Corrosion behaviour of carbon steel in aqueous solution containing Galena concentrate

Safira Fitri, Zulfiadi Zulhan, Bonita Dinasari
Metallurgical Engineering, Bandung Institute of Technology
E-mail: safiraafitri@gmail.com

Abstract. Carbon steel specimen was left in an aqueous solution containing galena concentrate for 15 days. Electrochemical Impedance Spectroscopy (EIS) method was conducted at 1st, 3rd, 5th, 7th, 9th, 11th, 13th and 15th days of immersion. Carbon steel was immersed in the lower solid region of 25 wt% and 75 wt% galena concentrate in solution. After 15 days of immersion, polarization resistance was measured using linear polarization resistance (LPR) technique. Analysis of impedance data from EIS method enables the determination of polarization resistance. The result showed that polarization resistance increases as a function of the solid percentage of galena concentrate and corrosion of carbon steel could be minimized.

1. Introduction
Corrosion of carbon steel causes major losses such as building structures, reduce process efficiency, product contamination, and may also lead to catastrophic accidents that endanger humanity. NACE International through the IMPACT program [1] has conducted the study to examine the global cost of corrosion. It was estimated to be $2.5 trillion, which was equivalent to 3.4% of the global Gross Domestic Product (GDP) in 2013.

Isaacson [2] has studied the effect of Galena on corrosion of carbon steel. Experiments were made to observe the corrosion processes of carbon steel grinding media in a mill used to crush sulfide minerals such as galena. The results showed that the corrosion rate of carbon steel decreases with increasing amount of galena when dissolved oxygen is present. The low corrosion rate of carbon steel is due to galena acting as oxygen scavenger which decreases the dissolved oxygen content in solution. The oxidation reaction does not occur only in carbon steel but also in Galena. Galena oxidation reaction at acidic pH can be expressed by reaction (1).

\[ \text{PbS} + 2H^+ + O_2 \rightarrow \text{Pb}^{2+} + S^0 + H_2O \]  

The elemental sulfur (S^0) released by galena oxidation can react with water and decrease pH of the solution due to the formation of H^+. Maldonado-Zagal and Boden [3] suggested total reaction of elemental sulfur in reaction (2).

\[ 4S^0 + 4H_2O \rightarrow SO_4^{2-} + 3H_2S + 2H^+ \]  

Hydrogen sulfide is one of the industrial aqueous corrosive solutes and corrodes carbon steel forming sulfide corrosion products [4].

Schaschi [5] also suggested a sulfur elemental reduction reaction that controls the corrosion of steel in the environment where sulfur is dissolved, following reaction (3).
\[ S^0 + H_2O + 2e^- \rightarrow HS^- + OH^- \]  

The iron sulfide film will continue to form as long as elemental sulfur is available in the solution. The formation of the iron sulfide is expressed by reaction (4) and (5).

\[ Fe^{2+} + HS^- + OH^- \rightarrow FeS + H_2O \]  

\[ Fe^{3+} + S^2- \rightarrow FeS \]  

A study by Miyasaka [6] concludes that the reduction of sulfur is controlled by mass transfer of oxygen in solution. If the solution contains a small amount of dissolved oxygen, then the corrosion rate will decrease. The presence of oxygen will accelerate the formation of iron oxide corrosion product. This iron oxide will react with \(S^2-\) to produce iron sulfide. Water content which can be expressed as a solid percentage becomes an important parameter in the corrosion process of carbon steel in galena concentrate as it affects pH, dissolved ions and oxygen, and electrolyte resistance.

Corrosion of carbon steel in a different solid percentage of galena concentrate was studied using Electrochemical Impedance Spectroscopy (EIS) to find the corrosion mechanism in the interface of carbon steel and galena concentrate. The results were used as references for preparing condition of galena concentrate in contact with carbon steel to minimize corrosion damage.

2. Materials and Methods

2.1 Materials

Carbon steel specimens used for this study are 1 cm\(^2\) in size for electrochemical measurement and 10 cm\(^2\) in size for immersion test. Its composition (in weight %) characterized using Optical Emission Spectroscopy (OES) is: 0.05% C, 0.06% Si, 0.006% S, 0.011% P, 0.22% Mn, 0.06% Ni, 0.03% Cr and the rest was Fe. Specimens were connected to copper wire using solder and mounted in epoxy resin for the electrochemical measurements. Then, specimens were wet grounded with silicon carbide abrasive papers from P120 to P2000, followed by rinsing with alcohol prior to testing. Only one plane of specimens was exposed to the Galena concentrate.

The Galena concentrate was crushed using a ball mill and sieved to get mineral particles with a diameter smaller than 75μm. After that, the sampling process was done using a riffle to obtain a galena concentrate with a homogeneous composition for XRD and XRF analysis. Galena concentrate was composed of 61% of pyrite (FeS\(_2\)), 25.2% of anglesite (Pb(SO\(_4\))), and 13.8% of galena (PbS) based on qualitative analysis XRD using MATCH! software. Then, XRF analysis is presented in Table 1. Galena concentrates were mixed with aquades to obtain 25 wt% and 75 wt% solid percentage. Aquades were added to the electrochemical cell on the 5th and 10th days of immersion to maintain the constant solid percentage of galena concentrate.

2.2 Electrochemistry

Electrochemical impedance measurement was conducted based on ASTM G-106 [7] and used three-electrode set-up. EIS measurements were performed using Potentiostat Reference 600 and software from Gamry Instrument. Impedance was measured at 1st, 3rd, 5th, 7th, 9th, 11th, 13th and 15th days of carbon steel immersion in galena concentrate. The amplitude of the sinusoidal potential signal was 10 mV concerning corrosion potential and the frequency range from 100 kHz to 1 mHz with 10 points/decade. The results of EIS measurement were analyzed to obtain electrical circuit model and electrical component value.

The aqueous and solid phase of a solution containing galena concentrate got separated after they were left for several hours without any disturbance. In this study, EIS was performed only on the solid region of 25 wt% and 75 wt% galena concentrate in solution. Schematic configuration of the electrochemical cell designed for this study is presented in Figure 1. The electrochemical cell consists of a cylindrical vessel 250 mL. There are holes in the top which are used to connect the potentiostat with the working, reference, and auxiliary electrode. The working electrode used in this study was
carbon steel specimen, while the reference electrode was Ag/AgCl reference electrode and the auxiliary electrode was graphite.

Figure 1. Schematic configuration of electrochemical cell for (a) 25 wt% and (b) 75 wt%

Table 1. XRF analysis of galena concentrate.

| Component | Pb  | Zn  | Cu  | Fe  | Si  | S   | Ca  | Al  |
|-----------|-----|-----|-----|-----|-----|-----|-----|-----|
| Result (wt%) | 31.5 | 3.59 | 1.23 | 23.5 | 1.06 | 38.1 | 0.36 | 0.36 |

Immersion test was also conducted based on NACE TM0169/G31-12a [8]. Carbon steel coupon was wet grounded with silicon carbide abrasive papers from P120 to P2000, followed by rinsing with alcohol prior to testing. As both planes of the coupon are exposed to the solution, mounting the carbon steel coupons in epoxy resin are not required. After 15 days of immersion, carbon steel surface was characterized using X-Ray Mapping to observe corrosion products. Linear polarization resistance (LPR) method was also conducted on the test cell after 15 days of immersion to determine polarization resistance value. This measurement was prepared based on ASTM G-59 [9] using potential ±30 mV concerning corrosion potential and the scan rate of 0.167 mV/s. The polarization resistance obtained from EIS were compared to polarization resistance obtained from LPR technique to conclude the trend of polarization resistance.

3. Results and discussions

3.1 Corrosion potential and pH
Corrosion potential of specimens in the aqueous solution containing galena concentrate for an electrochemical test is shown in Figure 2. The corrosion potential is expressed concerning Ag/AgCl reference electrode. It can be seen that the corrosion potential of carbon steel in 25 wt% and 75 wt% of Galena concentrate decreases as a function of time. The decrease in corrosion potential inferred that carbon steel tends to become nobler during immersion in solid region of galena concentrate. In addition to corrosion potential measurement, pH for all the variations of galena concentrate are also measured and shown in Figure 3. It was ranged from 4.2 to 5 which indicated the test solution is in acid condition during 15 days of the test.

Figure 2. Corrosion potential of carbon steel vs. Ag/AgCl (V)  
Figure 3. Electrolyte pH for all the variations of galena concentrate
3.2 Electrochemical impedance spectroscopy

3.2.1 Electrical circuit model.
Electrical circuit model used to simulate carbon steel in the aqueous solution containing galena concentrate are shown in Figure 4. The electrical circuit components are $R_s$ indicates the resistance of the solution, $R_i$ indicates passive layer resistance, $CPE_i$ indicates passive layer capacitance, $R_p$ indicates polarization resistance, $CPE_{dl}$ indicates double layer capacitance of electrode-electrolyte, $R_g$ indicates galena concentrate resistance, and $CPE_g$ indicates galena concentrate capacitance. Model 1 was used to describe the carbon steel surface where the passive layer begins to form well in all parts. Model 2 with addition of $CPE_g$ and $R_g$ arranged in parallel which means the galena concentrate got attached on the carbon steel surface. It can also indicate the presence of some species attached to the carbon steel surface.

Figure 4. Electrical circuit model used to simulate EIS measurement results

![Model 1 and Model 2](image)

3.2.2 Immersion of carbon steel in 25 wt% of Galena concentrate in solution.
The electrical circuit components value for carbon steel immersed in 25 wt% of Galena concentrate on the solid region are shown in Figure 5. The electrical circuit model chosen to simulate carbon steel immersed in 25 wt% of Galena concentrate on the solid part was model 2. It changed to model 1 after 13th days of immersion shows that galena concentrate was no longer attached to the carbon steel surface. It was indicated by the value of $\alpha_g$ and $R_g$ which continue to decrease as a function of time. $R_i$ tends to be stable for 15 days of immersion, while $R_p$ increases as a function time that indicates better
corrosion resistance of carbon steel. The value of capacitance tends to be constant which indicates the corrosion process on the carbon steel surface does not change as a function of time.

**Figure 6.** Immersion test coupon for carbon steel immersed in 25 wt% of Galena concentrate

**Figure 7.** Immersion test coupon for carbon steel immersed in 75 wt% galena concentrate

**Figure 8.** X-Ray Mapping analysis of carbon steel immersed in 25 wt% of Galena concentrate

The increasing of corrosion resistance of carbon steel in galena concentrate has been studied by Isaacson [2]. He stated that corrosion rate of carbon steel in galena concentrate decreases as increasing amount of galena concentrate which is caused by the oxidation process of Galena. Galena acts as an oxygen scavenger and consumes dissolved oxygen; hence, the corrosion rate of carbon steel decreases. The increasing of corrosion resistance is by the results of the immersion test in Figure 6 which shows the absence of corrosion products on the surface of carbon steel in solid region of galena concentrate. X-Ray Mapping analysis (Figure 8) shows that Fe and O dominate carbon steel immersed in the aqueous region of galena concentrate more uniformly than the solid region. It proves that corrosion damage of carbon steel immersed in a solid region of galena concentrate was hindered.

**Figure 9.** Electrical circuit components value for carbon steel immersed in 75 wt% of Galena concentrate on the solid region
3.2.3 Immersion of carbon steel in 75 wt% of Galena concentrate in solution.
The electrical circuit components value for carbon steel immersed in 75 wt% of Galena concentrate on the solid region are shown in Figure 9. Electrical circuit model used to simulate the carbon steel interface is model 2 with the capacitance value tends to be stable for 15 days of immersion. The increasing of $R_p$ indicates that carbon steel in contact with the solid of galena concentrate has low corrosion rate. It can be proven from the direct observation of the carbon steel surface as shown in Figure 7 where corrosion product slightly formed on the carbon steel surface immersed in solid region. The reduction of corrosion process of carbon steel in 75 wt% galena concentrate has the same characteristics as carbon steel immersed in 25 wt% galena concentrate. It was due to galena acts as oxygen scavenger that reduces dissolved oxygen in solution so that dissolved oxygen needed for carbon steel oxidation were not enough available.

3.2.4 Comparison of polarization resistance and corrosion rate of carbon steels.
Polarization resistance indicates carbon steel resistant to corrosion. The higher value of polarization resistance means the better corrosion resistant. Carbon steel in a higher percentage of galena concentrate shows excellent corrosion resistant than carbon steel in a lower percentage of galena concentrate. The corrosion rate of carbon steel immersed in 75 wt% of Galena concentrate is lower than the 25 wt%. Both EIS and LPR method shows the same trend for the measurement of polarization resistance and corrosion rate as shown in Table 2.

Table 2. Polarization resistance ($R_p$) and corrosion rate of carbon steel.

|            | $R_p$ EIS (Ohm) | $R_p$ LPR (Ohm) | Corrosion Rate EIS (mm/year) | Corrosion Rate LPR (mm/year) |
|------------|-----------------|-----------------|----------------------------|----------------------------|
| 25 wt%     | 3439            | 3843            | 0.074                      | 0.066                      |
| 75 wt%     | 25794           | 26520           | 0.006                      | 0.006                      |

4. Conclusion
Carbon steel immersed in an aqueous solution containing galena concentrate can be illustrated using electrical circuit model obtained from EIS measurement. Electrical circuit model analysis results in new information about carbon steel behavior especially the corrosion mechanism. The value of electrical circuit component can also be determined including polarization resistance ($R_p$) value which indicates carbon steel resistant to corrosion. The higher value of polarization resistance means the better corrosion resistance, was observed in the higher solid percentage of galena concentrate. The increase of the solid percentage of galena concentrate will increase the corrosion resistant to carbon steel.

References
[1] Koch G, Varney J, Thompson N, Moghissi O, Gould M, Payer J 2016 International Measures of Prevention, Application, and Economics of Corrosion Technologies Study (Texas : NACE International) ed G Jacobson
[2] Isaacson A E and Huiatt J L 1985 An electrochemical study of grinding media corrosion Annu. Meet. Assoc. Corros. Eng. NACE 364
[3] Maldonado Z S B and Boden P J 1982 Hydrolysis of Elemental Sulphur in Water and its Effect on the Corrosion of Mild Steel Br. Corros J 17 5–9
[4] Jones D A 1996 Principles and Prevention of Corrosion 2nd Edition (United State of America: Simon & Schuster)
[5] Schmitt G 1991 Effect of Elemental Sulfur on Corrosion in Sour Gas Systems Corrosion 47 285-308
[6] Miyasaka A, Denpo K and Ogawa H 1989 Environmental Aspects of SCC of High Alloys in Sour Environments Corrosion 87 5-10
[7] ASTM Comittee 1999 ASTM G106-89 Standard Practice for Verification of Algorithm and
Equipment for Electrochemical Impedance Measurements

[8] NACE International 2012 Standard Guide for Laboratory Immersion Corrosion Testing of Metals 1-10

[9] ASTM Committee 2003 ASTM G-59 Conducting Potentiodynamic Polarization Resistance Measurements 1–4