CHARACTERIZATION OF COPPER CORROSION PRODUCTS FORMED IN DRINKING WATER BY COMBINING ELECTROCHEMICAL AND SURFACE ANALYSES

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ABSTRACT

This study focuses on the application of electrochemical corrosion rate measurement and solid surface analysis approaches to understanding drinking water copper corrosion. Applying electrochemical approaches combined with copper solubility measurements, and solid surface analysis approaches are discussed. DC polarization (DCP) and Electrochemical Noise (ECN) measurements were carried out to obtain Stern-Geary constant and noise resistance, respectively. ECN has the advantage in that corrosion behavior can be monitored as a function of extended periods of time without the need to apply an artificial potential that can potentially alter the metal surface in an unnatural way. ECN allows for the prediction of how natural films on the corroding metal surface are impacted by changing water quality conditions. Specific film degradation and changes on copper metal were observed by Electrochemical Impedance Spectroscopy (EIS). Cyclic Potentiodynamic Polarization (CPP) measurements are applied to provide useful information about the properties of predicting pitting corrosion tendencies. These electrochemical methods, however, proved to be insufficient for understanding and predicting the build-up of corrosion products on copper surfaces. A study on the development of surface scales was carried out using X-ray Photoelectron Spectroscopy (XPS) and Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS). These approaches provided a better description of the mechanisms associated with the early build-up of corrosion products on the copper surface.

Keywords: copper corrosion, X-ray photoelectron spectroscopy (XPS), time-of-flight secondary ion mass spectrometry (ToF-SIMS)
INTRODUCTION

Copper has been one of the most widely used materials for pipes and fittings in the drinking water distribution system since copper can readily form copper oxide passivation layers of Cu$_2$O and/or CuO.\textsuperscript{1,2} In the past several decades, intensive studies have been performed on the corrosion behavior of copper in acid solution, neutral NaCl solutions, and alkaline solution.\textsuperscript{3-7} Some efforts were also made in the investigation of the corrosion behavior of copper in synthetic tap water and in very low conductivity electrolyte.\textsuperscript{2,8,9} However, the corrosion mechanism for copper is still not fully understood. Electrochemical methods, Tafel technique or Electrochemical Impedance Spectroscopy (EIS), are common electrochemical approaches used to investigate corrosion phenomena in aqueous solution. There are some advantages to conventional electrochemical techniques, such as; they can save time while accelerating corrosion behavior. The primary disadvantage is that most electrochemical techniques apply an artificially external potential which may potentially modify the metal surface. Spontaneous fluctuation of the current and potential of a corroding electrode which is commonly referred as electrochemical noise (ECN) has been extensively studied in the past decade in order to better understand the corrosion behavior in various conditions.\textsuperscript{10-12} Current and potential noises are typically acquired by monitoring two identical electrodes coupled through a zero resistance ammeter (ZRA) without external signal. The current between these two electrodes is measured in this ZRA mode while they are maintained with negligible potential difference. The voltage is measured simultaneously between one of the working electrodes and a reference electrode. In this study, electrochemical technique including conventional EIS and DC polarization techniques was applied to copper corrosion to obtain corrosion rate and compared each corrosion rate obtained from noise resistance after ECN test and from polarization resistance after EIS test. XPS analysis of copper compounds, copper oxide, sulfate, was used for studying copper corrosion products with various corrosion environments.\textsuperscript{13-15} In this study, two different copper oxidation states, Cu(I) and Cu(II), and copper compounds were investigated by XPS and ToF-SIMS.

EXPERIMENTAL

Sample preparation

Copper metal samples: Two different shapes, rod and coupon, of copper type C11000 (99.9 wt% Cu, 0.04 wt% O) from Metalsupermarkets (Cincinnati, OH) were used. A copper rod with 1.27 cm length and 0.95 cm diameter was used as a working electrode for Electrochemical Impedance Spectroscopy (EIS) and Tafel extrapolation. A cylindrical copper specimen was screwed tightly on the end of a threaded rod and was sealed by hot-melt gun between gasket and copper sample. The working electrode used in the Cyclic Potentiodynamic Polarization (CPP) test was copper coupon with dimensions 5.08 × 5.08 cm$^2$. Two identical copper coupons with dimensions 2.54 × 2.54 cm$^2$ and 0.08 cm thickness were used as two working electrodes without a counter electrode for Electrochemical Noise (ECN) measurement.

Before electrochemical tests, the working electrode was first polished with silicon carbide abrasive paper (grade 1200), rinsed with deionized water and finally degreased in acetone ultrasonically for 3 min at room temperature and air dried.\textsuperscript{(1)}

Synthetic tap water samples: Synthetic tap water used in this study contained 10 mg/L bicarbonate, 120 mg/L sulfate, 60 mg/L chloride and was adjusted to pH 9±0.1 unless stated otherwise. Deionized water

\textsuperscript{(1) ASTM G 1-90: Standard Practice for Preparing, Cleaning, and Evaluating Corrosion Test Specimens}
Electrochemical analyses

Electrochemical Impedance Spectroscopy (EIS)\(^{(2)}\): This technique was performed to evaluate the alternating current signals based on corrosion behavior with increasing immersion time. It was carried out on fresh copper rods by using a Gamry PCI4 with Framework\(^{\text{TM}}\) version 4.3 after immersing in test solutions for 2, 24 and 48 h and analyzed E-Chem Analyst version 1.3 application software. The initial frequency was 100 kHz and final was 0.02 Hz with AC excitation amplitude of 4 mV rms. Exposed sample area to the electrolyte was 4.5 cm\(^2\). Saturated calomel electrode (SCE) and a high purity graphite rod were used as a reference electrode and counter electrode, respectively. The electrochemical cell was made of Pyrex glass with 5 holes in which the working electrode, a graphite counter electrode, a reference SCE, air bubbler inlet and outlet were fitted. The tests were conducted in aerated condition to avoid diffusion controlled reaction.

DC Polarization (DCP): DCP was carried out to get the Stern-Geary constant (B) calculated from the Tafel slopes (\(\beta_a\) and \(\beta_c\)). Substituting the values \(\beta_a\) and \(\beta_c\) into the expression \(B = \frac{\beta_a \times \beta_c}{2.3 (\beta_a + \beta_c)}\) yielded B.

\[B = \frac{\beta_a \times \beta_c}{2.3 (\beta_a + \beta_c)}\]  \hspace{1cm} (1)

The initial potential was -0.25 vs OCP and the final was 0.25 V. The scan rate and sample period were 1 mV/s and 2 sec, respectively. Exposed sample area, electrode setup and electrochemical cell were the same as the EIS test above.

Cyclic Potentiodynamic Polarization (CPP)\(^{(3)}\): The initial and final potential were -0.5 and 0 V respectively. The forward and reverse scan rates were 0.5 and 2.5 mV/s, respectively. The working electrode was square 5.08 × 5.08 cm\(^2\) copper coupon and exposed sample area was 7.065 cm\(^2\). A graphite rod and SCE were used as a counter and reference electrode, respectively.

Electrochemical Noise (ECN): Both current and voltage noise were measured simultaneously on an electrochemical cell under control of a zero resistance ammeter. Unlike other electrochemical analyses, air was supplied to an auxiliary cell connected to the main cell with Tygon\(^{\text{TM}}\) tubing. The main ECN cell was covered by a Faraday cage preventing current and voltage noise from other electronic sources shown in Figure 1. Water flew from auxiliary cell to the ECN cell with a flow rate of 5.5 mL/s. Only one side of each two identical 2.54 × 2.54 cm\(^2\) copper coupons was exposed to the test electrolyte. The reference electrode was placed in the middle of the two working electrodes. Block time, sample period and repeat time were 4 s, 0.05 s and 15 s, respectively. ECN measurement recorded 48 h. All electrochemical measurements except ECN were performed in stagnant conditions.

Solid surface analyses

X-ray Photoelectron Spectroscopy (XPS): XPS measurements were performed using a Surface Science

\(^{(2)}\) ASTM G 3-89: Standard Practice for Conventions Applicable to Electrochemical Measurements in Corrosion Testing
\(^{(3)}\) ASTM G 61-86: Standard Test Method for Conducting Cyclic Potentiodynamic Polarization Measurements for Localized Corrosion Susceptibility of Iron-, Nickel-, or Cobalt-Based Alloys
Labs SSX-100 instrument fitted with a monochromatic Al Kα radiation (E=1486.6 eV). The absolute binding energies of different surface species were calibrated using the C1s line at 284.6 eV.

Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS): An ION-TOF model IV instrument equipped with a 25 kV liquid metal (69Ga) ion gun was used. The area analyzed was approximately 50 × 50 µm² and a flood gun was used for charge neutralization. The primary ion dose was 4.73 × 10⁹ ions/cm². An Ar gun with 3 keV and 70 nA current was used for sputtering for cleaning and depth profiling purposes. Sputtering and analysis area were 500 × 500 µm² and 100 × 100 µm² respectively.

## RESULTS AND DISCUSSION

### Electrochemical analyses

Figure 2 shows the Nyquist plots for copper immersed in control water (pH = 9±0.1) at different exposure times (2, 24, 48 hr) from high frequency (100 kHz) to low frequency (0.02 Hz). With increase of immersion time, the diameters of semicircles become larger. This Nyquist diagram indicated two time constants copper corrosion film made on the surface. One constant phase element (CPE1) indicates a charge transfer layer between the metal and electrolyte and the other CPE2 represents copper passivation films on the metal surface. The proposed physical structure of the corroded copper surface with an oxide film in the synthetic tap water and equivalent circuit model are proposed in Figure 3. The proposed equivalent circuit model seems to fit the physical structure and data quite well. Rs is the bulk solution resistance, Rct is the charge transfer resistance and Rp is the passivation film resistance. EIS parameters calculated from the proposed equivalent circuit model were shown in Table 1. The CPE can be used to fit an electrochemical system better than an ideal capacitor and calculated by 1/Z = Qo(jω)^n, where Qo is the admittance at ω (angular frequency) = 1 rad/s, j is an imaginary number and n is the CPE exponent. The factor n is usually between 0.5 and 1 indicating CPE is a non-ideal capacitor. The passivation film resistance was increased with time. The values of polarization resistance obtained from EIS data (Table 1) extrapolated to a low frequency.

The polarization resistance (Rp) which is the overall circuit resistance except solution resistance (Rs) in Figure 3 was used to other Icorr and corrosion rate using a Stern-Geary constant obtained from DCP. The anodic polarization curve of Figure 4 does not show well-defined Tafel behavior and cannot be used for determination of the Tafel constants since the surface may be roughened or otherwise changed as corrosion byproducts deposited and/or precipitated as oxide/hydroxide films on the surface while the cathodic polarization curve was measured. Anodic curve calculated from cathodic data and slopes of anodic and cathodic curve were considered as Tafel constants βa and βc. According to equation (1), B was calculated as 0.0382. This value was adopted to calculate corrosion rate in EIS and ECN afterward.

From EIS results, Icorr is readily obtained from equation (2) and the corrosion rate calculated from equation (3) below is shown in Figure 5. K is constant with 3272 mm/(amp·cm·year) and the equivalent weight of copper is 31.77g. Corrosion rate decreased with immersion time indicates inherent films formed initially and the passivated copper surface.

\[ I_{corr} = \frac{B}{R_p} \]  

\[ \text{p}_{corr} = \frac{K \times B}{R_p} \]

(4) ASTM G 102-89: Standard Practice for Calculation of Corrosion Rates and Related Information from Electrochemical Measurements
\[
CR = \frac{I_{corr} \times K \times EW}{d \times A}
\]
(3)

Where, CR: Corrosion rate (mm/year)

\(R_p\): Polarization resistance

K: 3272 mm/(amp·cm·year)

EW: 31.77 g

d: 8.96 g/cm³

A: exposed area

Figure 6 shows CPP data known as evaluating pitting tendency of test metal. Pitting loop after 2 hour immersion showed relatively large positive loop which implies a pitting tendency. The 24 h and 48 h very little positive loop is seen. It can be explained that copper corrosion byproduct became passivation layer prevent copper surface from further pitting corrosion or the changed pH affected less pitting tendency since pH was decreased initially from 9 to around 7.9 after 48 hour.

The noise resistance defined as the ratio of standard deviation of potential noise \(\sigma_{v(t)}\) and current noise \(\sigma_{i(t)}\) is shown in equation (4). The current measurements can be normalized for area. For example, the mean current divided by the area of one electrode.\(^{17}\) In Figure 7, current noise data is displayed as dotted line while potential noise recorded as the dashed line. Both noise signals showed fluctuations; mainly current range of 5 to 20 nA and potential range of 100 to 800 mV. ECN tests repeated in control water three times with new copper coupon are shown in Figure 8. The first measurement showed a high \(R_n\) of around 140 – 212, as where the 2\(^{nd}\) and 3\(^{rd}\) displayed comparatively low \(R_n\) of around 20 – 40. These results may be caused by surface scratches, an asymmetry of two working electrode or an incomplete coverage by the of Faraday cage since the bottom of ECN test cell was not covered by the Faraday cage. The corrosion current \((I_{corr})\) was also calculated from noise resistance with equation (5) and corrosion rate is obtained from equation (3) with a surface area of 12.9 cm². Based on results shown in Figure 8, noise resistance and corrosion rate are displayed average value with error ranges in Figure 9.

\[
R_n = \frac{\sigma_{v(t)}}{\sigma_{i(t)}}
\]
(4)

\[
I_{corr} = \frac{B}{R_n}
\]
(5)

Each corrosion rate for 2 h, 24 h and 48 h result from noise resistance from 1 s to 2 h, 1 s to 24 h and 1 s to 48 h, respectively. Similarly to EIS results, ECN also showed a decreased corrosion rate with increase time. However, the corrosion rate from EIS is higher than that from ECN. ECN does not apply any external potential, but in EIS an artificial 4 mV (rms) is applied to the metal sample. This is small, but this external potential may affect corrosion behavior, e.g., accelerate redox interaction on the metal surface.

**Solid surface analyses**

After electrochemical tests immersed in control water for 48 h, two distinct corroded samples were selected to investigate surface composition. Even observation with naked eye, two samples showed different surface. CPP tested sample had a dark colored surface while ECN tested was not discolored. It is noticed that ECN tested sample is at an earlier stage of corrosion compared with CPP tested.

The change of film composition was investigated by XPS analysis of corroded copper surface as
shown in Figure 10. Cu 2p\textsubscript{1/2} and 2p\textsubscript{3/2} peaks are at 953 and 933 eV, respectively. Copper has two different oxidation states, namely Cu\textsuperscript{1+} and Cu\textsuperscript{2+}. The spectral region of 934.2 eV was chosen for cupric oxide (CuO) of copper 2p\textsubscript{3/2} whereas that at 932.2 eV was chosen for cuprous oxide (Cu\textsubscript{2}O). XPS peaks of metallic copper, Cu\textsuperscript{0}, and cuprous, Cu\textsuperscript{1+}, are very close and overlap each other. Shake-up satellite peaks at 943 and 962 eV are evidence Cu\textsuperscript{2+}, namely CuO or Cu(OH)\textsubscript{2}. Figure 9 (a) shows that ECN sample has a Cu\textsuperscript{2+} dominant peak, whereas CPP sample has distinguish Cu\textsuperscript{1+} peak at 932.2 eV including Cu\textsuperscript{2+} at 934.2 eV. In the early stages of copper corrosion, it seems that copper metal oxidized as cupric ions and later on formed cuprous oxide layer.

Figure 11 displays positive ion depth profiling of each tested sample, (a) ECN and (b) CPP. Depth profiling was performed for 800 s. Depth profiling was recorded as a function of time which was converted as depth with 4.47 of sputtering yield and 8.45 \times 10\textsuperscript{22} atoms/cm\textsuperscript{3} of atomic density after analysis\textsuperscript{18}. The CPP tested sample has large Cu\textsubscript{2}O intensity whereas the ECN tested one does not. The CuO intensity of CPP tested sample was one order larger than that of ECN tested sample. In the first 10 nm layer, the amount of Cu\textsubscript{2}O increased whereas that of CuO decreased, which indicated the top most layer is Cu\textsuperscript{2+} rich and the lower layers contained Cu\textsuperscript{1+} more. Cu\textsubscript{2}O of CPP tested sample was thicker than ECN tested. It started to decrease at 10 nm and saturated around 40 nm since intensity of Cu\textsubscript{2}O does not decrease significantly until 140 nm.

CONCLUSIONS

Copper corrosion in drinking water distribution systems was studied by combining electrochemical and solid surface analysis. EIS and ECN were used to calculate copper corrosion rate first 48 hours after copper C11000 (99.9 wt% Cu, 0.04 wt% O) immersed in the control water (pH 9±0.1) while the Stern-Geary constant was obtained from the Tafel slope of the DC polarization technique. The initial pH 9±0.1 dropped to around 8±0.1 after the 48 hour experiment. The corrosion rate from the ECN technique was one order lower than that from EIS since ECN does not apply any external potential signal. However, ECN is very sensitive technique affected by even small electromagnetic wave. Although a Faraday cage was applied to prevent those effects, considerable variation was still detected. These variations may result from copper coupon preparation and incomplete coverage of whole ECN setup by Faraday cage. Even though ECN test presented results this time, this method is worthy to study further since only restricted methods exist to investigate localized corrosion. CPP known as pitting tendency can be detected was carried out in this control water, and distinct positive hysteresis was observed in the first 2 h and later on it was decreased. Electrochemical analyses showed inherent corrosion film was thickened as a function of time and decreased corrosion rate. XPS and ToF-SIMS results showed that the cuprous and cupric oxides formed on the copper surface. CPP tests accelerated the corrosion rate and more cuprous oxide was accumulated on the sample surface than in ECN tests. It can be concluded that cupric oxide (CuO) formed in the early stage of copper corrosion and CuO reduced to stable cuprous oxide (Cu\textsubscript{2}O) retarding further corrosion.

ACKNOWLEDGMENTS

This research was supported by the US Environmental Protection Agency, contact no. EP-C-05-056 and work assignment no. 0-11.
REFERENCES

18. Ion Spec, ToF SIMS application software
Table 1. EIS parameter of copper immersed in stagnant control water

<table>
<thead>
<tr>
<th>Time</th>
<th>$R_s$ (Ω)</th>
<th>CPE1 (F/cm$^2$)</th>
<th>$n_1$</th>
<th>$R_{ct}$ (Ω)</th>
<th>CPE2 (F/cm$^2$)</th>
<th>$n_2$</th>
<th>$R_{pf}$ (Ω)</th>
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<tbody>
<tr>
<td>2 h</td>
<td>150.7</td>
<td>161.1</td>
<td>0.752</td>
<td>195.2</td>
<td>369.4</td>
<td>0.632</td>
<td>4692</td>
</tr>
<tr>
<td>24 h</td>
<td>148.3</td>
<td>141.0</td>
<td>0.659</td>
<td>345.1</td>
<td>328.2</td>
<td>0.655</td>
<td>10210</td>
</tr>
<tr>
<td>48 h</td>
<td>147.0</td>
<td>83.45</td>
<td>0.728</td>
<td>901.7</td>
<td>212.4</td>
<td>0.650</td>
<td>29120</td>
</tr>
</tbody>
</table>
FIGURE 1 – Electrochemical noise experiments setup diagram
FIGURE 2 – Nyquist plots for copper immersed in control water
**Figure 3** – Proposed physical structure and equivalent circuit model

- \( R_s \): Bulk solution resistance
- CPE 1,2: Constant phase element 1,2
- \( R_{ct} \): Charge transfer resistance
- \( R_{pf} \): Passivation film resistance
FIGURE 4 – Cathodic polarization of copper data showing Tafel behavior in aerated control water after 48 hour
FIGURE 5 – (a) Polarization resistance and (b) Corrosion rate from EIS
FIGURE 6 – Cyclic Potentiodynamic Polarization curve of copper in the control water
FIGURE 7 – Current and potential noise fluctuations (root mean square)
FIGURE 8 – Noise resistance of copper coupon tested in control water, replica 1, 2, 3
FIGURE 9 – ECN tested in triplicate (a) Noise resistance and (b) Corrosion rate
FIGURE 10 – XPS spectra of copper (I), (II) after (a) ECN and (b) CPP test immersed for 48 h
FIGURE 11 – ToF-SIMS positive depth profiling of (a) ECN and (b) CPP tested; Sputtering yield of 4.47 and atomic density of $8.45 \times 10^{22}$ atoms/cm$^3$ were used