Corrosion Behavior of Carbon Steel in Concrete Material Composed of Tin Slag Waste in Aqueous Chloride Solution

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Abstract. Tin slag is a byproduct of tin ore smelting process which is rarely utilized. The main purpose of this work is to investigate the use of tin slag for concrete cement material application compared to the industrial Ordinary Portland Cement (OPC). Tin slag composition was characterized by XRD and XRF analysis. The characterization results showed the similar chemical composition of tin slag and OPC. It also revealed the semi crystalline structure of tin slag sample. Several electrochemical tests were performed to evaluate corrosion behavior of tin slag, OPC and various mixed composition of both materials and the addition of CaO. The corrosion behavior of OPC and tin slag were evaluated by using Cyclic Polarization, Electrochemical Impedance Spectroscopy (EIS) and Electrochemical Frequency Modulation (EFM) methods. Aqueous sodium chloride (NaCl) solution with 3.5% w.t concentration which similar to seawater was used as the electrolyte in this work. The steel specimen used as the reinforce bar (rebar) material of the concrete was carbon steel AISI 1045. The rebar was embedded in the concrete cement which composed of OPC and the various composition of tin slag including slag without addition of CaO and slag mixed with addition of 50% CaO. The electrochemical tests results revealed that tin slag affected its corrosion behavior which becoming more active and increasing the corrosion rate as well as decreasing the electrochemical impedance.

1. Introduction

Tin slag is byproduct of tin ore smelting process which is rarely utilized. The smelting process of tin ore produces slag-1 and slag-2. Slag-1 contains 20-30% tin, and slag-2/final slag which produced from smelting slag-1 contains only 2-3% tin [1]. The final slag (slag-2) is commonly discarded as waste material and usually it will be kept and controlled by the authorized environmental agency. Based on the XRD and XRF characterization analysis, it shows that the oxides composition of slag-2 (final slag) is quite similar to the Ordinary Portland Cement (OPC).

In addition, the similar characteristic between final slag and OPC is water absorption value. Water absorption value is the enhancement of weight percentage of a material to theoriginal weight expressed as the absorption value (in percent). The value of final tin slag was measured at 1.97% [2]. This value is quite moderate when compared with other slag, even close to the water absorption value for OPC, which is about 1.08%. This means the hydration reaction between water and final slag can happen quite
well. This is based on the study that the average absorbance value of cement should not be more than 5% with none being more than 7% [3].

Concrete is material that widely use for an infrastructure, that has constraint with damage caused by corrosion, especially by salinity in coastal area. Salinity is one of the major sources of damage in building on Coastal Zone [4]. The presences of aggressive chloride in coastal area can initiate corrosion in concrete reinforcement. The previous studies have suggested that there is a shoreline effect on the presence of destructive sea salt very quickly at the first 100 meters from the shore [5]. In fact, the wind can carry chlorides in the air up to distances beyond 3 km [6]. Whereas the concrete structure is generally expected to survive without repair and maintenance in a long time (up to 100 years). Therefore, concrete materials constructed as infrastructure in coastal areas should have good corrosion resistance to the presence of aggressive ions such as chloride so that innovation is required on the raw material of cement material in steel reinforcement to address this problem.

The chemistry in concrete involves hydration reaction by addition of water. Lime stone as main sources of CaO is used to form hydration product and bind other constituent including final tin slag. The addition of limestone has a purpose to increase the CaO content in final tin slag which only contain small amount of CaO. The important reaction on hydration reaction in concrete is given below:

\[
\begin{align*}
2(3\text{CaO}.\text{SiO}_2) + 6\text{H}_2\text{O} & \rightarrow 3\text{CaO}_2.\text{SiO}_2.3\text{H}_2\text{O} + 3\text{Ca(OH)}_2 \\
(2\text{CaO}.\text{SiO}_2) + 4\text{H}_2\text{O} & \rightarrow 3\text{CaO}_2.2\text{SiO}_2.3\text{H}_2\text{O} + 3\text{Ca(OH)}_2
\end{align*}
\]

This work focused on the aspect of corrosion behavior of OPC and final slag with CaO and without CaO addition in 3.5 % aqueous chloride solution (NaCl) which is evaluated by using electrochemical measurement testing methods which are: Cyclic Polarization, Electrochemical Impedence Spectroscopy (EIS) and Electrochemical Frequency Modulation (EFM) methods respectively.

2. Materials and Methods

Final tin slag used in this study comes from Bangka Island, Indonesia. Based on XRF characterization, the major component in final tin slag was SiO₂ and the other constituent component are shown in Table 1.

| SiO₂ | Al₂O₃ | Fe₂O₃ | TiO₂ | CaO | P₂O₅ | Na₂O | SnO₂ | ZrO₂ |
|------|-------|-------|------|-----|------|------|------|------|
| 39.7 | 13.2  | 8.70  | 6.84 | 5.64 | 5.26 | 4.30 | 4.10 | 3.75 |

In addition, this experiment used AISI 1045 as reinforced steel that will be embedded in concrete material which composed of tin slag waste. The composition of reinforced steel is shown in Table 2.

| C   | Si  | Mn  | P   | Cr  | Ni  | Cu  |
|-----|-----|-----|-----|-----|-----|-----|
| 0.40| 0.23| 0.67| 0.011| 0.06| 0.01| 0.02|

The resistivity and pH of the various composition materials: OPC, final tin slag without CaO addition and tin slag material mixed with 50 % CaO addition were measured to provide preliminary corrosivity data prior to performing electrochemical testing. The cement and tin slag sample materials were put in the soil box in wet condition by adding some distilled water then measured by resistivity meter to obtain resistivity data followed by simply measured by using pH meter.

Cylindrical concrete specimens used for the electrochemical testing were prepared with diameter 100 mm and length 140 mm which steel bar was embedded in symmetrical position. The exposed area of 700 mm² was made prior to the measurements testing (Fig. 1). All of the concrete specimens were exposed in NaCl 3.5% at room temperature.
The electrochemical measurements testing were conducted with Cyclic polarization, EIS and EFM methods by using Gamry Instruments Potentiostat PCI4G750 completed with Global Software. The measurements apparatus consists of reference and counter electrodes with steel rebar testing specimen was treated as working electrode as shown in Fig. 2.

3. Results and Discussion

3.1 Resistivity and pH Measurement

Prior to electrochemical testing, the resistivity and pH of OPC and tin slag in wet condition were measured as preliminary corrosivity data. The testing results can be seen in Fig. 3, which shows that the resistivity and pH increases with increasing CaO content in the mixture.
The effect of CaO content on pH that is the value increases with increasing CaO content as resulted from basic or alkaline property of CaO compound and will further hydrated to form Ca(OH)$_2$ followed by curing process.

### 3.2 Cyclic Polarization Testing

The results of cyclic polarization measurement are shown in Fig. 4.

![Cyclic Polarization Curves for OPC, Slag with CaO addition, and Slag without CaO addition](image)

**Figure 4.** Cyclic Polarization Curves for OPC, Slag with CaO addition, and Slag without CaO addition

The Cyclic Polarization testing of steel rebar which embedded in OPC shows that the significant passive condition behavior takes place without the occurrence of pitting breakdown. Steel rebar embedded in tin slag without CaO addition shows the active condition of corrosion behavior. There is pitting breakdown encountered by steel bar embedded in tin slag with CaO addition caused by the aggressive ion chloride (penetration) in aqueous 3.5% NaCl solution which contains dissolved oxygen.

### 3.3 Electrochemical Impedance Spectroscopy (EIS) Test

The results from EIS test can be shown in Fig.5 which represented by Nyquist plot curves.

![Nyquist Plot from EIS Test Results](image)

**Figure 5.** Nyquist Plot from EIS Test Results

As can be shown by Nyquist plots, OPC material which represented by (a) curve shows with nearly 45° line slope indicates diffusion and passive corrosion behavior. Slag without CaO addition shows nearly semi-circle curve which indicates active condition with charge transfer corrosion behavior. Slag with CaO addition also shows nearly semi-circle curve which indicates relatively in active condition or controlled
by charge transfer corrosion behavior but has higher magnitude of electrochemical impedance which compared to the impedance magnitude of slag without CaO addition.

3.4 Electrochemical Frequency Modulation (EFM) Test

The results of EFM test can be shown in Fig. 6 (a), 9 (b) and 9 (c) curves which represent the materials: OPC, slag without CaO and slag with CaO respectively.

![Figure 6. EFM Inter-modulation Spectrum for (a) OPC, (b) Slag without CaO addition (c) Slag with CaO addition.](image)

Resulted from the above EFM curves, the following corrosion rates results analysis can be shown in Table 3.

|               | OPC  | Slag with CaO | Slag without CaO |
|---------------|------|---------------|------------------|
| Current (μA)  | 92.77| 44.99         | 88.13            |
| Corrosion Rate (mpy) | 1.70 | 13.70         | 26.85            |

The corrosion rates decreased with increasing CaO content and influenced by the cement mixture composition like the presence of specific oxide compounds which cause the occurrence of passivity corrosion behavior and contribution of curing process especially in OPC concrete material.
4. Conclusions
The following conclusions can be made from this work is the corrosion rates decreased with increasing CaO content due to the occurrence of passivity corrosion behavior and the magnitude of impedance increased. Furthermore, the addition of approximately 50% CaO with final tin slag was required to improve its corrosion property so that it can be used for concrete cement application properly.

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