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Development of an Instantaneous Corrosion Rate Monitoring System for Metal and Metal Alloys in Recirculating Cooling Systems

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ABSTRACT: An instantaneous corrosion rate (ICR) monitoring technique, suitable for application in recirculating cooling water systems, is useful for rapid appraisal of corrosiveness of the aqueous system with respect to metal and metal alloys of interest. In this study the instantaneous corrosion rates of mild steel, copper, and cupronickel alloys were measured at various times during an exposure period by electrochemical polarization resistance measurements using a three-electrode system. The average corrosion rates (ACR) were also determined by the gravimetric weight loss method to correlate with the ICR data. Stainless steel was used as the reference electrode to replace the standard saturated calomel electrode for increased robustness of the system in pilot-scale cooling systems. A side-streamflow channel unit was designed to hold the three electrodes in flowing cooling water. Use of stainless steel as a reference electrode was reliable and ICR was monitored intermittently for 28 days. Integration of the ICR data from the pilot-scale cooling towers correlated well with the ACR results, with similar correlation coefficients obtained from bench-scale experiments.

INTRODUCTION

A number of methods have been used to assess the corrosion rate of metals and metal alloys in contact with aqueous systems.^{1,2} Some of the methods give time averaged corrosion rates, while others provide instantaneous corrosion rates of the metals and metal alloys. Each of these methods has its advantages and disadvantages in terms of the applicability and accuracy of results when considered for use in open recirculating cooling water systems. The methods used most commonly to evaluate metal and metal alloy corrosion rates are the gravimetric weight loss method, the electrical resistance method, the electrochemical Tafel extrapolation method, and the electrochemical polarization resistance method. The first two methods yield average corrosion rates, while the latter two methods yield instantaneous corrosion rates. In many cases, the instantaneous corrosion rate (ICR) of a metal specimen in a cooling system is of interest in order to be able to respond rapidly in corrosion management to a sudden change in solution condition and in the corrosion rate of metal and metal alloys in the system.

The conventional gravimetric weight loss method (WLM) utilizes the weight difference of a metal or metal alloy specimen before and after its exposure to the corrosive environment. It is an inexpensive and simple method with well-documented standard operational procedures.^{3,4} However, this method provides only an average corrosion rate over the entire contact period of the metal or metal alloy specimen.¹

The electrical resistance (ER) method measures the change in electrical resistance of a corroding metal with a metal or metal alloy probe in situ and permanently exposed to the process stream. Increase in the electrical resistance is related directly to the metal loss and thus the corrosion rate.⁵ The ER method provides average corrosion rates over periods of several days.⁶ However, the presence of pitting corrosion, corrosion

product, and mineral precipitation severely hampers the efficiency of ER method.²

The electrochemical Tafel extrapolation method is commonly used for ICR determination.^{1,7,8} This method requires higher anodic/cathodic polarizing voltage, which may alter the surface properties of an electrode. Hence, this method is not suitable for continuous corrosion monitoring.¹

The electrochemical polarization resistance method (PRM) can respond to small variations in the corrosiveness of the aqueous systems toward metal and metal alloys, and the measurement can be done instantaneously.^{1,9} This method is suitable for long-term continuous corrosion monitoring. A standard test method is available for polarization resistance measurement.¹⁰ However the coefficients used to convert polarization resistance to instantaneous corrosion rate are not constant and vary between systems.¹¹

The weight loss method and polarization resistance method can be combined for quantitative ICR analysis.^{11–13} WLM and PRM measurements on the same metal–water system can be used to calibrate PRM measurements and determine a coefficient (B') relating polarization resistance to ICR. The coefficient was found to vary with metal alloy, water quality, and exposure time.¹¹ It was observed that a stable coefficient is achieved for a metal or metal alloy immersed in an aqueous system for more than 3 days. The WLM and PRM measurements were conducted in bench-scale experiments.¹¹

A major limitation identified in applying WLM-PRM results from bench-scale measurements to pilot-scale cooling water systems is the typical use of a delicate standard reference electrode in the PRM system, e.g., a saturated calomel (glass)

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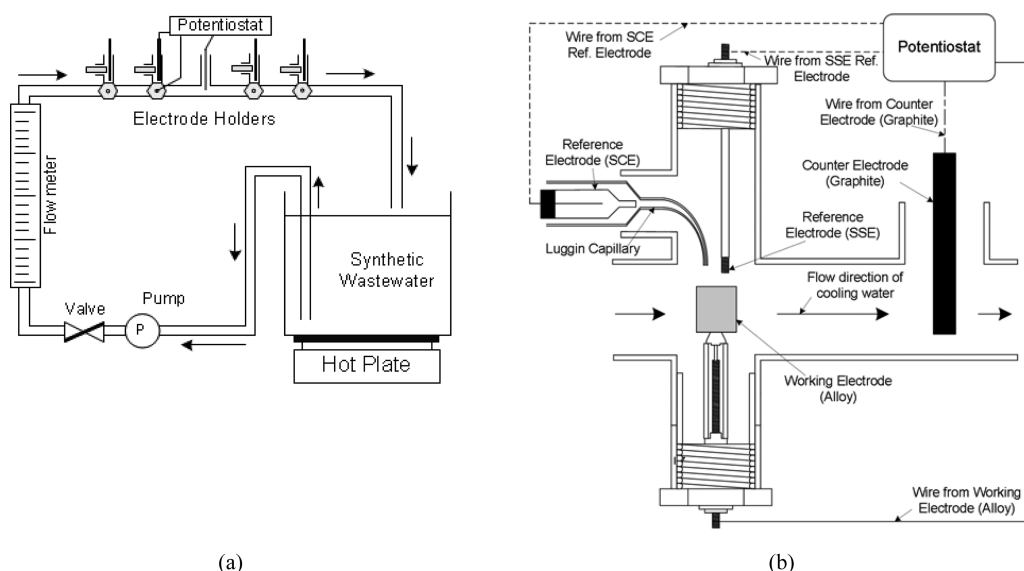


Figure 1. Schematic diagrams of (a) bench-scale recirculating system and (b) metal alloy specimen holder and ports for counter electrode and reference electrodes in the bench-scale recirculating system.

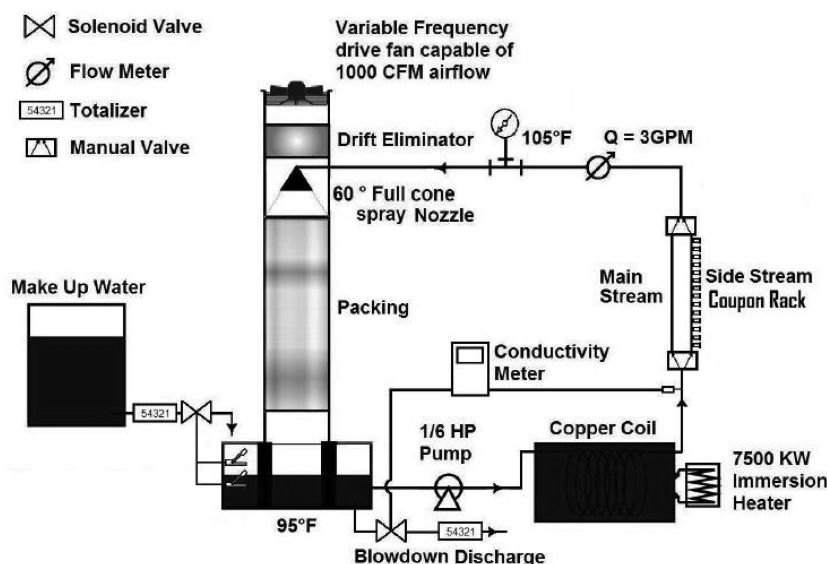


Figure 2. Schematic of pilot-scale cooling tower design. The coupon rack design details are given in Figure 3.

electrode (SCE). A standard reference electrode is difficult to maintain in a pilot-scale system with fast flowing recirculating cooling water. The Luggin capillary in which the reference electrode is placed is easily fouled by the recirculating cooling water. Hence a substitute for a standard glass reference electrode is necessary to employ the ICR measurement technique in a pilot-scale cooling water system.

In this study stainless steel was selected as an alternative reference electrode. Stainless steel electrodes are inexpensive and more durable in flowing water systems like recirculating cooling water systems. The stainless steel electrode (SSE) was selected to serve the purpose of a robust, stable reference electrode for ICR measurement in pilot-scale cooling systems.

The objectives of this study were to (a) modify the bench-scale recirculation system developed previously to facilitate WLM and PRM measurements of metals and metal alloys immersed in flowing water possessing chemical compositions and temperature pertinent to cooling systems; (b) conduct a

series of bench-scale experiments to determine the reliability of using SSE as the reference electrode for PRM measurements; (c) determine the coefficient (B') to convert polarization resistance (R_p) measurements to ICR values with SSE as the reference electrode; (d) design and construct a field-deployable PRM system for R_p measurement of different metal alloys in pilot-scale cooling systems.

METHODOLOGY

Bench-Scale Recirculation System. In a previous study, a bench-scale recirculation system was used to expose metal and metal alloy samples to temperature, flow velocity, and water quality similar to those in recirculating cooling water systems.¹¹ The bench-scale recirculating water system consisted of a centrifugal pump, a water bath on a hot plate (to control the water temperature), and a 1.91 cm (0.75 in) nominal diameter PVC pipe circulation system with a pipe rack to hold different electrodes. For the present study, the design of the pipe rack

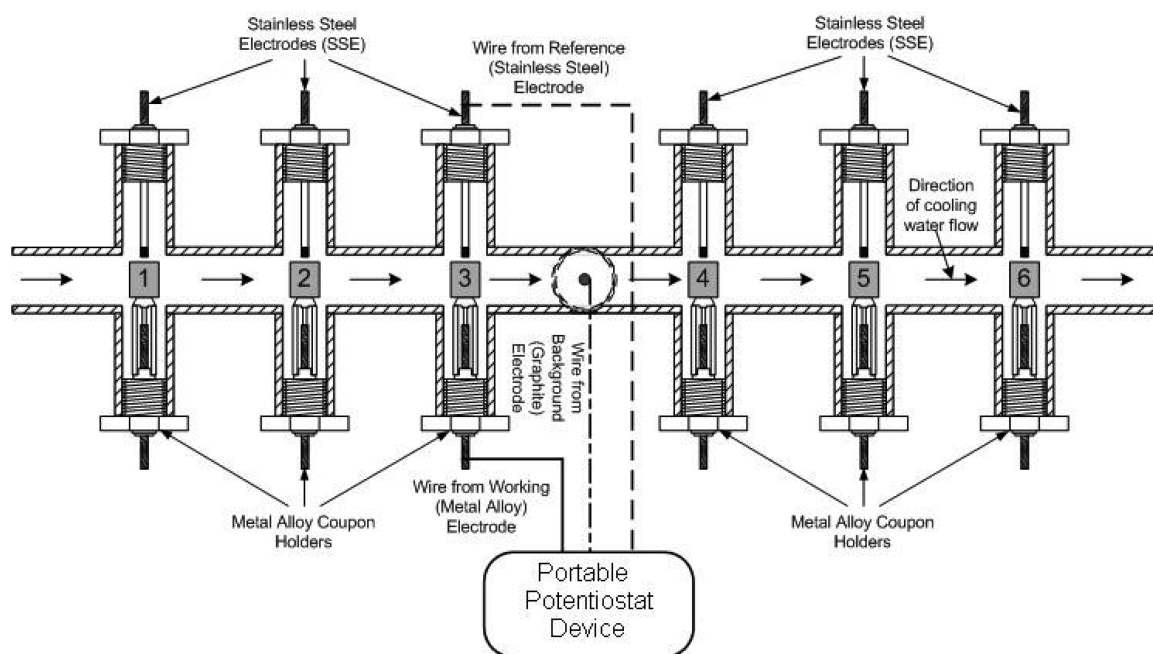


Figure 3. Schematic of side stream coupon rack holding metal alloy specimens, stainless steel (reference) electrodes, and graphite (counter) electrode in flowing cooling water with connections to a portable potentiostat.

Table 1. Range of Key Parameters of Synthetic Recirculating Water Quality

pH	total ammonia ^a	total phosphate	inhibitors ^b		free chlorine/chloramine
			TTA	SHMP	
7.1–8.8	0–40 ppm	0–45 ppm	0–5 ppm	0–10 ppm	0–3 ppm

^aAmmonia was added separately in the synthetic secondary treated cooling water recipe to observe its corrosive effect. ^bTTA: tolyltriazole. SHMP: sodium hexametaphosphate.

holder was modified to accommodate two different reference electrodes (Figure 1a). The pipe rack holder included four tee sections into which alloy specimen holders were mounted. Each tee section was connected to another tee section, which accommodated two different reference electrodes (Figure 1b) for side by side polarization resistance measurement analysis. The temperature of the recirculating water was maintained at 40 °C in the bench-scale system to simulate the temperature of cooling water in the pilot-scale recirculating cooling water systems.¹⁴

Both WLM and PRM corrosion monitoring were carried out in the bench-scale recirculation system. The reference electrode was placed close (within 2 mm) to the working electrode: the SCE was placed in a Luggin capillary and the SSE was located at one of the tee section ends (Figure 1b). The pipe rack holder also accommodated a graphite counter electrode and a metal specimen holder (made of an end-cap plug containing a threaded stainless steel rod with an alloy specimen attached at the end). The metal alloy specimen, reference electrode (either SCE or SSE), and counter electrode were connected to a potentiostat for polarization resistance (R_p) measurements (Figure 1b). After the desired immersion period, the metal and metal alloy specimens were removed for weight loss analysis.

Pilot-Scale Recirculation System. Two pilot-scale cooling towers, setup as shown in Figure 2, were installed at the Franklin Township Municipal Sanitary Authority (FTMSA) wastewater treatment facility for evaluation of different corrosion, scaling, and biofouling control programs when treated municipal wastewater is used as makeup water.¹⁴ The

cooling towers were operated with the following conditions: (a) cooling water at four cycles of concentration; (b) flow rate 0.189 L/s (3 gpm) (passing through a 1.91 cm nominal diameter PVC pipe rack); (c) recirculating water temperature of 40.6 °C (105 °F) delivered to the cooling tower and 35 °C (95 °F) in the collection basin. A side-streamflow channel was installed in the pilot-scale cooling system for placement of metal and metal alloy samples and corrosion analysis.

For the present study, the side-stream coupon rack was designed to hold the metals and metal alloys of interest, reference electrode (SSE), and a counter electrode (graphite) in flowing cooling water. Figure 3 shows details of the side-stream coupon rack with the location of different electrodes, metal alloy specimens, and cables connecting the electrodes to the potentiostat. Both WLM and PRM corrosion analysis was carried out on six metal alloy specimens mounted in the side-stream coupon rack unit of each cooling tower.

Synthetic Cooling Water Preparation. Synthetic cooling water was used in the bench-scale system to assess the reliability of using SSE as a reference electrode for electrochemical PRM measurement and to determine the coefficient (B') relating R_p to ICR. Synthetic cooling water was prepared considering typical concentrations of inorganic constituents of different treated (secondary or tertiary) municipal wastewater at four cycles of concentration (4CoC). The average inorganic water quality of different treated municipal wastewater at four cycles of concentration was obtained from previous pilot-scale experiments.¹⁴ The synthetic secondary treated cooling water at 4CoC was prepared using the following composition (mM):

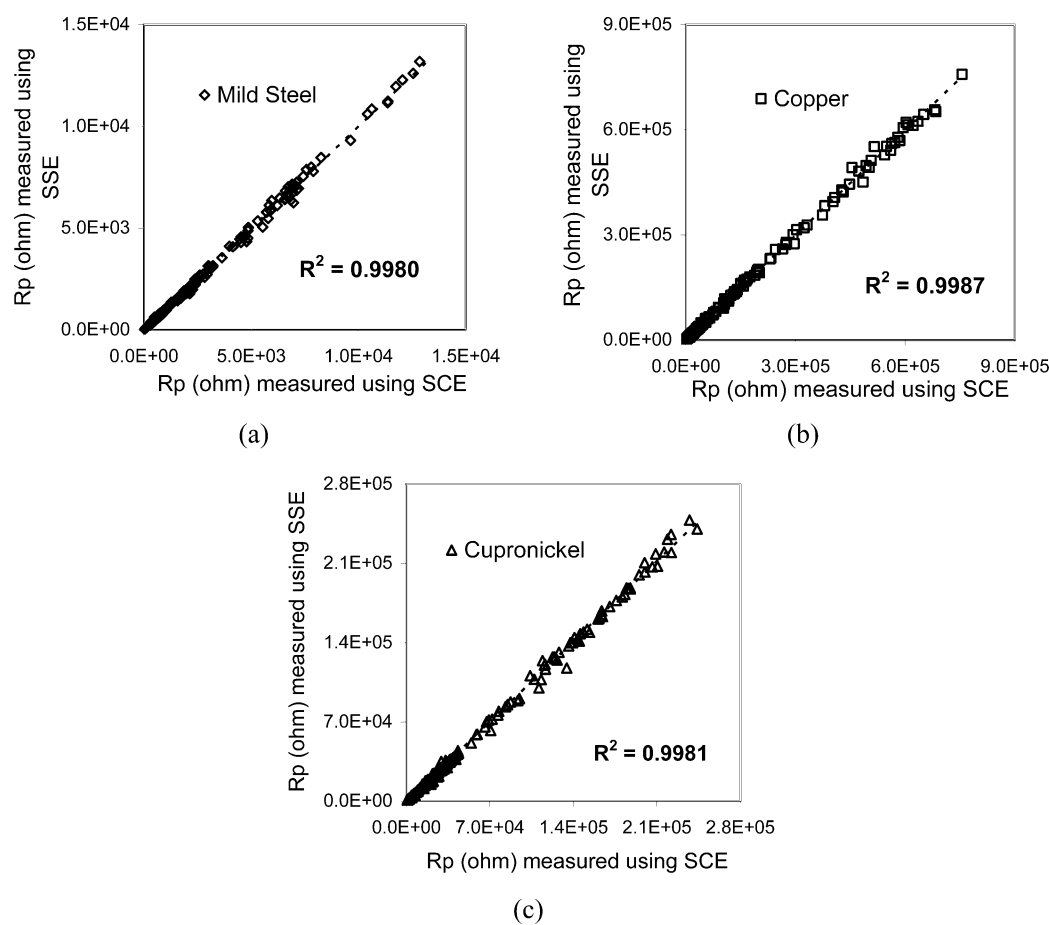


Figure 4. Comparison of polarization resistance (R_p) measurements using standard saturated calomel electrode (SCE) and stainless steel electrode (SSE) as reference electrodes. R_p values were measured using both the electrodes as reference electrodes consecutively for (a) mild steel, (b) copper, and (c) cupronickel samples immersed in synthetic recirculating cooling water in different bench-scale experiments.

K^+ , 0.48; Na^+ , 13.0; Mg^{2+} , 1.60; Ca^{2+} , 4.00; Cl^- , 11.2; CO_3^{2-} , 6.00; SO_4^{2-} , 3.50; PO_4^{3-} , 0.48. The synthetic tertiary treated (secondary treatment followed by nitrification and filtration) cooling water at 4CoC was prepared using the following composition (mM): K^+ , 0.48; Na^+ , 8.60; Mg^{2+} , 1.60; Ca^{2+} , 4.00; Cl^- , 11.2; CO_3^{2-} , 0.40; SO_4^{2-} , 3.50; NO_3^- , 1.20; PO_4^{3-} , 0.48.

The pH values for the secondary and tertiary treated cooling water were 8.7 ± 0.1 and 7.1 ± 0.1 respectively, prior to any modification. Table 1 shows the parameters varied in different bench-scale experiments to provide a wide range of corrosiveness in the synthetic cooling water. These parameters included pH, ammonia, phosphate, inhibitors, and disinfectants.

Metal Alloy Pre-exposure and Postexposure Treatment. The metal and metal alloys chosen for this study were mild steel (UNS G10180), copper (UNS C10100), and cupronickel (UNS C70600) as they are suitable for cooling water systems using municipal wastewater as makeup water.^{14,15} The specimens were cylinder-shaped with a nominal diameter of 0.375 in. and nominal length of 0.5 in. and were obtained from Metal Samples Co. (Munford, AL). Before immersing the metal and metal alloy samples in recirculating cooling water (both in bench-scale and pilot-scale systems), they were wet polished with SiC paper to a 600 grit surface finish, dried, weighed to 0.1 mg, degreased with acetone, and rinsed in distilled water.

During exposure of the metal alloy specimens in the bench-scale experiments, the R_p of the specimens was semi-

continuously monitored and specimens were withdrawn after approximately 1, 3, 5, and 7 days of exposure to measure the weight loss. After withdrawal, the specimens were cleaned following the ASTM G1 and then reweighed to 0.1 mg to determine the weight loss.³

In the pilot-scale cooling system tests, the metal and metal alloy specimens were immersed for periods of 7 and 28 days. Semicontinuous R_p measurements on the specimens were performed at different time intervals. The WLM was also used to determine the average corrosion rate during the exposure period. After withdrawal, similar postexposure treatments were performed on the metals and metal alloys as was done in the bench-scale experiments.

Electrochemical Polarization Resistance Measurement. Electrochemical polarization resistance (R_p) was measured using a portable VersaSTAT3 potentiostat (Princeton Applied Research, a subsidiary of AMETEK, Inc., USA). R_p measurement involved a three-electrode system. Metal and metal alloy specimens immersed in the recirculating cooling water were directly used as working electrodes. Both SSE and SCE were used as reference electrodes in the bench-scale experiments, whereas in pilot-scale experiments only SSE was used as reference electrode. Graphite was used as a counter electrode in the system. Each polarization scan was performed from -30 to $+30$ mV with respect to the stable corrosion potential at a scan rate 0.167 mV/s.¹⁰

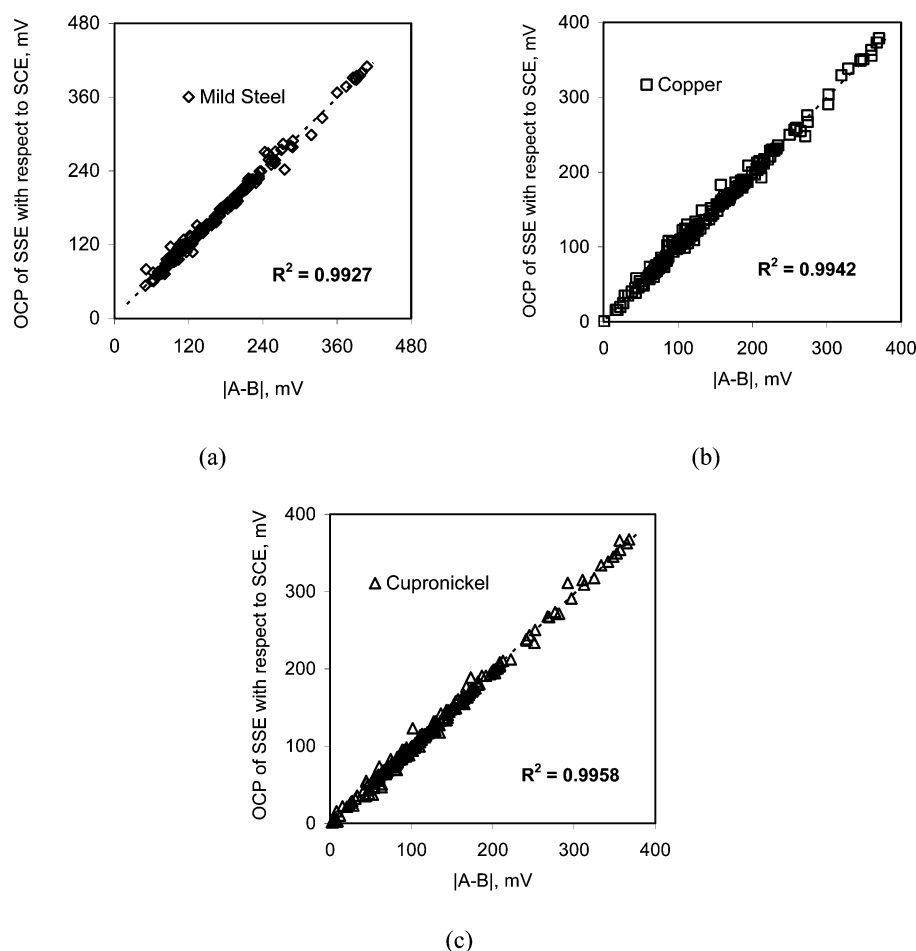


Figure 5. Comparison of open circuit potential (OCP) of SSE (measured with respect to SCE) and the absolute difference of corrosion potential of (a) mild steel, (b) copper, and (c) cupronickel measured with respect to SSE and SCE as reference electrodes. (Here, A and B are corrosion potentials of a metal or metal alloy sample measured with respect to SSE and SCE as a reference electrode, respectively).

ICR Calculated from R_p Measurements of Metals in Pilot-Scale Cooling Towers. The value of B' determined by combining WLM and PRM measurements in the bench-scale system were used to calculate instantaneous corrosion rate of the metals and metal alloys immersed in pilot scale cooling water systems using the following equation:

$$\text{ICR} = \frac{B'}{A\rho R_p} \quad (1)$$

where, B' = modified Stern–Geary constant, A = surface area of metal alloys exposed to recirculating cooling water, ρ = density of metal alloy specimen, and R_p = polarization resistance of the metal/metal alloy of interest.¹¹ The modified Stern–Geary constant (B') is a proportionality constant for a particular type of metal alloy in a particular aqueous system. From the derivation of eq 1 given in the work of Hsieh et al.,¹¹ it is evident that the modified Stern–Geary constant depends on material properties like average molecular weight (M , g/mol), average charge of metal (z , mol e^- /mol), and Faraday's constant (F , 96 485 coulomb/mol e^-) and the Stern–Geary constant (B , volt).¹¹ The Stern–Geary constant (B) depends on the anodic and cathodic Tafel constants which in turn are related to material properties and water chemistry. However as demonstrated in the previous study, the value of B' can be expressed as the ratio of weight loss to $\int 1/R_p dt$.¹¹ Exposed surface area (A) of each metal and metal alloy sample was

determined before the insertion of the samples in the cooling system. Hence by measuring the R_p in the pilot scale cooling system, eq 1 can be used to determine the corresponding ICR of the different metals and metal alloys.

RESULTS AND DISCUSSION

Reliability of Using SSE as Reference Electrode for R_p Measurement. Results of semicontinuous R_p measurements of the metals and metal alloys tested are plotted in Figure 4. For each material, the R_p measurements were performed successively using both the SSE and SCE reference electrodes.

High R^2 values for mild steel, copper, and cupronickel indicate reliability of the linear relationship between the R_p values of these materials measured using both reference electrodes. During every bench-scale experiment, open circuit potential (OCP) of SSE was recorded (with respect to SCE) following each set of R_p measurements. The corrosion potentials of the metal and metal alloys were also determined prior to the R_p measurements with respect to both SSE (A) and SCE (B), respectively. In order to confirm reliable behavior of SSE as a reference electrode, the absolute value of OCP of SSE with respect to SCE must be equal to the absolute difference between A and B. Figure 5 shows plots of OCPs of SSE with respect to SCE against the absolute difference of A and B for mild steel, copper, and cupronickel. High R^2 values in these

plots also indicate the consistent behavior of SSE as a reference electrode in waters having varying corrosiveness.

Correlation between Weight Loss and R_p Measurements in a Bench-Scale Recirculating System. (i) *Synthetic Tertiary Treated Municipal Wastewater.* The modified Stern–Geary coefficient (B') was determined for mild steel, copper, and cupronickel using combined WLM and PRM with SSE as the reference electrode. The synthetic water chemistry was varied to have different corrosiveness toward the metal and metal alloys (Table 1). Figure 6 shows the

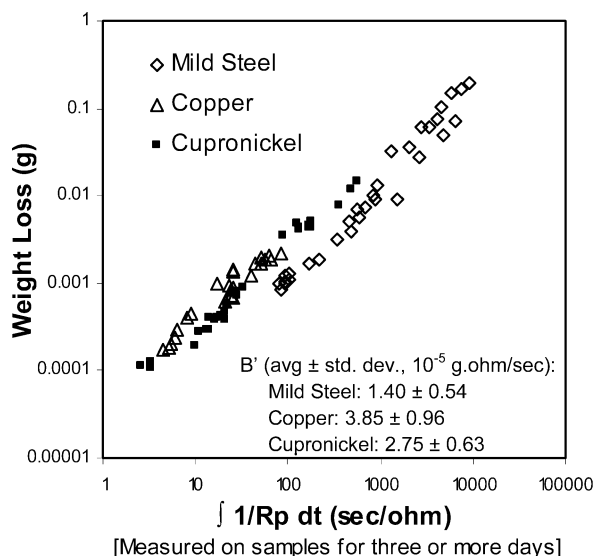


Figure 6. Relationship between weight loss and integration of polarization resistance over time ($\int 1/R_p dt$) for metal and metal alloy samples immersed in synthetic recirculating cooling water for approximately 3–7 days (B' reaches relatively stable value after 3 days).

relationship between weight loss and $\int 1/R_p dt$ for specimen immersion times longer than 3 days. The immersion time of longer than 3 days was determined based on knowledge obtained from previous experiments (discussed in a published paper by Hsieh et al. 2010), in which it was found that B' (or the relationship between weight loss and $\int 1/R_p dt$) could reach stability after 3 days of exposure.¹¹ Bench-scale experiment results from this study also showed that B' reached a stable value for metal and metal alloy samples immersed in synthetic recirculating cooling water after three days. B' is determined from the ratio of weight loss to $\int 1/R_p dt$ for samples immersed in different synthetic recirculating cooling water. Average and standard deviation values of B' determined for mild steel, copper, and cupronickel are given in Figure 6. The data presented in Figure 6 are in logarithmic scale, since the variation in weight loss and $\int 1/R_p dt$ are over 3 orders of magnitude.

The B' values determined in the present study varied from those obtained in a related previous study, likely due to a wider range of pH considered in the bench-scale tests performed in this study.¹¹ This conforms to the findings of the previous study as B' varied with changing water quality.¹¹

CORRATER (Rohrback Cosasco Systems), an existing commercially available tool for ICR monitoring, uses a polarization resistance measurement technique.¹⁶ However, this technique uses a single coefficient relating ICR to polarization resistance measurement for a particular metal or

metal alloy for all waters.^{2,16} CORRATER does not consider the influence of varying water quality on the coefficient correlating ICR to R_p . The present ICR measurement technique enables calibration of B' with changing water quality and incorporates this factor in ICR measurement.

For any particular type of water chemistry, the B' value will be determined from bench-scale experiments by combining electrochemical polarization resistance measurement and gravimetric weight loss measurement. Previous work showed that changing water quality from municipal wastewater to tap water resulted in a different B' value for various metals and metal alloys.¹⁷ Hence calibration of B' is very important with the type of water used in the system. Once calibration of B' is done for a particular type of water chemistry, it can be used to correlate polarization resistance (R_p) values measured in the pilot-scale system to instantaneous corrosion rate of specific metal alloys in the calibrated aqueous system.

Mechanistic changes in the assembly of the electrochemical system can impact the measurement of polarization resistance (R_p). For example, increase in the distance between reference electrode and working electrode will increase the R_p value due to ohmic drop in the solution between the two electrodes. Careful setup was made with the stainless steel electrode used in this study, so that the reference electrode did not touch the working electrode (this will cause short circuit in the system). Also a distance of 2–3 mm was maintained between the two electrodes to minimize the ohmic drop contribution to R_p .¹⁰ Higher ohmic drop in solution will lead to a high measured R_p value which consequently will indicate an erroneous low instantaneous corrosion rate.

The development of a passive layer on the metal surface could influence the relationship between weight loss and integrated polarization resistance. In a previous study,¹¹ it was found that the correlation of the measurement became stable after 3 days, which could result from the development of a passive layer on the metal surface in the initial stage. In the present study, it was found that for an exposure time of 3–7 days, the relationship between weight loss and $\int 1/R_p dt$ was approximately linear for the bench scale tests and also for exposure time of up to 28 days in the pilot scale experiments. For even longer exposure time, actual data are needed to confirm the stability of B' (or the relationship between weight loss and integrated polarization resistance).

(ii) *Actual Tertiary Treated Municipal Wastewater.* Similar bench-scale experiments were carried out with actual tertiary treated municipal wastewaters at 4CoC, with and without the addition of tolyltriazole (TTA) as a corrosion inhibitor. The tertiary treated wastewaters used were: (a) secondary effluent with pH controlled to 7.7 (MWWpH), (b) secondary effluent with nitrification-filtration (MWWNF), and (c) secondary effluent with nitrification-filtration and granular activated carbon adsorption (MWWNFG). The treated wastewaters collected from FTMSA wastewater treatment facility were concentrated in the laboratory by heated evaporation (40 °C) to reach 4CoC. The temperature (40 °C) used for heated evaporation in the lab, to concentrate the municipal wastewater to 4 CoC, simulates the temperature of recirculating cooling water in the pilot-scale cooling systems.¹⁴

Figure 7 shows the relationship between weight loss and integration of polarization resistance over time for mild steel, copper, and cupronickel samples immersed in recirculating cooling water for 5 and 7 days in the bench-scale system. Tolyltriazole dosings in different tertiary treated municipal

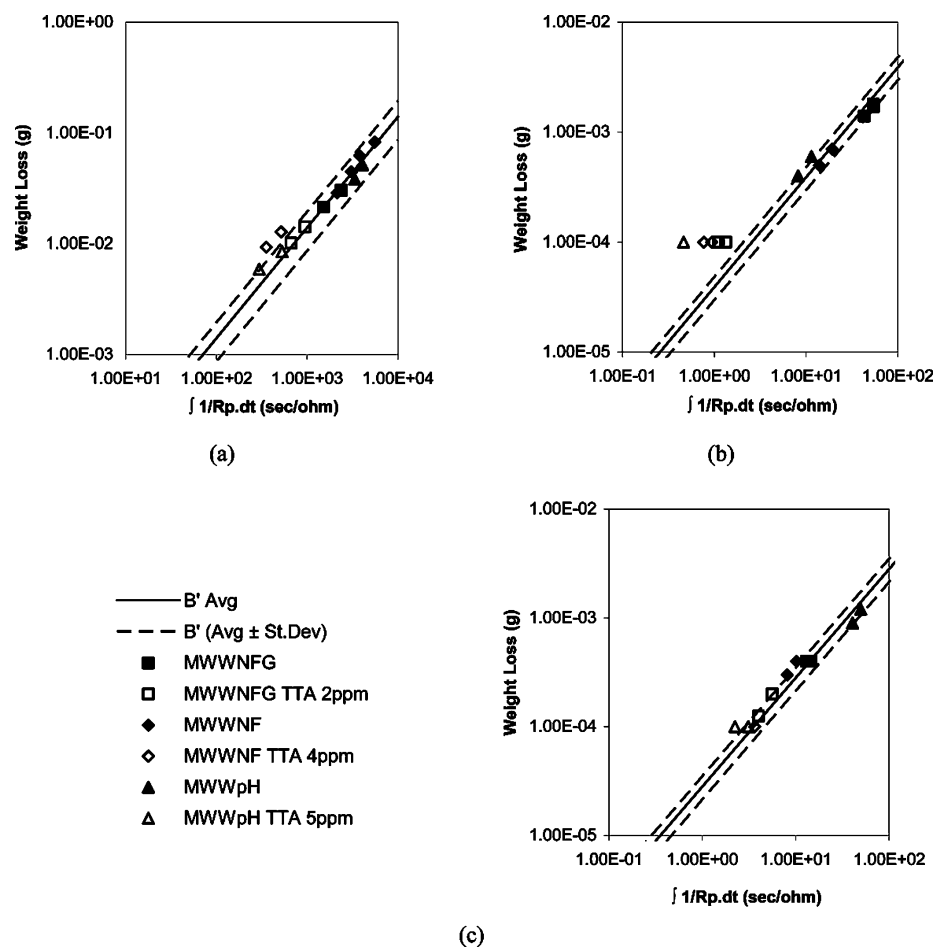


Figure 7. Relationship between weight loss and integration of polarization resistance over time ($\int 1/R_p dt$) for (a) mild steel, (b) copper, and (c) cupronickel samples immersed in bench-scale recirculating cooling water using different actual tertiary treated municipal wastewater for 5 and 7 days.

wastewaters are also indicated in the figure. The solid lines and dashed lines in Figure 7 correspond to the average and standard deviation values of B' for respective metal and metal alloys, as determined from bench-scale recirculating experiments using synthetic cooling water.

Weight loss and $\int 1/R_p dt$ values from bench-scale experiments using actual tertiary treated municipal wastewaters were found to correlate well with previously determined relationships using synthetic treated wastewater. However in the lower corrosion range, for copper and cupronickel, limitation of measured weight loss to a detection limit of 0.1 mg prohibits demonstration of good correlation in the low corrosion range. Since the relationship is well maintained in the higher corrosion rate range for copper and cupronickel, B' values determined in the higher range can be extended to the lower corrosion range. Such extrapolation of B' is based on the assumption that weight loss and $\int 1/R_p dt$ will follow similar relationship in the lower corrosion range.

ICR Calculated from R_p Measurements of Metal and Metal Alloy Samples in Pilot-Scale Cooling Systems. ICR measurements were carried out in two different pilot-scale cooling systems using tertiary treated municipal wastewater from FTMSA as makeup water. The cooling towers are designated here as cooling tower A (CTA) and cooling tower B (CTB). Mild steel, copper, and cupronickel coupon samples were inserted in both CTA and CTB for durations of 7 and 28 days. After the first 7 days, coupon samples were withdrawn

from CTB, and another set of coupon samples were inserted in CTB for 6 days (days 22–28 of a total of 28 days of operation). CTA and CTB used continuous dosing of sodium hypochlorite and chlorine dioxide (ClO_2) as biocide to control biofouling, respectively. A residual of sodium hypochlorite (1–2 ppm as free chlorine) and chlorine dioxide (0.5–1 ppm as ClO_2) were maintained in CTA and CTB, respectively. Addition of chlorine dioxide to CTB caused the pH of recirculating cooling water to decrease rapidly. Hence sodium hydroxide was used after the first 7 days to maintain the desired cooling water pH of 7.5. The pH of the cooling water was also influenced by the pH of the makeup water.¹⁸ CTB was also dosed with 2 ppm of the corrosion inhibitor TTA. The scaling propensity of the recirculating cooling water was measured using the Langelier saturation index (LSI). The detailed calculation procedure for LSI given by EPRI (2003) was employed.¹⁹ Average LSI values of CTA and CTB were 0.68 and 0.07, respectively, thereby indicating that recirculating cooling water in CTA had more scaling potential than that in CTB.

Figure 8 shows the corrosion rate profiles for the 28-day metal and metal alloy samples with the average corrosion rates for each sample. Similar corrosion rate profiles were also determined for the 6- and 7-day metal and metal alloy samples. Daily ICR measurements were carried out for the 6- and 7-day samples inserted in the cooling systems. For 28-day coupon samples, semicontinuous ICR measurements were carried out as well (Figure 8). The average corrosion rates of metal and

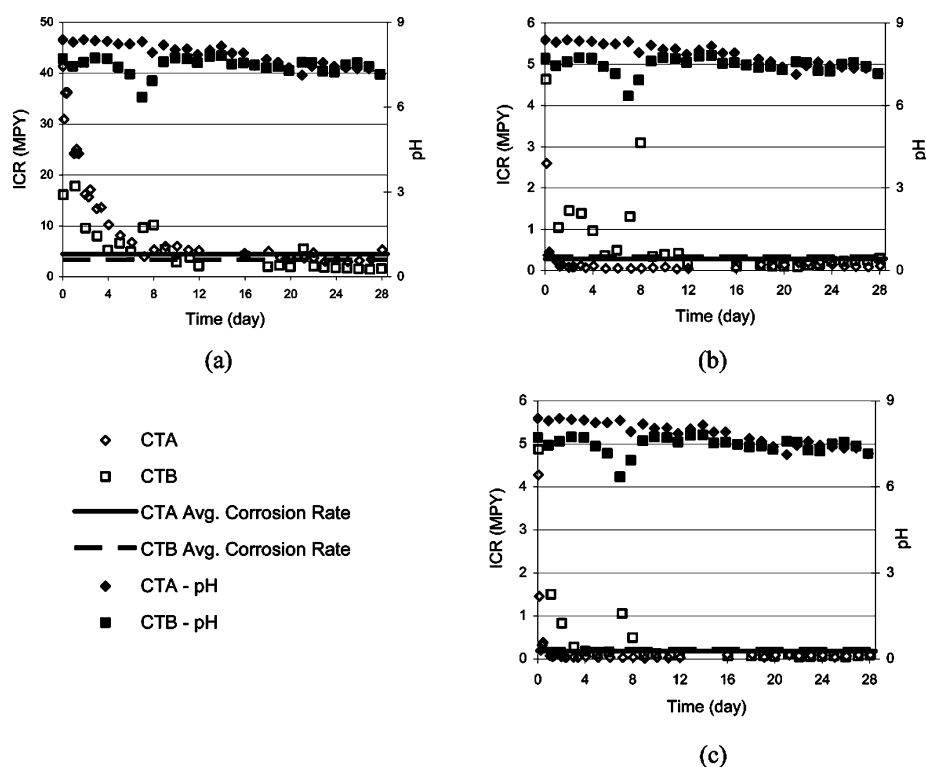


Figure 8. Instantaneous corrosion rate (ICR) measurements of (a) mild steel, (b) copper, and (c) cupronickel samples immersed in recirculating cooling towers (CTA, CTB) for 28 days. The average corrosion rates, determined from weight loss measurement, are indicated by horizontal lines. The pH profile of cooling waters in CTA and CTB are also shown in the figure.

metal alloy samples immersed in CTA and CTB are given in Table 2.

Table 2. Average Corrosion Rates of Mild Steel, Copper, and Cupronickel Samples Immersed in Pilot-Scale Cooling Tower Systems CTA and CTB for Different Durations

pilot-scale cooling tower system	immersion period	average corrosion rate (MPY ^a)		
		mild steel	copper	cupronickel
CTA	7 days	11.5	0.17	0.22
	28 days	4.47	0.28	0.18
CTB	6 days	3.44	0.89	0.76
	7 days	7.85	0.98	0.67
	28 days	3.39	0.34	0.23

^aMPY: Milli-inch per year.

An equilibration time period, ranging from 10 to 30 min, was necessary to reach stable corrosion potential before each R_p measurement was taken in the pilot scale system. Equilibration time required in the higher corrosion rate range was more than that in the lower corrosion rate range. The weight loss of each metal and metal alloy sample was determined after the designated immersion period to obtain corresponding average corrosion rates.

From the instantaneous corrosion rate profiles, the following is observed:

- Most of the corrosion of metal and metal alloy samples occurred in the initial 3–4 days of exposure.
- A lower corrosion rate in the initial time period resulted in lower average corrosion rate.

- Corrosion rates were greatly influenced by sudden changes of pH, as seen on days 7 and 8 in CTB (Figure 8).
- The 28-day ICR profile shows that after the initial immersion period the corrosion rates of different metal and metal alloys fall within acceptable limit due to formation of scaling and corrosion products on the surface of the specimens.^{14,16,20}

Comparison of Approximate B' Values Obtained from Pilot-Scale Cooling Towers to Those Obtained from Bench-Scale Experiments. Similar to the bench-scale experiments, R_p values obtained at different time intervals facilitate determination of $\int 1/R_p dt$ in pilot-scale cooling systems. From the ratio of weight loss and $\int 1/R_p dt$, an approximate B' value was obtained. The B' values obtained from the pilot-scale experiments may not be as accurate as those determined in bench-scale experiments.

The durations between successive R_p measurements were longer in the pilot-scale testing, and there was no information on the ICR profile between two such measurements. However, an approximate B' value can be determined assuming no abrupt change in the corrosion rate trend in between two successive R_p measurement.

Figure 9 shows a comparison between the approximate B' values of mild steel, copper, and cupronickel determined from the pilot-scale experiments, to similar B' values determined in the bench-scale experiments using synthetic cooling water.

Standard deviations associated in weight loss measurements are also indicated in Figure 9. The weight loss values were very small compared to the initial and final weights of the coupon samples. Hence there may be some error in the measurement of small weight losses, especially for copper and cupronickel.

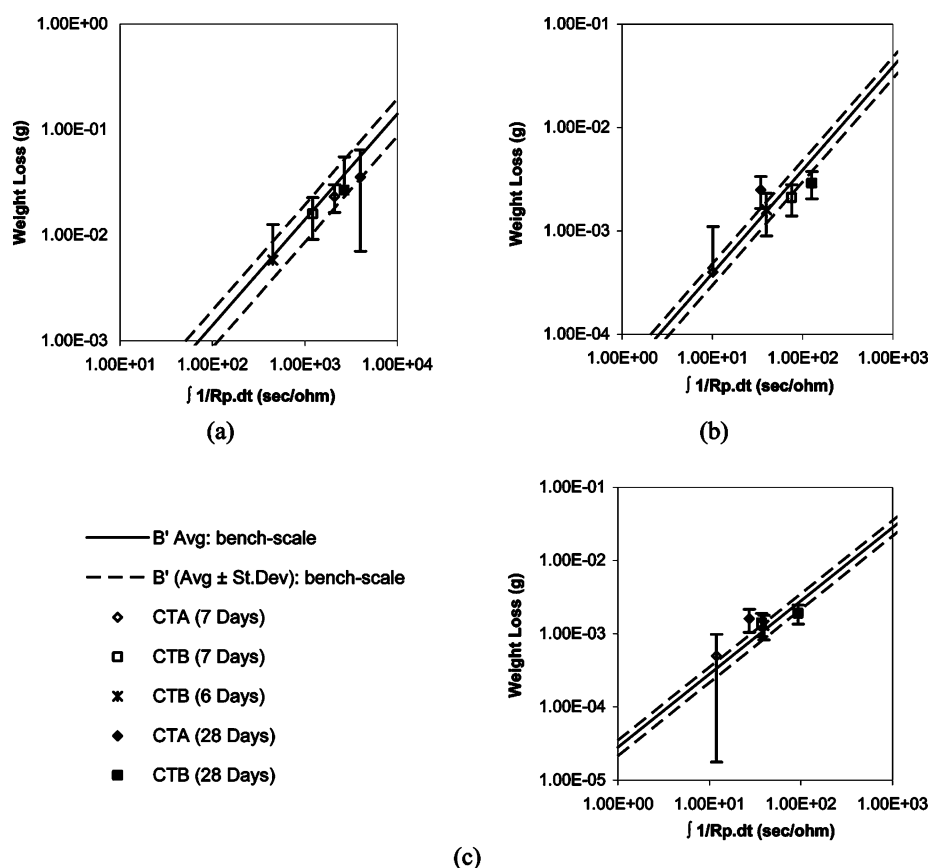


Figure 9. Comparison of the relationship between weight loss and integration of polarization resistance over time for data from pilot-scale experiments and the average correlation previously determined from bench-scale experiments for (a) mild steel, (b) copper, and (c) cupronickel.

Standard deviations in weight loss measurements were determined from initial and final weights of coupon samples immersed in similar type of cooling water for 7 or 28 days in the pilot-scale cooling systems. With the standard deviations in weight loss measurements plotted in Figure 9, the ICR data in the pilot-scale system showed similar relationship between weight loss and $\int 1/R_p dt$ as observed in the bench scale experiments.

CONCLUSION

This study developed an instantaneous corrosion rate measurement technique based on electrochemical polarization resistance for metals and metal alloys used in power-plant cooling systems. The technique may be used for similar aqueous systems where metals are exposed to a flowing aqueous stream.

Use of stainless steel as a reference electrode made the polarization resistance measurement technique reliable and robust for deployment in pilot-scale cooling systems. Stainless steel electrodes performed just as well as standard saturated calomel electrode while treated municipal wastewater was used as makeup water in the cooling system. Existing instantaneous corrosion rate measurement techniques use a single constant for a particular metal alloy to relate polarization resistance to instantaneous corrosion rate, regardless of water quality. The technique developed in this study considers water quality in instantaneous corrosion rate analysis. With changing water quality, calibration of the modified Stern–Geary constant (B') is needed to relate polarization resistance to weight loss for a particular metal or metal alloy. Since the corrosion rate may vary with changing water quality, calibration of B' values in the

bench-scale recirculating system developed here will enable consistent instantaneous corrosion rate measurement in pilot or full-scale cooling water systems. In this study B' values determined in bench-scale studies were comparable to B' values determined from measurements conducted for a period of 28 days in the pilot-scale studies. Reliability of using the B' value for longer time duration (>28 days) was not investigated. However B' value for extended exposure time period can be obtained using bench-scale testing as shown in this study. Long-term study is necessary to demonstrate effectiveness of the instantaneous corrosion rate monitoring technique over a longer period for corrosion monitoring of metal and metal alloys in a recirculating cooling system.

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Notes

The authors declare no competing financial interest.

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