10, tower C: 11).

Table 5 – Concentrations of anionic species and other chemical additives (for corrosion and biofouling control) in makeup water (secondary effluent) and recirculating water (CoC 4–5) in field testing with pilot-scale cooling towers (unit: mg/L).

Species	Raw water	First Run			Second Run	
		Tower A	Tower B	Tower C	Tower A	Tower B
ALK	113 ± 34	283 ± 54	364 ± 53	324 ± 25	232 ± 68	244 ± 79
SO ₄	75 ± 7	357 ± 39	388 ± 49	378 ± 76	323 ± 30	356 ± 27
Cl	142 ± 22	955 ± 135	937 ± 74	917 ± 152	859 ± 133	1050 ± 115
PO ₄	11.5 ± 1.8	5.9 ± 1.1	4.1 ± 1.0	5.2 ± 0.6	7.5 ± 2.7	8.1 ± 3.3
TKPP	–	–	0.6 ± 0.4	0.6 ± 0.4	–	–
PBTC	–	–	0.8 ± 0.3	0.9 ± 0.7	–	–
TTA	–	1.0 ± 0.8	2.0 ± 0.9	1.8 ± 1.0	–	1.8 ± 1.0
Total Cl ₂	–	1.2 ± 0.9	1.0 ± 0.7	1.5 ± 0.8	3.2 ± 1.3	3.6 ± 2.2

For ALK, the unit is mg/L as CaCO₃.

continuous addition of makeup water (secondary-treated MWW) to the cooling towers. Unlike the scaling patterns observed in bench-scale tests where a plateau was obvious after about 12 h, scale was continuously formed over the entire test period (24 d) in cooling towers.

After day 8 (or 4 days after reaching steady state of CoC 4), an accelerated mass accumulation of solids on the coupon discs in all three towers was obvious. An analysis of solid composition revealed that biomass (the fraction burnable at 500 °C) accounted for 30–50% of the total accumulated solids, indicating that biofilm growth played an important role in surface fouling in the cooling towers using secondary-treated MWW. However, the total amount of biomass cannot be completely accounted for by the volatile organic matter burnable at 500 °C. For example, the mineral content of cells remaining after burning still contributed to the mass gain measurements. Moreover, the dynamic process of simultaneous biofouling and mineral scaling might enhance each other mutually—the mineral scales can provide a coating layer conducive to biofilm development compared to a smooth metal surface, and at the same time the organic matrix consisting of extracellular polymeric substances (EPS)

of the biofilm can help trap more mineral solids. For example, the inorganic mineral fraction of EPS can be as much as 77% of the EPS dry weight (d'Abzac et al., 2010).

3.3. Experimental observation vs. equilibrium prediction

The use of chemical equilibrium modeling with the model MINEQL+ (Schecher and McAvoy, 1992, 1999) allowed estimation of the mineral precipitation potential, the chemical composition of solid precipitates, and their relative abundance. In this study, mineral precipitates predicted by MINEQL+ were compared with the actual species that comprised the deposits collected from experiments conducted at both bench-scale water recirculating systems and pilot-scale cooling towers.

The precipitated solids from the bench- and pilot-scale tests were inspected using Scanning Electron Microscopy (SEM) and their elemental composition determined by Energy Dispersive X-ray Spectroscopy (EDS) analyses. The total mass of the solids collected in various tests was also compared to the amount predicted by MINEQL+ for the conditions tested. The information obtained from these comparisons was used to discuss the usefulness of the equilibrium modeling as a predictive tool in assessing the cooling water scaling behavior.

Based on the chemical composition of the synthetic MWW (Table 2), chemical equilibrium modeling predicted that hydroxyapatite (HAP) and dolomite would precipitate at CoC 4 (modeling condition: ionic strength corrected, 40 °C, and closed system) with the following amounts:

HAP [Ca₅(PO₄)₃OH](s): 0.07 mM (35.2 mg/L)
 Dolomite [CaMg(CO₃)₂](s): 6.44 mM (1187.5 mg/L)

Based on the modeling results, the elemental composition of the predicted solids is shown in Table 6 (Condition (1)).

For the simulations of synthetic MWW, the initial TDS of the water (CoC 4) was 3455 mg/L, of which 1223 mg/L were predicted to precipitate at equilibrium (35.4 wt%), leaving 65% of the initial TDS in solution (roughly, a 1:2 distribution in terms of precipitated vs. soluble total solids). Of particular interest is the distribution of Ca and Mg at equilibrium: precipitated, complexed, and free ions. Equilibrium prediction by MINEQL+ for synthetic MWW illustrated that almost 90% of the initial Ca and Mg should precipitate out of solution. Ca and

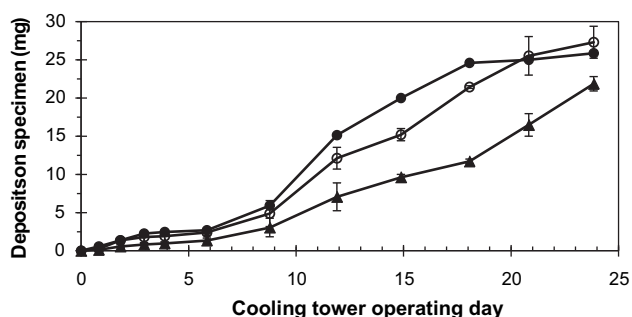


Fig. 7 – Deposit mass measurements in the pilot-scale cooling tower tests using secondary-treated MWW. Tower A, no inhibitors (○), Tower B, 10 mg/L of PMA (▲), Tower C, 20 mg/L of PMA (●). Deposits were collected on stainless steel disc specimens immersed in recirculating pipe flow. Effective collection area 5.61 cm², flow velocity 0.6 m/s (3 GPM flowrate in 3/4" pipe), water temperature 40 ± 1 °C (104 ± 2 °F), measured pH 8.5 ± 0.3. Error bars indicate the data range of measurements from duplicate tower tests.

Table 6 – Elemental composition of the precipitates from synthetic MWW: Modeling prediction vs. experimental observation.

Condition		Elemental Percentage					
		Ca	Mg	P	C	O	H
Modeling without kinetic constraints (1)	Molar	10.3	9.8	0.3	19.5	60.0	0.1
	Mass	22.3	12.8	0.5	12.7	51.8	0.0
Modeling with kinetic constraints (2) ^a	Molar	20.1	0	0.6	19.2	60.0	0.2
	Mass	40.0	0	0.9	11.4	47.7	0.0
Observed in bench experiments (3) ^b	Molar	28.7 ± 2.4	1.3 ± 0.2	0.0 ± 0.1	24.2 ± 1.1	45.8 ± 3.7	0.0 ± 0.1
	Mass	52.2 ± 3.1	1.4 ± 0.2	0.0 ± 0.1	13.2 ± 1.0	33.2 ± 3.4	0.0 ± 0.1

a No Mg precipitation.

b Data are mean values ± 1 sd based on triplicate measurements.

Mg are thus disproportionately removed from the solution compared to other aqueous species.

Stainless steel disc specimens immersed in the bench-scale recirculating system using the synthetic MWW were used to collect mineral deposits. After 6 days, the discs were removed from the recirculating water and air-dried prior to SEM/EDS analysis. The SEM image shows well-shaped crystalline morphologies of calcite (Fig. 8). Based on the EDS analysis, the average abundance of the elements in the collected solids is listed in Table 6 (Condition (3)). Both molar and mass concentrations were directly obtained from the EDS analysis (triplicate measurements). Compared to the model prediction (Table 6 Condition (1)), the sampled solids contained excess Ca but were deficient in Mg. This observation that Mg did not participate in the solids formation was confirmed by the essentially unchanged aqueous concentration of Mg over the course of experiment (Fig. 9). What the model predicted may be the most stable crystalline phases under equilibrium conditions. Deposits precipitated from the experimental water, while ultimately driven by thermodynamics, can experience different pathways of mineral formation which involved different kinetic constraints and/or inhibitory factors imposed by water chemistry amendments.

Since Mg was only marginally observed in the collected deposits, a second set of modeling calculations was performed with the added modeling constraints: 1) Mg-containing solids (e.g., dolomite, huntite, artinite, brusite, and magnesite) were not allowed to form, and 2) Calcium carbonate takes the form of aragonite, a faster-forming crystalline phase of $\text{CaCO}_3(\text{s})$ that is also more soluble than calcite (Ogino et al., 1990; Gutjahr et al., 1996). Under these conditions, a total of 759 mg/L of precipitates in the form of HAP and aragonite were predicted to form, resulting in a 22% decrease in solution TDS.

HAP [$\text{Ca}_5(\text{PO}_4)_3\text{OH}(\text{s})$]: 0.07 mM (35.2 mg/L)

Aragonite [$\text{CaCO}_3(\text{s})$]: 7.23 mM (723.6 mg/L)

The elemental composition of the solids predicted under these conditions is shown in Table 6 (Condition (2)). The result is in a closer agreement with the experimental observation in terms of elemental composition. However, the total amount of solids predicted by modeling (759 mg/L) was still significantly greater than that precipitated experimentally (150–200 mg/L), implying that precipitation equilibrium had not been established during the experimental conditions, i.e., 3–4 days of limiting hydraulic residence time in the cooling water.

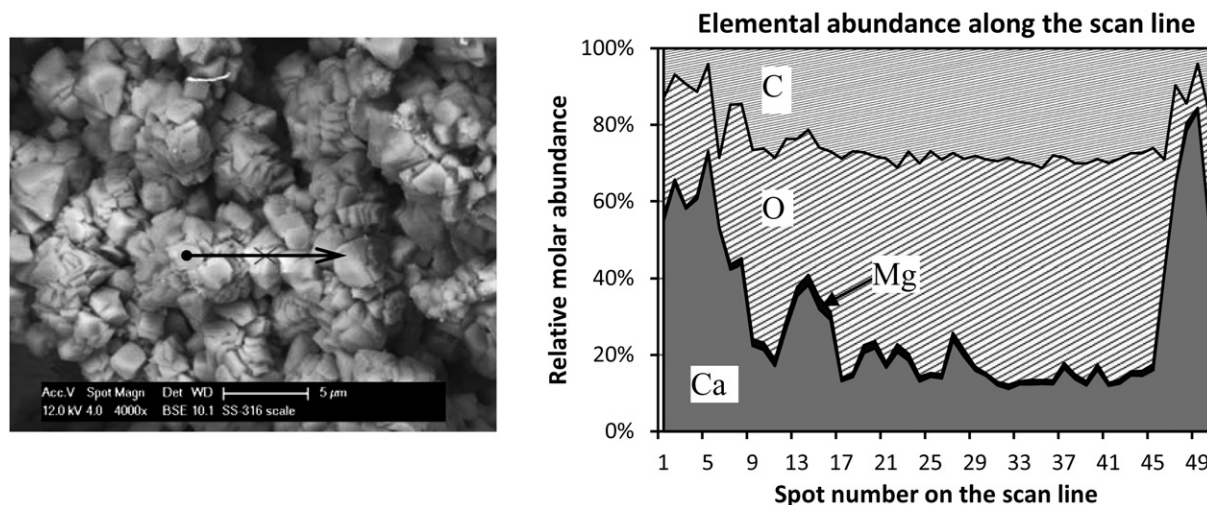


Fig. 8 – SEM image (left) and quantitative 1D EDS analysis (right) of the deposits collected on a stainless steel disc immersed in synthetic MWW in bench-scale water recirculating system. The arrow line (10 μm in length) on the SEM image indicates the scan line for the EDS analysis of elemental abundance. P and H are not detected.

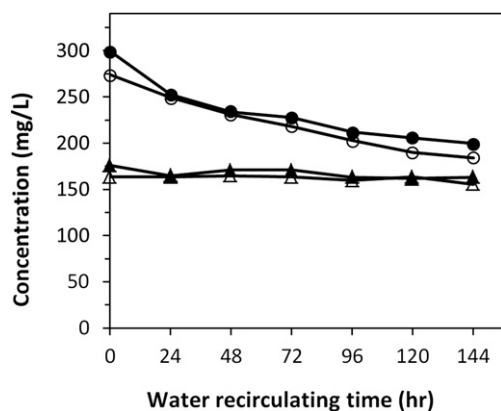


Fig. 9 – Changes in the aqueous concentrations of Ca and Mg in bench-scale water recirculating system using a synthetic MWW (without chemical addition). Closed data points represent concentrations of unfiltered water samples while open points filtered samples. The filtration is carried out using 0.45 μm HA type membrane filters (Millipore) to remove suspended solids. Ca unfiltered (●), Ca filtered (○), Mg unfiltered (▲), Mg filtered (△).

Compared to the modeling prediction of 90% Ca precipitation, only about 35% of Ca actually precipitated during the 6 days of bench-scale tests with synthetic MWW (Fig. 9). A similar percentage of Ca precipitation (35–40%) was observed in pilot-scale cooling tower tests with secondary-treated MWW. Tower A, which received no PMA, precipitated the greatest amount of Ca, while Towers B and C, with PMA addition, retained higher amounts of Ca in water. This suggests that PMA retarded Ca precipitation, resulting in higher Ca concentrations during the course of tower tests. It is clear therefore that kinetic constraints

of precipitation exerted by the PMA addition are not captured by the equilibrium modeling that is entirely based on thermodynamic calculations.

For pilot-scale cooling tower experiments, SEM/EDS analyses were performed on deposits collected from Tower A after 6 days of operation at CoC 4 (Fig. 10). The EDS spectra show very low amounts of Mg, thereby confirming the results shown in Figs. 8 and 9 from bench tests with synthetic MWW. However, the SEM data indicated solids of more amorphous character as opposed to those depicted in Fig. 8. Alvarez et al. (2004) observed that the Ca–P complexes preferentially precipitate in amorphous forms in the presence of soil organic matter. In addition, amorphous $\text{CaCO}_3(\text{s})$ has been collected on steel surfaces when organic additives are present in solution (Kjellin et al., 2001; Kjellin, 2003; Wei et al., 2004, 2005). The interactions of mineral precipitates with organic matter present in the actual MWW suggest more complex chemistries occurring in pilot-scale cooling tower water than in the bench-scale system where synthetic MWW was used to simulate only the inorganic constituents.

The EDS analyses conducted on the solids collected from pilot experiments indicate that the deposits consisted primarily of calcium carbonates and phosphates, which is in qualitative agreement with the revised model predictions discussed earlier. However, the quantity of phosphates appears to be greatly enriched when compared to that in the deposits collected from the bench-scale studies using synthetic MWW. This is likely because of the higher P concentration in the actual MWW (i.e., 12 mg/L vs. 5 mg/L in the synthetic water). In addition, P-containing chemicals, in the form of TKPP (10 mg/L) and PBTC (5 mg/L), were also added to the cooling towers for corrosion/scaling control. Chemical analyses indicated that these added phosphates quickly became undetectable in the liquid phase, suggesting their precipitation

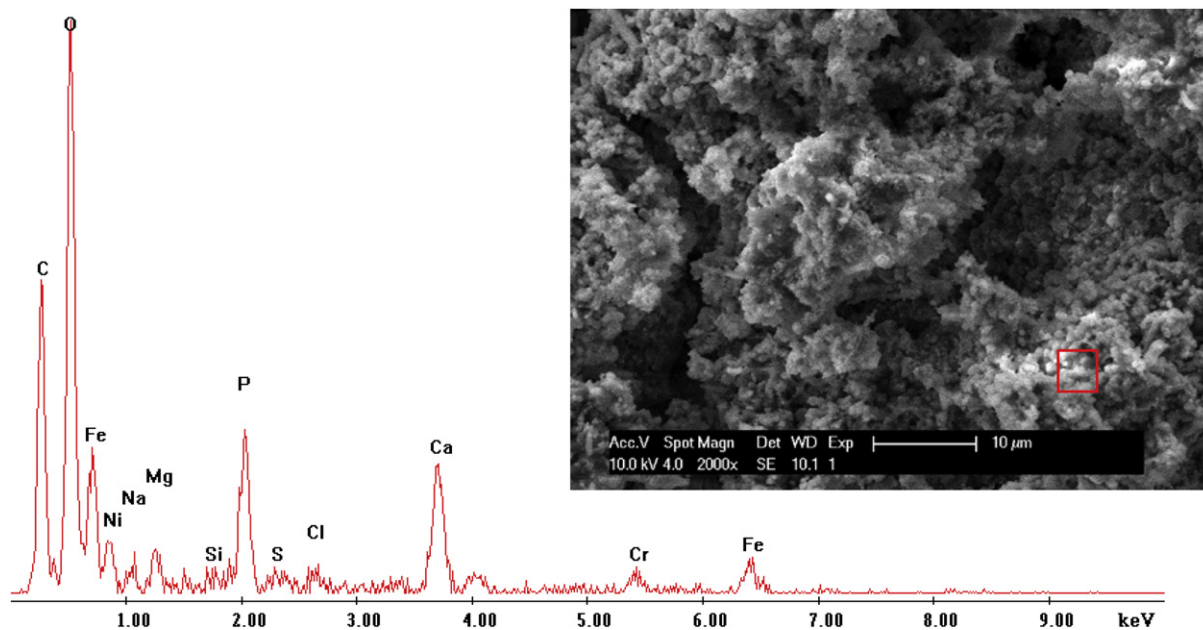


Fig. 10 – SEM image and the elemental composition of the solid deposits collected on a stainless steel disc immersed in the secondary-treated MWW in the pilot-scale cooling tower (Tower A) operated at CoC 4. EDS scan was performed on the area outlined by the square box on the SEM image.

that further contributed to the relatively high P signal in the EDS spectra (Fig. 10).

4. Conclusions

This study demonstrates the feasibility and challenges of using secondary-treated municipal wastewater as an alternative cooling system makeup water to replace freshwater. The scaling behavior and control of it in recirculating cooling systems was evaluated. Based on the results from bench-scale experiments performed in this study, it was determined that commonly used polymer-based scaling inhibitors can be effective in controlling potentially severe scaling when using this impaired water as makeup in recirculating cooling systems. PMA reduced scaling significantly in the absence of chlorine biocide but was only partially effective in the presence of chlorine. Ammonia present in the wastewater could suppress the aggressiveness of free chlorine on PMA. Preformed monochloramine was found to be less aggressive than free chlorine, while still being an effective biocide. Pilot-scale cooling tower experiments indicated that mineral scaling control by PMA was much more challenging due to biofouling.

Overall, for scaling control of MWW that is concentrated to CoC 4 in recirculating cooling systems, 1) PMA can be applied at 10 mg/L level for effective mineral scaling inhibition in the absence of biofouling, 2) monochloramine is better suited as biocide than free chlorine because of the reduced impact of monochloramine on antiscalants programs, and 3) phosphorous-based scaling and corrosion inhibitors are not appropriate due to their precipitation with Ca.

Acknowledgements

This work was supported by the U.S. Department of Energy, National Energy Technology Laboratory, Grant No. DE-FC26-06NT42722. The authors gratefully acknowledge the Franklin Township Municipal Sanitary Authority, and especially manager James Brucker, for allowing and supporting performance of the pilot-scale cooling tower tests at their facility.

REFERENCES

- American Public Health Association, et al., 2005. *Standard Methods for the Examination of Water and Wastewater*, 21st ed., Washington, DC.
- Alvarez, R., et al., 2004. Effects of humic material on the precipitation of calcium phosphate. *Geoderma* 118 (3–4), 245–260.
- Anderson, H.A., Russell, J.D., 1976. Possible relationship between soil fulvic acid and polymaleic acid. *Nature* 260 (5552), 597.
- Beardwood, T., 17 December 2009. Common Antiscalants Used in Cooling Industry. Ashland Chemical Co./Drew Industrial, Tuscon, AZ. personal communication.
- Chien, S.-H., et al. Chloramination as biofouling control strategy when using secondary-treated municipal wastewater as power plant cooling system makeup, submitted for publication.
- Chowdhury, S., et al., 2009. Models for predicting disinfection byproduct (DBP) formation in drinking waters: a chronological review. *Science of the Total Environment* 407 (14), 4189–4206.
- Christophersen, D., 19 December 2007. Common Antiscalants Used in Cooling Industry. Crown Solutions/Veolia Water, Vandalia, OH. personal communication.
- d'Abzac, P., et al., 2010. Characterization of the mineral fraction associated to extracellular polymeric substances (EPS) in anaerobic granular sludges. *Environmental Science & Technology* 44 (1), 412–418.
- Du, K., et al., 2009. Fluorescent-tagged no phosphate and nitrogen free calcium phosphate scale inhibitor for cooling water systems. *Journal of Applied Polymer Science* 113 (3), 1966–1974.
- Ehrhardt, R.F., et al., 1986. *Analysis of Alternate Sources of Cooling Water (EPRI-EA-4732)*. Electric Power Research Institute, Palo Alto, CA.
- EPRI, 2003. *Use of Degraded Water Sources as Cooling Water in Power Plants (1005359)*. Energy Commission, Public Interest Energy Research Program Sacramento, CA.
- EPRI (2008). *Use of Alternate Water Sources for Power Plant Cooling*. Palo Alto, CA.
- Eriksson, R., et al., 2007. The calcite/water interface: I. Surface charge in indifferent electrolyte media and the influence of low-molecular-weight polyelectrolyte. *Journal of Colloid and Interface Science* 313 (1), 184–193.
- Ficara, E., Rozzi, A., 2004. Coupling pH-stat and DO-stat titration to monitor degradation of organic substrates. *Water Science and Technology* 49 (1), 69–77.
- Frayne, C., 1999. *Cooling Water Treatment-Principles and Practices*. Chemical Publishing Co, New York, NY.
- Gehrke, N., et al., 2005. Superstructures of calcium carbonate crystals by oriented attachment. *Crystal Growth & Design* 5 (4), 1317–1319.
- Gutjahr, A., et al., 1996. Studies of the growth and dissolution kinetics of the CaCO₃ polymorphs calcite and aragonite I. Growth and dissolution rates in water. *Journal of Crystal Growth* 158 (3), 296–309.
- Hassan, K.Z.A., et al., 2006. Iron oxide enhanced chlorine decay and disinfection by-product formation. *Journal of Environmental Engineering-ASCE* 132 (12), 1609–1616.
- Hess, A.N., Chin, Y.-P., 1996. Physical and chemical characteristics of poly(maleic acid), a synthetic organic colloid analog. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 107, 141–154.
- Hsieh, M.-K., et al. Corrosion control when using secondary-treated municipal wastewater as alternative makeup water for cooling tower systems, in press.
- Johnstone, D.W., Miller, C.M., 2009. Fluorescence excitation-emission matrix regional transformation and chlorine consumption to predict trihalomethane and haloacetic acid formation. *Environmental Engineering Science* 26 (7), 1163–1170.
- Kielemoes, J., et al., 2000. Influence of denitrification on the corrosion of iron and stainless steel powder. *Environmental Science & Technology* 34 (4), 663–671.
- Kirmeyer, W.D., et al., 1993. *Optimizing Chloramine Treatment*, second ed.. American Water Works Research Foundation, pp. 20–23.
- Kitis, M., et al., 2001. The reactivity of natural organic matter to disinfection byproducts formation and its relation to specific ultraviolet absorbance. *Water Science and Technology* 43 (2), 9–16.
- Kjellin, P., 2003. X-ray diffraction and scanning electron microscopy studies of calcium carbonate electrodeposited on

- a steel surface. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 212 (1), 19–26.
- Kjellin, P., et al., 2001. A new method for the study of calcium carbonate growth on steel surfaces. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 194 (1–3), 49–55.
- Li, C.W., et al., 2000. Use of UV spectroscopy to characterize the reaction between NOM and free chlorine. *Environmental Science & Technology* 34 (12), 2570–2575.
- Li, H., 2010. Mineral precipitation and deposition in cooling systems using impaired waters: mechanisms, kinetics, and inhibition. Ph.D. Thesis. Department of Civil and Environmental Engineering, University of Pittsburgh.
- Metcalf & Eddy, 2007. *Water Reuse: Issues, Technologies, and Applications*. McGraw-Hill.
- Miller, W.G., 2006. Integrated concepts in water reuse: managing global water needs. *Desalination* 187 (1–3), 65–75.
- Nalepa, C.J., et al., 1999. A comparison of bromine-based biocides in a medium-size cooling tower. *Journal of Cooling Tower Institute* 20, 42–60.
- Nowack, B., 2003. Environmental chemistry of phosphonates. *Water Research* 37 (11), 2533–2546.
- Ogino, T., et al., 1990. The rate and mechanism of polymorphic transformation of calcium carbonate in water. *Journal of Crystal Growth* 100 (1–2), 159–167.
- Roccaro, P., et al., 2008. Differential absorbance study of effects of temperature on chlorine consumption and formation of disinfection by-products in chlorinated water. *Water Research* 42 (8–9), 1879–1888.
- Scandolari, L., 12 March 2008. Common Antiscalants Used in Cooling Industry. PA (Kroft Chemical Co.), personal communication, Pittsburgh.
- Schecher, W.D., McAvoy, D.C., 1992. MINEQL+: a software environment for chemical equilibrium modeling. *Computers, Environment and Urban Systems* 16 (1), 65–76.
- Schecher, W.D., McAvoy, D.C., 1999. MINEQL+ Chemical Equilibrium Modeling System, Version 4 for Windows. Environmental Research Software, Hallowell, ME.
- Shakkthivel, P., et al., 2005. Water soluble copolymers for calcium carbonate and calcium sulphate scale control in cooling water systems. *Journal of Applied Polymer Science* 96 (4), 1451–1459.
- Shakkthivel, P., Vasudevan, T., 2006. Acrylic acid-diphenylamine sulphonic acid copolymer threshold inhibitor for sulphate and carbonate scales in cooling water systems. *Desalination* 197 (1–3), 179–189.
- Snoeyink, V.L., Jenkins, D., 1980. *Water Chemistry*. Wiley, New York.
- Sonnenberg, L., et al., 2007. Quantitative single molecule measurements on the interaction forces of poly(L-glutamic acid) with calcite crystals. *Journal of the American Chemical Society* 129 (49), 15364–15371.
- Sperandio, M., Paul, E., 1997. Determination of carbon dioxide evolution rate using on-line gas analysis during dynamic biodegradation experiments. *Biotechnology and Bioengineering* 53 (3), 243–252.
- Stumm, W., Morgan, J.J., 1996. *Aquatic Chemistry: Chemical Equilibria and Rates in Natural Waters*, second ed.. Wiley, New York.
- Vidic, R.D., Dzombak, D.A., 2009. Reuse of treated internal or external wastewaters in the cooling systems of coal-based thermoelectric power plants, In: Final Technical Report to US DOE/NETL, project number DE-FC26–06NT42722.
- Wang, L.L., et al., 1997. Adsorption of (poly)maleic acid and an aquatic fulvic acid by goethite. *Geochimica Et Cosmochimica Acta* 61 (24), 5313–5324.
- Wei, H., et al., 2004. Crystallization habit of calcium carbonate in presence of sodium dodecyl sulfate and/or polypyrrolidone. *Journal of Crystal Growth* 260 (3–4), 545–550.
- Wei, H., et al., 2005. On the crystallization of calcium carbonate modulated by anionic surfactants. *Journal of Crystal Growth* 27 (9(3–4)), 439–446.
- Weinberger, L.W., et al., 1966. Solving our water problems – water renovation and reuse. *Annals of the New York Academy of Sciences* 136, 131–154.
- Weissenbacher, N., et al., 2007. Determination of activated sludge biological activity using model correct CO₂ off-gas data. *Water Research* 41 (7), 1587–1595.
- Williams, R.B., Middlebrooks, E.J., 1982. *Wastewater Reuse – An Assessment of the Potential and Technology*. Water Reuse. Ann Arbor Science Publishers, Ann Arbor, MI.
- Zhang, P., et al., 2009. Waste activated sludge hydrolysis and short-chain fatty acids accumulation under mesophilic and thermophilic conditions: effect of pH. *Water Research* 43 (15), 3735–3742.
- Zhang, Y., et al., 2008. Nitrification in premise plumbing: role of phosphate, pH and pipe corrosion. *Environmental Science & Technology* 42 (12), 4280–4284.