Evaluation of coating performance on carbon steel A-36 in copper concentrate environment using electrochemical impedance spectroscopy

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Abstract. The presence of chalcopyrite increases the corrosion rate of carbon steel through a galvanic couple. In this study, five organic coating systems were evaluated for their strength against consequent corrosion in the presence of copper concentrate by electrochemistry impedance spectroscopy (EIS) measurement. The coating system studied are a single application epoxy coating (C1); a three-layer epoxy system with zinc-rich epoxy primer base coat, surface tolerant epoxy middle layer, and a top layer polyurethane (C2); a three-layer epoxy system that has the advantages of fast dry time consist of epoxy zinc phosphate base coat primer, the middle layer of the epoxy primer containing the pigment zinc phosphate and top layer polyurethane (C3); metallic pigmented polyurethane coating (C4), and an epoxy coating which can be applied to wet surfaces or in water (C5). All those systems have been tested by the EIS. The test results showed that C2, C3, C4, and C5 coating systems maintained good barrier properties during the immersion process, the low frequency |Z| is more than 10^8 Ω.cm^2 after 30 days of immersion exposure. Epoxy modified coating (C1) had the lowest impedance with resistance under 10^6 Ω.cm^2 provide poor corrosion protection.

1. Introduction
The percentage of copper present in the copper concentrate is in the range of 20 to 40 %. Thus, chalcopyrite is preferable to get a large amount of copper at the end of the extraction [1]. The remainder of the concentrate is iron and sulfur in the chalcopyrite, and unwanted impurities such as silicate gangue minerals or other sulfide minerals, typically minor amounts of pyrite, sphalerite, or galena.

During the handling process, the concentrate spill mixed with rainwater, causing the steel structural members to be corroded. A contact between wet concentrate and steel structure occurs, which results in a galvanic couple. The presence of chalcopyrite increases the corrosion rate of carbon steel through a galvanic couple [2]. Carbon steel was anodic relative to pyrite and chalcopyrite, and therefore the electrons flowed from carbon steel to the minerals. Pyrite or chalcopyrite with a high rest potential acted as the cathode, while the carbon steel with a low rest potential acted as the anode. That happened when they were electrochemically contacted in the single mineral-media system [3]. About 80% wt/wt of the constituent minerals of the concentrate are sulfides [4].

The primary function of protective coatings is their barrier properties. However, if the integrity of the coating is compromised and the substrate is exposed, the corrosion of either the substrate (in case of organic and cathodic coatings) or the coating (in case of sacrificial anodic coatings) will develop [5]. Since no one protective coating is suitable for all potential applications, the selection of a coating for a
particular application always means balancing economic and technical considerations to achieve a solution [6].

Organic coatings play a significant role in the protection of materials. Epoxy zinc-rich coatings are usually used as a primer coating and have good corrosion resistance [7], which is very important for steel anticorrosion in atmosphere and water environments. Epoxy coatings offer a wide variety of benefits. They are often effective when used as corrosion protective systems, attributed to their excellent chemical resistance, strong adhesion, and good electrical insulating properties. Epoxy coatings protect against corrosion by forming a physical barrier and, when integrated with corrosion inhibitors, resist the attack of aggressive species. It has been determined when nanoparticles are incorporated into epoxy resins, the corrosion rate is significantly reduced [8].

The aliphatic polyurethane is based on aliphatic isocyanate, which reacts with acrylic ester containing hydroxy and has strong adhesion, good chemical resistance, and aging resistance. But aliphatic polyurethane is easy to become yellow because of the decomposition of urethane bonds. Therefore, acrylic polyurethane topcoat is widely used in offshore oil platforms, bridges, ships and automobile industries [9].

This paper aims to study five coating systems and find the most durable coating system for copper concentrate environment. The corrosion protection effectiveness of the coating systems was assessed according to ISO 16773 standard by performing electrochemical impedance spectroscopy (EIS) in an aqueous solution. Finally, results of the EIS measurement were simulated and analyzed by equivalent electrical circuits (EEC).

2. Materials and Methods

2.1. Material and sample preparation
Carbon steel A-36 with a dimension of (70x50x3 mm) was used as a metallic substrate for applying the coating. Chemical composition was determined through Optical Emission Spectrometer (OES) (Table 1). Samples of copper concentrate and rainwater were collected from the Dewatering plant located in Amamapare port, Timika (Indonesia). Representatives samples were chemically analyzed by x-ray diffraction (Table 2), and rainwater was analyzed by APHA method 4500 (Table 3).

| Table 1. Chemical composition of the A-36 Steel, %. |
|-----------------------------------------------|
| C  | Si  | Mn  | P   | S   | Cr  | Mo  | Ni  | Cu  | Fe  |
|----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| Low Carbon | 0.116 | 0.2 | 0.481 | 0.018 | 0.015 | 0.031 | 0.008 | 0.013 | 0.037 |
| Steel A-36 | Bal. |

| Table 2. Chemical composition of the copper concentrate. |
|-----------------------------------------------|
| Mineral | Chemical Composition | Wt (%) |
|--------|----------------------|--------|
| Quartz | SiO₂ | 1 |
| Chalcopyrite | CuFeS₂ | 76.6 |
| Pyrite | FeS₂ | 4.7 |
| Alluaudite | NaCO₃(PO₄)(HPO₄)₂ | 7.2 |
| Zeolite X | Ag₉₂₄O₃₅₆Al₆₉O₃₈₄ | 3.5 |
| Inyonite | (Ca(H₂O)₃(B₂O₃)(OH)₃)(H₂O) | 3.9 |
| Pyrophyllite | Al₂Si₄O₁₀(OH)₂ | 3 |
| Total Clay | | 0.0 |
| Total | | 100 |
Table 3. Chemical composition of rainwater in Dewatering plant.

| No. | Test       | Unit | Result | Methods       |
|-----|------------|------|--------|---------------|
| 1   | pH         |       | 6.82   | APHA 4500-H   |
| 2   | Chloride   | mg/L | 5.743  | APHA 4500-C1 |
| 3   | Sulphate   | mg/L | 9      | APHA 4500-SO4|
| 4   | Ammonia    | mg/L | < 0.01 | APHA 4500-NH3|
| 5   | CO₂        | mg/L | 13.19  | APHA 4500-CO2|
| 6   | Dissolved Oxygen | mg/L | 8.81  | APHA 4500-O |

Steel samples were surface treated to Sa 2½ standard according to ISO 8501-1 before coating applied to the steel surface. The coating systems examined in this study were epoxy modified coating (C1), three coat system consisting of a zinc-rich epoxy primer, an epoxy build coat and a polyurethane topcoat (C2), three coat system consisting of a fast cure epoxy primer, a fast cure epoxy build coat and a polyurethane topcoat (C3), single component moisture cure weatherable aliphatic polyurethane topcoat (C4), and a two-component epoxy coating 100% solids and VOC free (C5).

Table 4. Coating systems.

| Type | Coating System (Dry Film Thickness, DFT µm) | Total DFT (µm) |
|------|--------------------------------------------|---------------|
|      | Primer | Intermediate | Top |            |
| C1   | Epoxy (modified) | Epoxy (modified) | Epoxy (modified) | 320 ± 20 |
|      | 100     | 100           | 120          |            |
| C2   | Zinc-Rich Epoxy | Epoxy | Polyurethane | 340 ± 20 |
|      | 90      | 190           | 60           |            |
| C3   | Fast Cure Epoxy primer | Fast Cure Epoxy | Polyurethane | 320 ± 10 |
|      | 90      | 170           | 60           |            |
| C4   | Single Component Moisture Cure Weatherable Aliphatic Polyurethane | 320 ± 20 |
|      | 120     | 100           | 100          |            |
| C5   | Underwater Epoxy | Underwater Epoxy | Underwater Epoxy | 440 ± 20 |
|      | 150     | 150           | 150          |            |

Five kinds of coatings were processed with various compositions and thicknesses, as presented in Table 4. The test samples were fabricated as 70x50x3 mm steel plates. Then the sample is immersed in a copper concentrate slurry to accelerate corrosion. The composition of each electrolyte used in this experiment is shown in Table 5.

Table 5. Electrolyte for immersion test.

| Corrosive Medium | Volume (ml) | Immersion Period (days) |
|------------------|-------------|-------------------------|
| **Solution 1**   | With Pneumatic agitation | 7, 14 and 30 |
| (65% Concentrate Slurry) | Rainwater | 87.5 |
|                   | Copper Concentrate | 162.5 |
| **Solution 2**   | Without agitation | 7, 14 and 30 |
| (65% Concentrate Slurry) | Rainwater | 42 |
|                   | Copper Concentrate | 78 |
| **Solution 3**   | Without agitation | 7, 14 and 30 |
| (35% Concentrate Slurry) | Rainwater | 52 |
|                   | Copper Concentrate | 28 |
2.1.1. Electrochemical impedance spectroscopy (EIS) test. The EIS has conducted on the electrochemical workstation of PGSTAT302N 100 V/250 mA by using a three electrode electrochemical cell with the coated steel panel as working electrode, an Ag/AgCl (Sat KCl) as reference electrode, and platinum as the counter electrode (Figure 1). The exposed area of 15.21 cm$^2$ was delimited by attaching a glass tube with neutral curing silicone adhesive to the coated specimens. The sine wave with an amplitude of 10mV rms, open circuit potential and the frequency of 10 mHz –100 kHz were adopted in the EIS test.

The sample was soaked in concentrate slurry solution for 7, 14, and 30 days. Then the electrochemical impedance spectra of the sample were determined. The measured impedance spectrum of Nyquist map and bode map were fitted for analysis using Nova 1.11 software, and the impedance spectrum fitting parameters were obtained.

Figure 1. EIS testing three-electrode cell set-up: the colored leads area the working (red), reference (blue), and counter (black) electrodes.

3. Results

3.1. The result of EIS test

The data analysis proceeded by a categorization of coating types. The EIS results appear in the subsequent sections of this report along with a simplified interpretation of the raw data, plotted by impedance magnitude, $|Z|$, and phase angle, left and right y-axis, respectively, versus the measurement frequency [10]. Greater impedance correlates with less corrosion rate, as electron flow decreases with increasing resistance in the system. The data showed that straighter lines correlate with better corrosion resistance, as the lines have greater impedance [11].

The impedance diagrams (Figure 2) were obtained after 7, 14 and 30 days of immersion in the solution of the coated samples without defect. For coating system C1, the final impedance falls to the values around $10^5$ Ω.cm$^2$ (Figure 2a) in solutions 1 and 2, although initially being by about two orders of magnitude higher for solutions 2 and 3. This would imply that more severe corrosive solutions are attained during the immersion test in solution 1 than immersion test in solutions 2 and 3. Solution 1 is the most aggressive environment than others. This shows that the more severe environments generally have more moisture or chemical constituents and galvanic interaction between steel and copper concentrate promotes the corrosion rate of the substrate.
The coating systems C2 and C3 (Figure 2b and 2c) after immersion for 30 days, the impedance modulus |Z| at low frequency 10 mHz is above $10^9 \Omega \cdot \text{cm}^2$ indicates that the three coats systems (zinc-rich primer, epoxy, and polyurethane) have high corrosion resistance. In solution 1 system C2, after 30 days immersion, the impedance value decreased to $1.22 \times 10^7 \Omega \cdot \text{cm}^2$.

Lalic et al. [12] investigated two coating systems A and B during exposure to 3.5% NaCl by EIS, system A is made up of zinc-rich basecoat and an epoxy topcoat applied at a thickness of 270 μm. Hence, the drop in low-frequency impedance is larger for system A around $10^7 \Omega \cdot \text{cm}^2$ than for the system B around $10^{10} \Omega \cdot \text{cm}^2$, which has an extra layer of polyurethane and a total thickness of 460 μm.

The coating system C4 (Figure 2d) shows a constant impedance modulus value above $10^9 \Omega \cdot \text{cm}^2$, after 30 days in immersion exposure which indicates good corrosion resistance performance. This is influenced by the content of aluminum flakes in the coating increasing corrosion resistance due to low water absorption into the coating. The corrosion resistance of aluminum flakes is very important, as low corrosion resistance results in deterioration of the metallic appearance of the coating in contact with humid or corrosive environments [13].

In the coating system C5 (Figure 2e), the impedance modulus decreased slightly and was constant with the immersion time, indicating that the penetration of the solution into the layer reached a saturation state. The impedance value at a frequency of 10 mHz is very high, more than $10^9 \Omega \cdot \text{cm}^2$. 

a) ![Graph A](image1.png)

b) ![Graph B](image2.png)
Figure 2. Bode plots of magnitude of impedance for the coating systems after being immersed in three solutions at different times. (a) C1, (b) C2, (c) C3, (d) C4, and (e) C5.

Figure 3 shows the EIS diagrams obtained for the different solutions under the study. The EIS diagrams show that C2, C3, C4, and C5 coating systems maintained good barrier properties during the immersion process; the low frequency |Z| is more than $10^8 \ \Omega$ after 30 days in immersion exposure. The lowest impedance modulus value was obtained for the C1 coating system with the impedance mode value of the coating reduced under $10^8 \ \Omega \cdot \text{cm}^2$, which means that the aggressive medium continuously penetrates the coating.
Figure 3. Impedance change of the five coating systems in the low frequency (10 mHz) at different times.

3.2. Fit and Simulation

The processing of the experimental data for all the five coating systems allowed the identification of two equivalent circuits with which the surface properties can be analyzed after 7, 14, and 30 days of immersion in the solution. When choosing these circuits, it was taken into account that the value of the factor $\chi^2$ and the relative measurement error of the impedance $\varepsilon_z$ to be as small as possible [14].

EIS results are usually discussed using an equivalent electrical circuit that represents the physical properties of the steel/coating system. Two different equivalent electrical circuits (Figure 4) were used to fit the measured spectra, depending on the type of coating. The circuit in Figure 4a includes a resistor ($R_s$) modeling the resistance of the electrolyte, in series with a coating capacitance ($C_c$) in parallel with pore resistance ($R_{po}$), that model the properties of the coating, and in series with a double layer capacitance by $C_{dl}$ and $R_{ct}$ elements in parallel modeling the double-layer capacitance and the charge transfer resistance, which is responsible for the kinetics of the corrosion process.

The constant phase elements representing the double layer capacitance between the metal surface/electrolyte solution (CPE) [15]. In general, it was proposed that CPE could be originated from surface inhomogeneity by the adsorbate diffusion, or the electrodes roughness surface. In electrochemical systems the diffusion can create an impedance called Warburg impedance ($W$), as shown in Figure 4b, commonly used to describe phenomena such as diffusion, adsorption, or desorption of electroactive substances at interfaces metal/coating [16].

![Equivalent electrical circuit for (a) C2, C3, C4 and C5; (b) C1 coating systems.](image)

Figure 4. Equivalent electrical circuit for (a) C2, C3, C4 and C5; (b) C1 coating systems.

Figure 5a shows the calculated result of the pore resistance ($R_{po}$) for each coating system after immersion test in solution 1 for 30 days. The $R_{po}$ of C1, C2 and, C3 decreases, while for the C4 and C5 coating system, the $R_{po}$ increases. This confirms the presence of aluminum flakes in coating C4, which
increases the pore resistance from penetration electrolyte, and coating system C5 with high solid has low porosity.

The coating capacitance value (Cc), which shows the level of absorption of the electrolyte solution for the five coating systems (Figure 5b) increase with the elapse of time until a constant value is attained when the coating is saturated with water, coating capacitance values are smaller for thicker polymer films (C5).

![Pore Resistance (Rpo)](image1)

![Coating Capacitance (Cc)](image2)

**Figure 5.** Evolution of pore resistance $R_{po}$ (a); Coating Capacitance $Cc$ (b) in solution 1 versus time for five coating systems.

The charge transfer resistance ($R_{ct}$) was the control step of corrosion process in Figure 6a for the five coating systems decreased after being immersed for 30 days. C1 has the lowest charge transfer resistance, and therefore, more corrosion occurs.

The double layer capacitance ($C_{dl}$) in Figure 6b shows the corrosion reactions level at the interface layer between coating and substrate. The $C_{dl}$ value for coating system following order $C1 > C3 > C2 > C5 > C4$ respectively. The C1 coating system has the highest $C_{dl}$ value, and C4 has the lowest. The amount of electrolyte absorption into the coating, the large coating capacitance indicates the poor performance of coating protection.

![Charge Transfer Resistance (Rct)](image3)

![Capacitance Double Layer (Cdl)](image4)

**Figure 6.** Evolution of charge transfer resistance $R_{ct}$ (a), Capacitance double layer $C_{dl}$ (b) in solution 1 versus time for five coating systems.

### 4. Conclusion

The effectiveness of five coating systems for the corrosion protection of carbon steel A-36 in copper concentrate environment has been evaluated according to the ISO 16773 standard by performing electrochemical impedance spectroscopy (EIS) in aqueous solution. This study shows that in solution 1 (65% slurry concentrate + 35% rainwater with agitation), epoxy modified coating (C1) had the lowest impedance with resistance under $10^6$ Ω.cm$^2$ provide poor corrosion protection. The corrosion
mechanism for all coating systems was determined by an equivalent circuit containing two time constants, which described two electrochemical processes in the electrolyte/ coating and coating/ substrate interfaces. The C2, C3, C4, and C5 coating systems were reached resistance over $10^8 \, \Omega \cdot \text{cm}^2$ provide good corrosion protection after 30 days of immersion in copper concentrate environment. Electrochemical impedance measurements in copper concentrate solution confirmed good protective properties of metallic pigmented polyurethane coating (C4) on steel, i.e., greater values of pore resistance and charge-transfer resistance, and smaller values of coating capacitance and double-layer capacitance were obtained for these protective systems.

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