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Bridging Gravimetric and Electrochemical Approaches To Determine the Corrosion Rate of Metals and Metal Alloys in Cooling Systems: Bench Scale Evaluation Method

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The gravimetric weight loss method and the electrochemical polarization resistance methods were combined to evaluate instantaneous corrosion rates for metals and metal alloys in industrial cooling-water systems. Metal and metal–alloy samples were exposed to synthetic cooling water in a bench-scale recirculating system constructed to study corrosion under flow conditions similar to those of a cooling-water system. The measurements yielded by both methods were related through a coefficient, B' , to convert polarization resistance measurements to instantaneous corrosion rates. The metals and metal alloys tested in this study included mild steel, aluminum, copper, and cupronickel. B' was observed to change with time initially but approach a constant value for long-term exposure (>3 days) for most metal materials. B' values varied with metal or metal alloy studied. It was concluded that combining both methods to determine the B' value for a metal or a metal alloy under particular exposure conditions provides a means of obtaining an accurate instantaneous corrosion rate.

1. Introduction

Corrosion criteria for commonly used metals and metal alloys in cooling systems have been proposed in trade publications and cooling-water-system practice guides.^{1–3} The criteria are used as a tool to evaluate the corrosivity of waters and the effectiveness of corrosion inhibitors in cooling-water systems. While there is no universal agreement about specific values for the criteria, the various proposed criteria are generally similar.

Three methods have been used most commonly to assess metal and metal alloy corrosion: the gravimetric weight loss method, the electrochemical Tafel extrapolation method, and the electrochemical polarization resistance method.

The conventional gravimetric weight loss method is the least expensive and simplest method for corrosion monitoring, and operational procedures for conducting the weight loss method are well established.^{4,5} This method simply measures the weight change of an alloy specimen after surface cleaning, over a period of time in which the specimen was exposed to corrosive environment studied. The weight loss measured is converted to a uniform corrosion rate over the exposure period. Although this method is simple to perform, it only gives an average corrosion rate. In many cases, the instantaneous corrosion rate is of greater interest to enable a real-time response to a sudden increase of corrosion rate.

The electrochemical Tafel extrapolation method is commonly used for corrosion mechanism studies and instantaneous corrosion rate determination.^{6–8} This method requires high anodic/cathodic polarizing voltage (e.g., ± 250 mV) and thus might change the surface properties of an electrode. It is only suitable for one-time measurement and not for continuous monitoring. The often poor linearity of anodic polarization curves also limits the application of this method for corrosion rate determination.

If only the cathodic polarization curve is determined, the cathode/anode area ratio influences the accuracy of the results.

The electrochemical polarization resistance method is a sensitive, time-saving method that can detect small changes in relative corrosiveness of water to metal alloys studied, and the measurement can be done real-time, semicontinuously and rapidly.^{6,9} Thus, the polarization resistance method is the most applicable among the three methods for long-term, continuous corrosion monitoring. A standard test method for polarization resistance measurements exists.¹⁰ However, the coefficients used to convert polarization resistance to instantaneous corrosion rate vary with metal of interest and with water chemical composition and thus are system specific. Variation of the coefficient for a metal or metal alloy in a particular type of water with time has not been studied. The variation could influence the accuracy of instantaneous corrosion rate measurements. A previous study¹¹ showed anomalous corrosion rate prediction via comparison of polarization resistance and weight loss measurements, probably due to the variation of the coefficient.

It has been proposed that the combination of the weight loss method and the polarization resistance method offers means of quantitative instantaneous corrosion analysis.^{12,13} However, studies on the relationship between the weight loss method and the polarization resistance method are limited and most studies conducted the two methods on different sets of metal or metal alloy specimens.^{14–17}

The objectives of this study were to (1) design and construct a bench-scale recirculating system in which metal and metal alloy specimens can be exposed to water chemical compositions and temperatures relevant to cooling systems, and the weight loss measurement and the polarization resistance measurement can be applied to study metal alloy corrosion, (2) conduct a series of experiments to examine the relationship between the weight loss method and the polarization resistance method of several alloys in synthetic cooling water, (3) develop a method of combining weight loss data and polarization resistance

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measurements to obtain quantitative instantaneous corrosion rates in industrial cooling systems.

2. Theory of Polarization Resistance

The theory underlying the polarization resistance method is based on charge balance and the current–potential relationship (Tafel relationship) for electron-transfer reactions. Polarization resistance, R_p (Ω), is defined as the differential of the overpotential, η (volt), over the withdrawn current, I_{app} (amp), when η approaches zero, i.e., the slope of polarization curve at the corrosion potential.^{18,19}

$$R_p \equiv \frac{d\eta}{dI_{app}} \bigg|_{\eta=0} = \frac{\beta_a \beta_c}{2.3 I_{corr} (\beta_a + \beta_c)} = \frac{B}{I_{corr}} \quad (1)$$

where β_a and β_c are anodic and cathodic Tafel constants (volt), I_{corr} is the corrosion current (amp/cm²), and B is the Stern–Geary constant (volt) defined as $\beta_a \beta_c / 2.3 (\beta_a + \beta_c)$. Equation 1 is known as the Stern–Geary equation. The main assumptions underlying eq 1 are (1) the corrosion reaction rate is controlled by charge transfer; (2) the corrosion mechanism only involves one anodic and one cathodic reaction; (3) the corrosion potential is not near either the anodic or the cathodic reaction potential.¹⁹

R_p can be related to the instantaneous corrosion rate, ICR (cm/s), through the following equation:

$$ICR = \frac{MB}{AFz\rho R_p} \quad (2)$$

where M is average molecular weight of the metal or metal alloy (g/mol), A is the surface area (cm²), F is the Faraday constant [96 485 coulomb/(mol e[−])], z is the average charge of the metal [(mol e[−])/mol], and ρ is the density of the metal (g/cm³).

The main benefit of using the polarization resistance method to determine the instantaneous corrosion rate is that only a small polarization range very close to corrosion potential is needed to acquire R_p in eq 2. Thus, the surface properties of the metal or metal alloy remain similar after each measurement. This feature makes semicontinuous measurement of R_p for a metal or metal alloy electrode possible without affecting the surface properties of that electrode.

The major difficulty of employing eq 2 is the acquisition of B since the Tafel constants are usually not known precisely. The Tafel constants can be estimated from the higher range of a polarization curve as in the Tafel extrapolation method, but this procedure can alter the surface, which makes continuous measurement infeasible, as discussed previously. Another approach is to measure and correlate R_p and weight loss (WL) for the same material, determine B empirically,^{12,13} and relate R_p semiempirically to ICR. This approach requires many measurements to confirm the value of B for a certain metal or metal alloy.^{14,15}

Stern and Weisert²⁰ compiled data from several different sources and generalized the relationship between corrosion current density and polarization resistance and found that in most corroding systems, B ranges from 0.013 to 0.052 V. Thus, by measuring polarization resistance and using $B = 0.026$ V, corrosion rates can be estimated to within a factor of 2. The data Stern and Weisert²⁰ used were generated from experiments with nickel, iron, steel, cast iron, and measurements of ferric–ferrous ions in different aqueous media. However, inconsistent results between weight loss measurements and polarization resistance measurements were found.^{16,17} Limited studies on B values for metal and metal alloys commonly used

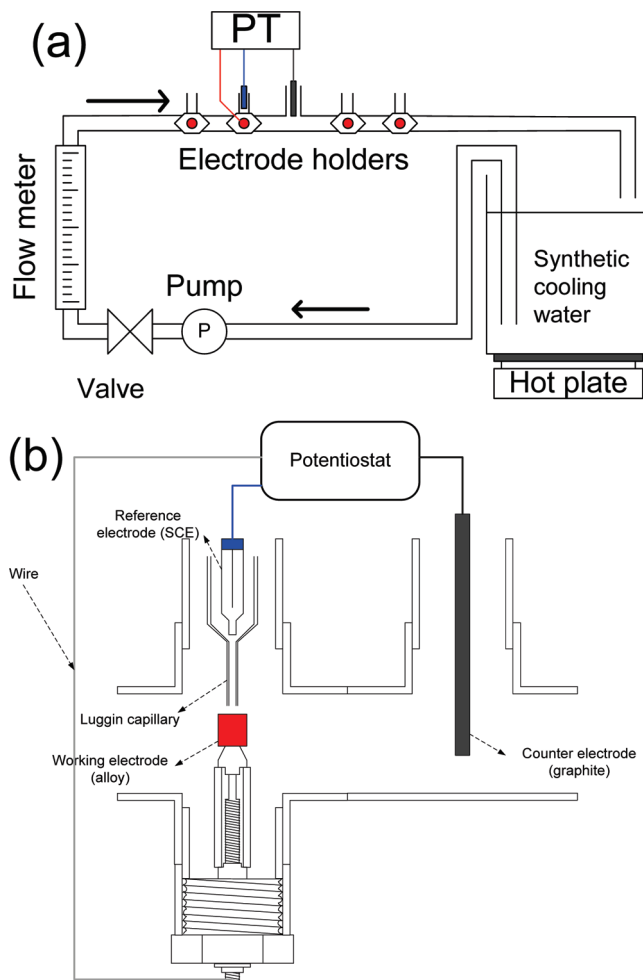


Figure 1. (a) Schematics of the bench-scale recirculating system and (b) detail of mild steel specimen holder and ports for counter electrode and reference electrode installed in the bench-scale recirculating system.

in heat exchangers in the cooling industry, such as aluminum and copper alloys, have been performed.¹⁴

Most studies on the determination of B values have been performed with the metal or metal alloy immersed in aqueous solutions for a short time. The stability of the B value with time for metals or metal alloys in various aqueous environments has not been studied.

To apply eq 2 successfully, z needs to be specified accurately or significant errors in reporting ICR can result.¹⁴ While the determination of z for a specific metal or metal alloy is difficult since many metal elements can have variable valence, the combination of the weight loss method and the polarization resistance method avoids the determination of z and can be used to acquire an empirical constant to convert R_p to ICR directly, as explained in detail later.

3. Experimental Section

3.1. Bench-Scale Recirculating System. A bench-scale recirculating system was designed and constructed for exposure of metal or metal alloy specimens to temperature, flow velocity, and water quality similar to those in a recirculating cooling-water system. The bench-scale recirculating system included a centrifugal pump, a water bath on a hot plate to control the water temperature, and a 0.75 in. nominal diameter PVC pipe rack to hold metal and metal alloy specimens (Figure 1a). The pipe rack consisted of several tee sections into which specimen holders were mounted.

Table 1. Ranges of Key Parameters of Synthetic Cooling-Water Quality^a

pH	ammonia	phosphate	inhibitors							free chlorine/ monochloramine
			TTA	SHMP	TKPP	HEDP	PBTC	AR540	Zn	
7.6–8.8	0–100 ppm as N	0–20 ppm as PO ₄	0–4 ppm	0–10 ppm ^b	0–10 ppm ^b	0–4 ppm	0–10 ppm	0–10 ppm	0–4 ppm	0–1 ppm as Cl ₂

^a TTA: tolyltriazole. SHMP: sodium polyphosphates. TKPP: tetrapotassium pyrophosphate. HEDP: 1-hydroxyethylidene-1,1-diphosphonic acid. PBTC: 2-phosphonobutane-1,2,4-tricarboxylic acid. AR540: AR540 is commercial scaling inhibitor, marketing name Aquatreat AR540 (Alco Chemical, Chattanooga, TN). ^b As PO₄.

To employ gravimetric and electrochemical corrosion measurements in the bench-scale recirculating system, the pipe rack was equipped to accommodate a saturated calomel reference electrode (RE, 0.242 V vs standard hydrogen electrode) in a Luggin capillary, and a graphite counter electrode (CE). Also, each specimen holder was made of an end-cap plug containing a threaded stainless steel rod with a metal or metal alloy specimen attached. The specimen, RE, and CE were connected to a potentiostat for electrochemical corrosion analysis (Figure 1b). After exposure, each specimen was removed for gravimetric corrosion analysis after surface cleaning.

3.2. Synthetic-Cooling-Water Preparation. Synthetic cooling water was prepared to test the applicability of the bench-scale recirculating system for electrochemical and gravimetric corrosion analysis. The synthetic-cooling-water quality was based on an estimated average inorganic composition of secondary treated municipal wastewater concentrated four times. It was chosen to be concentrated four times because water in recirculating cooling systems usually is concentrated several times compared to makeup water due to evaporation. The synthetic cooling water was prepared using the following recipe (mM): NaHCO₃, 13.44; CaCl₂, 7.62; MgSO₄, 2.84; NH₄Cl, 7.01; K₂HPO₄, 0.21; KCl, 0.28; MgCl₂, 4.24. The pH of the water was 8.7 ± 0.1 before further adjustment. The water provided a

corrosive aqueous environment for the metals and metal alloys studied due to the presence of ammonia. Some parameters were changed in various tests to create a range of corrosivity of the synthetic cooling water (Table 1). These parameters included pH, phosphate, inhibitors, and disinfectants. The synthetic cooling water was recirculated and aerated in the bench-scale system at 40 °C. Semicontinuous *R_p* measurements and WL measurements were performed for the metal and metal alloy specimens in contact with the synthetic water.

3.3. Metal and Metal Alloy Pre-Exposure and Postexposure Treatment. The metals and metal alloys chosen for study were mild steel (UNS G10180), aluminum (UNS A91100), copper (UNS C10100), and cupronickel (UNS C70600) as they are commonly used in cooling-water systems.²¹

Metal and metal alloy specimens tested were cylinder-shaped with the diameter of 0.375 in. and length of 0.5 in. and were obtained from Metal Samples Co. (Munford, AL). Prior to being exposed to synthetic cooling water, they were wet polished with SiC paper to a 600 grit surface finish, dried, weighed to 0.1 mg, degreased with acetone, rinsed in distilled water, and then mounted in the bench-scale recirculating system. During the exposure, the *R_p* of the specimens was semicontinuously monitored and specimens were withdrawn after approximately 12 h and 1, 2, 3, 4, and 7 days of exposure to determine the

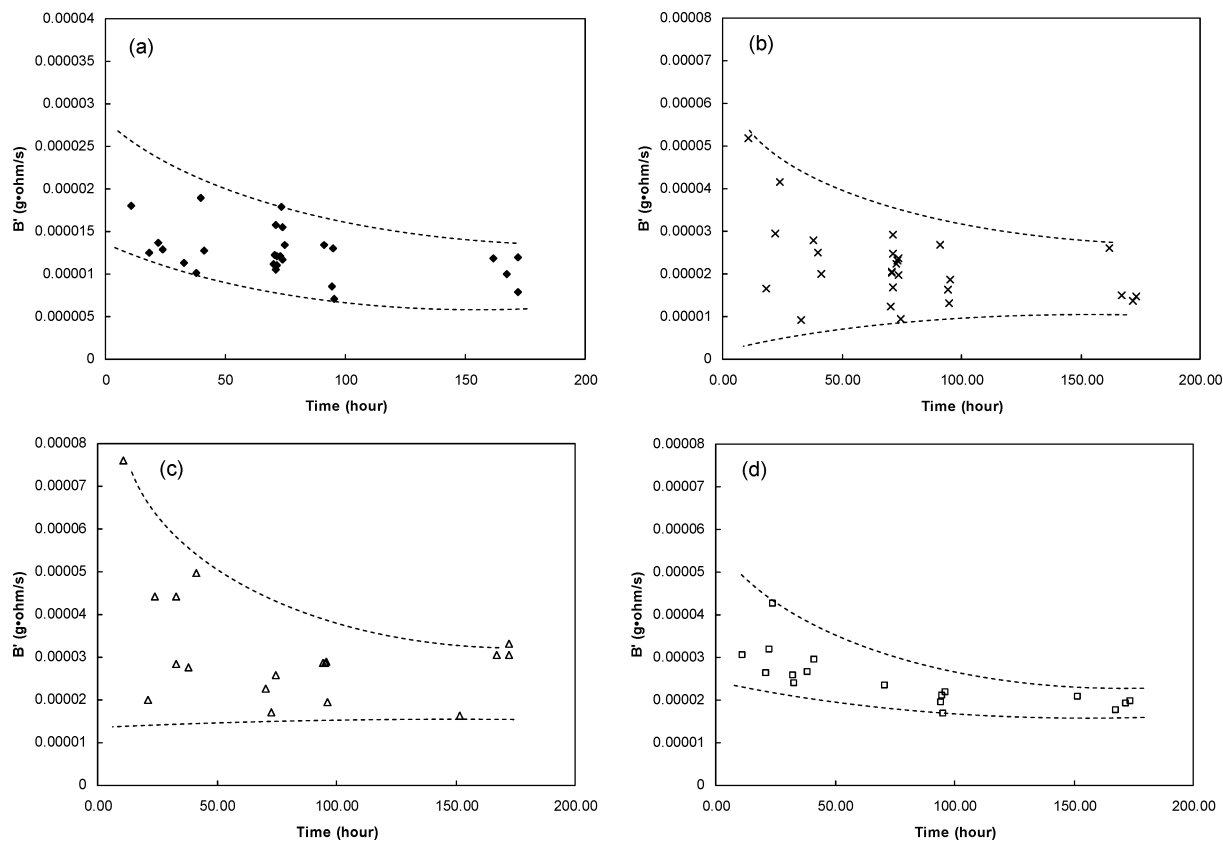


Figure 2. B' versus time for (a) mild steel, (b) aluminum, (c) copper, and (d) cupronickel immersed in synthetic cooling water. The B' values were determined by combining the gravimetric weight loss method and the electrochemical polarization resistance method for tests of varying duration. Hand drawn curves are used to indicate the converge of the B' values with time.

Table 2. Metal Alloys Corrosion Potential (E_{corr} , V vs SCE), Integration of Polarization Resistance with Time ($\int(1/R_p) dt$, s/ Ω), Weight Loss (WL, g), B' [(g· Ω)/s], and B (V) Determined from Bench-Scale Recirculating System Testing with Synthetic Cooling Water with Varied Key Parameter Conditions^a

(a) Mild Steel								
key parameter conditions	pH	time (h)	E_{corr} vs SCE (V)	$\int(1/R_p) dt$ (S/ Ω)	WL (g)	B' [10^{-5} (g $\cdot\Omega$)/s]	B (V) EW 28	
GPM1.5	7.6	95.4	−0.663	3352	0.0239	0.71	0.025	
GPM1.5	7.6	172.1	−0.663	6162	0.0483	0.78	0.027	
DKP10, GPM1.5	7.6	95.0	−0.631	1279	0.0166	1.30	0.045	
DKP10, GPM1.5	7.6	171.8	−0.647	2182	0.0262	1.20	0.041	
DKP10, GPM1.5	8.4	94.2	−0.650	540	0.0046	0.86	0.030	
DKP10, GPM1.5	8.4	167.1	−0.625	788	0.0079	1.00	0.034	
DKP20, SHMP10, TTA4, HEDP4, Zn4, GPM1.5	8.8	91.0	−0.607	79	0.0011	1.35	0.046	
DKP20, SHMP10, TTA4, HEDP4, Zn4, GPM1.5	8.8	161.7	−0.599	185	0.0022	1.19	0.041	
NH100, DKP20, TKPP10, TTA4, PBTC10, GPM3	8.5	73.3	−0.572	34	0.0006	1.79	0.062	
NH100, DKP20, TKPP10, TTA4, PBTC10, MCA < 1,GPM3	8.7	71.2	−0.564	86	0.0009	1.05	0.025	
NH100, DKP20, TKPP5, TTA2, PBTC5, GPM3	8.4	70.2	−0.545	80	0.0009	1.12	0.039	
NH100, DKP20, GPM3	8.5	74.6	−0.568	1093	0.0147	1.34	0.046	
DKP20, TKPP10, TTA4, PBTC10, GPM3	8.8	72.3	−0.589	70	0.0011	1.58	0.054	
DKP20, TKPP10, TTA4, PBTC10, FC1, GPM3	8.8	73.7	−0.601	231	0.0027	1.17	0.040	
NH100, DKP20, TKPP10, TTA4, PBTC10, MCA1, GPM3	8.4	70.9	−0.587	147	0.0016	1.09	0.038	
NH100, DKP20, TKPP10, TTA4, PBTC10, AR10, GPM3	8.5	73.6	−0.622	77	0.0012	1.55	0.054	
NH100, TKPP10, PBTC10, GPM3	8.7	71.5	−0.545	164	0.0020	1.22	0.042	
NH100, TTA4, PBTC10, GPM3	8.7	72.3	−0.538	173	0.0021	1.21	0.042	
NH100, TKPP10, TTA4, GPM3	8.7	71.3	−0.565	27	0.0003	1.11	0.038	
DKP20, GPM3	8.6	70.6	−0.586	181	0.0022	1.22	0.042	
(b) Aluminum								
key parameter conditions	pH	time (h)	E_{corr} vs SCE (V)	$\int(1/R_p) dt$ (s/ Ω)	WL (g)	B' [10^{-5} (g $\cdot\Omega$)/s]	B (V)	
							EW 9	EW 27
GPM1.5	7.6	95.5	−1.137	128	0.0024	1.88	0.201	0.067
GPM1.5	7.6	173.2	−1.070	203	0.0030	1.47	0.158	0.053
DKP10, GPM1.5	7.6	94.9	−1.083	161	0.0021	1.32	0.141	0.047
DKP10, GPM1.5	7.6	171.9	−1.046	227	0.0031	1.37	0.147	0.049
DKP10, GPM1.5	8.4	94.3	−1.079	486	0.0079	1.62	0.174	0.058
DKP10, GPM1.5	8.4	167.2	−1.042	647	0.0097	1.50	0.161	0.054
DKP20, SHMP10, TTA4, HEDP4, Zn4, GPM1.5	8.8	91.1	−0.983	91	0.0025	2.69	0.288	0.096
DKP20, SHMP10, TTA4, HEDP4, Zn4, GPM1.5	8.8	161.9	−0.660	99	0.0026	2.61	0.280	0.093
NH100, DKP20, TKPP10, TTA4, PBTC10, GPM3	8.5	73.4	−0.450	99	0.0023	2.31	0.248	0.083
NH100, DKP20, TKPP10, TTA4, PBTC10, MCA < 1,GPM3	8.7	71.3	−0.476	314	0.0092	2.93	0.314	0.105
NH100, DKP20, TKPP5, TTA2, PBTC5, GPM3	8.4	70.3	−0.614	72	0.0009	1.24	0.133	0.044
NH100, DKP20, GPM3	8.5	74.7	−0.680	1308	0.0124	0.95	0.102	0.034
DKP20, TKPP10, TTA4, PBTC10, GPM3	8.8	71.3	−0.739	105	0.0026	2.47	0.264	0.088
DKP20, TKPP10, TTA4, PBTC10, FC1, GPM3	8.8	73.8	−0.533	141	0.0028	1.98	0.213	0.071
NH100, DKP20, TKPP10, TTA4, PBTC10, MCA1, GPM3	8.4	70.9	−0.728	228	0.0046	2.02	0.216	0.072
NH100, DKP20, TKPP10, TTA4, PBTC10, AR10, GPM3	8.5	73.8	−0.702	151	0.0036	2.38	0.255	0.085
NH100, TTA4, PBTC10, GPM3	8.7	72.9	−0.633	319	0.0071	2.23	0.239	0.080
NH100, TKPP10, TTA4, GPM3	8.7	71.4	−0.670	42	0.0007	1.67	0.179	0.060
DKP20, GPM3	8.6	70.8	−0.878	175	0.0036	2.05	0.220	0.073
(c) Copper								
key parameter conditions	pH	time (h)	E_{corr} vs SCE (V)	$\int(1/R_p) dt$ (s/ Ω)	WL (g)	B' [10^{-5} (g $\cdot\Omega$)/s]	B (V)	
							EW 31.8	EW 63.6
GPM1.5	7.6	95.7	−0.053	55	0.0016	2.90	0.088	0.044
GPM1.5	7.6	172.4	−0.046	82	0.0027	3.30	0.100	0.050
DKP10, GPM1.5	7.6	95.1	−0.081	41	0.0012	2.86	0.087	0.043
DKP10, GPM1.5	7.6	172.3	−0.056	74	0.0023	3.06	0.093	0.046
NH100, GPM1.5	7.6	96.2	−0.188	1039	0.0203	1.95	0.059	0.030
NH100, GPM1.5	7.6	151.6	−0.182	1659	0.0269	1.62	0.049	0.025
DKP10, GPM1.5	8.4	94.5	−0.017	17	0.0005	2.87	0.087	0.043
DKP10, GPM1.5	8.4	167.3	−0.019	24	0.0007	3.05	0.093	0.046
NH100, DKP20, GPM3	8.4	74.8	0.011	31	0.0008	2.59	0.079	0.039
NH100, GPM3	8.3	70.6	−0.062	313	0.0071	2.27	0.069	0.034
NH100, TKPP10, PBTC10, GPM3	8.7	72.8	−0.046	441	0.0076	1.72	0.052	0.026
(d) Cupronickel								
key parameter conditions	pH	time (h)	E_{corr} vs SCE (V)	$\int(1/R_p) dt$ (s/ Ω)	WL (g)	B' [10^{-5} (g $\cdot\Omega$)/s]	B (V)	
							EW 31.5	EW 56.9
GPM1.5	7.6	95.0	−0.012	95	0.0020	2.11	0.065	0.036
GPM1.5	7.6	173.7	−0.006	167	0.0033	1.98	0.061	0.034
DKP10, GPM1.5	7.6	95.4	−0.010	38	0.0007	1.69	0.052	0.029
DKP10, GPM1.5	7.6	172.1	−0.025	99	0.0019	1.93	0.059	0.033
NH100, GPM1.5	7.6	96.3	−0.025	194	0.0042	2.19	0.067	0.037
NH100, GPM1.5	7.6	151.7	−0.015	209	0.0043	2.07	0.063	0.035
DKP10, GPM1.5	8.4	94.6	−0.102	31	0.0006	1.94	0.059	0.033
DKP10, GPM1.5	8.4	167.4	−0.191	52	0.0009	1.76	0.054	0.030
NH100, GPM3	8.3	70.7	−0.044	132	0.0031	2.34	0.072	0.040

^a The corrosion potential shown in the table was that of the electrode right before the electrode removal. For the tests with pH lower than 8, sulfuric acid was added to control the pH. EW: possible equivalent weight of a metal or metal alloy. GPM#: water flow rate of # gpm. DKP#: dipotassium orthophosphate # ppm as PO₄. SHMP#: sodium polyphosphate # ppm as PO₄. TKPP#: tetrapotassium pyrophosphate # ppm as PO₄. TTA#: tolyltriazole # ppm. HEDP#: 1-hydroxyethylidene-1,1-diphosphonic acid # ppm. PBTC#: 2-phosphonobutane-1,2,4-tricarboxylic acid # ppm. Zn#: zinc nitrate # ppm as Zn. NH#: ammonia # ppm as N. FC#: free chlorine # ppm as Cl₂. MCA#: monochloramine # ppm as Cl₂. AR#: Aquatreat AR540 (Alco Chemical, Chattanooga, TN) # ppm.

relationship between WL and R_p measurements with time for a particular metal or metal alloy. After withdrawal, the specimens were cleaned following the ASTM G1⁴ and then reweighed to 0.1 mg for determining the WL.

3.4. Polarization Resistance Measurement. The metal alloy specimens in the bench-scale recirculating system were used directly for electrochemical polarization resistance (R_p) measurements. R_p was measured using a PGSTAT100 potentiostat (ECO CHEMIE, The Netherlands). A three electrode system was employed with the alloy specimen as a working electrode, graphite as a counter electrode, and saturated calomel electrode as a reference electrode in a Luggin capillary probe. Each polarization scan was performed from -30 to $+30$ mV with respect to the corrosion potential at a scan rate of 0.3 mV/s.

4. Results and Discussion

4.1. Equation Derivation To Relate Weight Loss and Polarization Resistance. The weight loss that occurs over time of exposure of a metal or metal alloy specimen of surface area A can be related to ICR by integrating both sides of eq 2 and rearranging the equation:

$$WL = \int ICR \cdot A \rho \, dt = \frac{M}{Fz} \int \frac{B}{R_p} \, dt \quad (3)$$

where M , F , z , A , and ρ are constant with time.

Under the assumption that B does not change with time for a metal or metal alloy in a certain aqueous solution, one can define

$$B' = \frac{BM}{Fz} = \frac{WL}{\int (1/R_p) \, dt} \quad (4)$$

where B' [(g·Ω)/s] is of interest since it can be determined from WL and R_p and without knowledge of z . For B' determined through eq 4, ICR can be determined directly through R_p measurement:

$$ICR = \frac{B'}{A \rho R_p} \quad (5)$$

The assumption of B' or B being constant is examined below.

4.2. B' Value vs Time for Metal Alloys. The variation of B' calculated by using eq 4 versus time of exposure was determined through tests of different duration and results are shown in Figure 2. As can be seen from Figure 2, B' values for mild steel were relatively stable but B' values for other metals and metal alloys tested in this study were generally not constant with time as they gradually reached steady state values. Thus, the assumption that B' is constant with time is incorrect for short-term measurements but reasonable for long-term (>3 days) measurements. Figure 2 indicates that the B' values for the metals and metal alloys tested converged with time and reached relatively stable after 3 days. Thus, to acquire a stable B' for a metal or metal alloy in a particular aqueous environment, longer immersion time is necessary. The assumption that B' is constant allows the use of eq 4 for long-term (>70 h) B' determination. This time to steady state behavior may not be relevant to other metals and metal alloys and aqueous systems and additional testing is necessary to ascertain the time required for B' to achieve a constant value in each case. The B' values of metals and metal alloys determined from tests with exposure time more 70 h are presented in Table 2. Table 2 also shows the testing key parameter conditions, exposure time, corrosion potential,

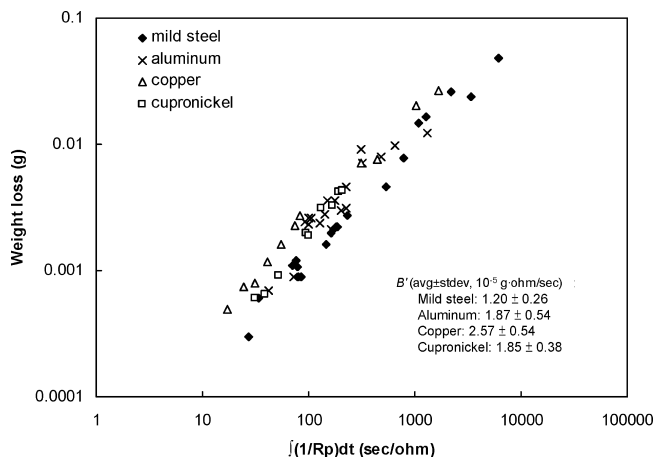


Figure 3. Relationship between gravimetric weight loss and the integration of polarization resistance over time. The data points were selected only for these with metal alloy immersed over 3 days when B' reached relatively stable values.

integration of polarization resistance with time, as well as the calculated Stern–Geary constants.

Overall, the electrochemical polarization resistance method in combination with the gravimetric weight loss method used in this study can track the change of B' with time, and give more accurate instantaneous corrosion rate estimation.

4.3. Relationship between Weight Loss and Polarization Resistance. Data points of weight loss vs $\int (1/R_p) \, dt$ from at least 3 days and a maximum of 7 days immersion of all metals and metal alloys tested in this study were used to determine B' values for metals and metal alloys in particular systems since B' was found to be relatively more stable after 3 days of immersion in synthetic cooling water. The results are shown in Figure 3 in which data are presented in logarithmic scale since WL and $\int (1/R_p) \, dt$ data for each metal or metal alloy varied over 3 orders of magnitude. Figure 3 shows that for each alloy immersed in synthetic cooling water subjected to different chemical treatments (Table 1), WL and $\int (1/R_p) \, dt$ were approximately proportional. The slope of the linear WL vs $\int (1/R_p) \, dt$ plot gives the value of B' for that particular system. The averages and standard deviations of B' values determined for the metals and metal alloys tested are given in Figure 3.

The consistency of B' values over a wide range of aqueous conditions for any of the tested metals and metal alloys demonstrates the utility of combining weight loss and polarization resistance measurements to determine a long-term B' and thus instantaneous corrosion rates for a particular metal or metal alloy in a particular solution. In industrial cooling systems, the recirculating cooling water might be subjected to various kinds of chemical treatments to prevent corrosion, scaling, and biofouling. As shown here, it appears that these chemical treatments of a particular water (i.e., synthetic cooling water tested in this study) do not vary the long-term B' significantly for the metal and metal alloys tested. The observed consistency of the B' values also indicates that accurate instantaneous corrosion rate measurements are possible via polarization resistance if B' is determined a priori for the system of interest. The instantaneous corrosion rate measured by polarization resistance can thus be used as an indication of whether a particular water has an acceptable or unacceptable corrosivity with respect to the metal or metal alloy of interest.

Experiments of similar approach were performed to study the B' values for metals and metal alloys in contact with tap water. The results showed that mild steel and aluminum had

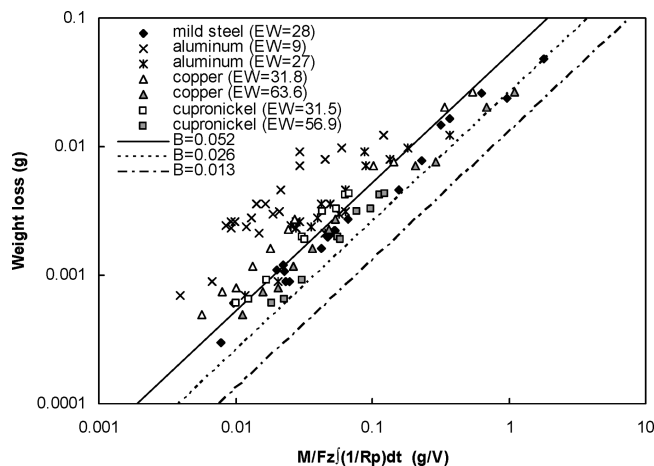


Figure 4. Comparison of the relationship between weight loss and the integration of polarization resistance with time between data points from this study (only data points from the metal alloy immersion time over 3 days were used) and generalized conclusion from the study by Stern and Weisert.²⁰

quite different B' values for tap water and synthetic cooling water. It was concluded that for the same metal or metal alloy the B' might vary with waters having significant different chemistry.²²

4.4. Comparison of Results from This Study with Other Studies. As discussed earlier, Stern and Weisert²⁰ identified that B ranges generally from 0.013 to 0.052 V. According to eq 4, if M/z , the equivalent weight of a metal or metal alloy, is known, B' determined from the present study can be converted to B and the results can be compared with the general B range compiled by Stern and Weisert.²⁰ According to eq 4, the generalized B range can be expressed as the relationship between WL and $(M/Fz)f(1/R_p) dt$, which is shown as the solid straight lines in Figure 4. The upper line in Figure 4 represents the B

value of 0.52 V, the middle line 0.26 V, and the lower 0.13 V, spanning the range established by Stern and Weisert.²⁰

In this study, z assigned for iron is +2 ($\text{mol}\cdot\text{e}^-/\text{mol}$), for aluminum is +1 or +3 ($\text{mol}\cdot\text{e}^-/\text{mol}$),¹⁸ for copper is +1 or +2 ($\text{mol}\cdot\text{e}^-/\text{mol}$),¹⁸ and for nickel is +2 ($\text{mol}\cdot\text{e}^-/\text{mol}$).¹² The resulting equivalent weight (EW) obtained from ASTM G102¹² are 28.0 $\text{g}/(\text{mol}\cdot\text{e}^-)$ for mild steel, 27.0 or 9.0 $\text{g}/(\text{mol}\cdot\text{e}^-)$ for aluminum, 63.6 or 31.8 $\text{g}/(\text{mol}\cdot\text{e}^-)$ for copper, and 56.9 or 31.5 $\text{g}/(\text{mol}\cdot\text{e}^-)$ for cupronickel. The calculated relationship between WL and $(M/Fz)f(1/R_p) dt$ for all metals and metal alloys tested in this study with over 3 days immersion is shown in Figure 4.

In Figure 4, B values of mild steel, copper (EW = 63.6 $\text{g}/(\text{mol}\cdot\text{e}^-)$), and cupronickel (EW = 56.9 $\text{g}/(\text{mol}\cdot\text{e}^-)$) are in the range 0.013–0.052 V. For mild steel, B values range from 0.026 to 0.052 V, which is consistent with B values for iron in various natural and synthetic waters. For aluminum, most data points are not located in the range of B values identified by Stern and Weisert.²⁰ Figure 4 also shows B values of copper (EW = 31.8 $\text{g}/(\text{mol}\cdot\text{e}^-)$) and cupronickel (EW = 31.5 $\text{g}/(\text{mol}\cdot\text{e}^-)$). Most of those B values are not in the range of 0.013 to 0.052 V.

Overall, the B value range identified in the study of Stern and Weisert²⁰ does not apply to all metals and metal alloys in contact with synthetic cooling water. Thus, using the general B value to estimate metal or metal alloy corrosion rate in cooling-water systems is not appropriate to determine accurate instantaneous corrosion rates.

4.5. Influence of the Key Parameters on the Polarization Curves. In this study, each polarization resistance was determined from a polarization curve. Here only the polarization curves of mild steel with an exposure time of 3 days and flow rate of 3 gpm were shown in Figure 5. Clearly, both corrosion potential and polarization curves were influenced by the key parameter conditions. The key parameters could shift the corrosion potential toward either the positive or negative

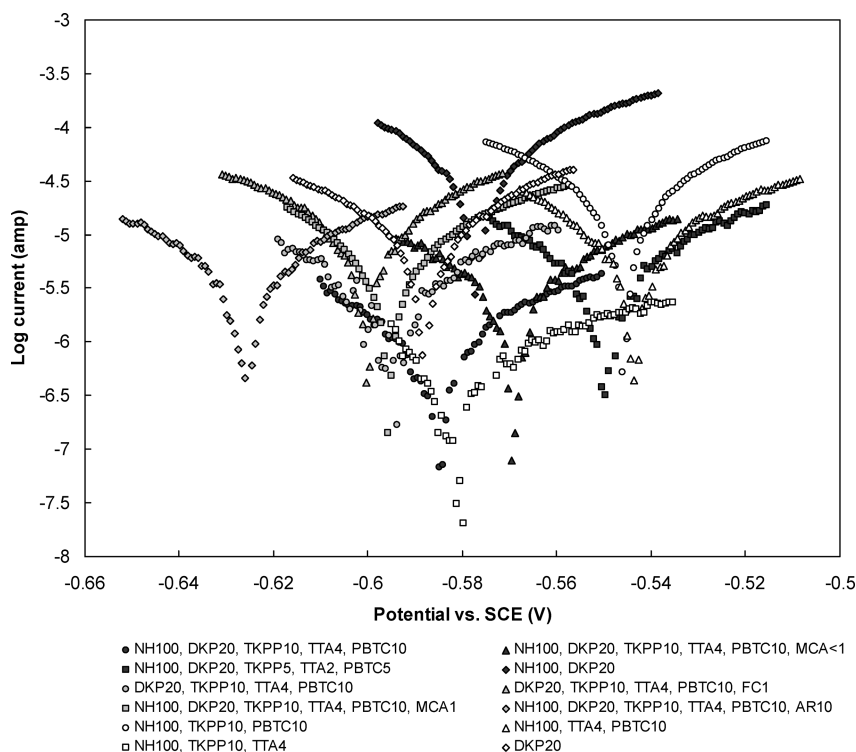


Figure 5. Polarization curves of mild steel exposed to synthetic cooling water with varied key parameter conditions in a bench-scale recirculating system at flow rate 3 gpm for 3 days. The figure indicates that the polarization curves were influenced significantly by the key parameters.

direction. However, the increase or decrease of the corrosivity of the water could not be directly suggested by the shift of the corrosion potential. Investigations of the influence of key parameters on the polarization curves are continuing.

5. Summary and Conclusions

In this study, metals and metal alloys (mild steel, aluminum, copper, and cupronickel) commonly used in industrial cooling systems were used to examine the relationship between weight loss measurements and polarization resistance measurements of corrosion in synthetic cooling water. Results indicated the semiempirical constant B' , which is the constant of proportionality between WL and time-integrated polarization resistance, changes with time but reached a stable value after 3 days. The long-term (>3 days) B' value for each metal and metal alloy was generally constant over a wide range of corrosivity of water. With knowledge of B' for a particular system, polarization resistance measurements can be used to obtain an accurate instantaneous corrosion rate. Thus, the combination of both the gravitational weight loss method and the electrochemical polarization resistance method is useful for assessment of instantaneous corrosion rate.

Additional research is needed to relate the results obtained to fundamental electrochemical properties of the metals and metal alloys studied. Recommended follow-up research based on the results obtained in this study includes (1) conduct potentiodynamic polarization experiments to study the change of anodic and cathodic behaviors of a metal or metal alloy with time in the pilot-scale system at different exposure times up to 2 months, (2) examine a wide variety of water qualities to elucidate the main factors influencing the value of B' for a particular metal or metal alloy exposed to a particular type of water, and (3) apply spectroscopic surface characterization techniques (X-ray diffraction, scanning electron microscopy, etc.) to understand the relationship of surface property changes and B' values.

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