The Study of the Effect of Final Tin Slag as Partial Substitution in Portland based Concrete towards Corrosion Resistance of Reinforcement Steel against Chloride Environment with Linear Polarization Method

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Abstract. The final tin slag is the final product of the tin smelting process which contains oxide compounds such as SiO$_2$, CaO, Al$_2$O$_3$, and Fe$_2$O$_3$ which have similarities to the content of the oxide compounds found in Portland cement (OPC). The existence of the final tin slag has not been widely used. For that reason, the final tin slag will be very useful if it is used as a cement substitute as a raw material for making concrete. This study aims to analyze the resistance of cement and steel reinforcement mixtures on concrete to a corrosive environment using linear polarization method. In this study, the composition of the final tin slag used was 10%, 20%, 30%, and 40%. The final tin slag used came from PT. Timah Tbk on Bangka Island Indonesia. Then, the 0.5 w/c ratio concrete will be cured for 28 days and will be immersed with a 3.5% NaCl solution for 6 days. The results presented that the reinforcement steel embedded in concrete OPC60-FTS40 was the sufferest towards corrosion since it had the highest corrosion rate in each immersion day among all the concrete samples and followed by OPC80-FTS20, OPC70-FTS30, OPC100, and OPC90-FTS10 in six days of immersion.

Keywords: final tin slag, Portland cement (OPC), concrete, corrosion resistance, linear polarization

1. Introduction
Major development of infrastructures raises the demand for concrete and its aggregates significantly [1]. Concrete is a mixture of cement, aggregate, and water which is commonly used in construction of a building. A common issue in building is corrosion in reinforcing steel of concrete due to chemical reaction between the steel and outer environment through porosity within the concrete. The porosity in concrete allows reaction between environment and systems within the concrete and eventually leads to corrosion. Furthermore, Indonesia is a maritime nation with a huge risk for corrosion occurring in construction concretes resulting from high salinity of its seawater. Aggressive ions, including chloride, in such environment accelerate the corrosion process. The corrosion is detrimental for any construction as it reduces quality and lifetime of a building [2]. The corrosion in reinforcement steel occur due to
the oxide compounds form hydroxides that are very alkaline (pH 12-13) when there is additional water in the hydration reaction [3]. Those alkaline condition trigger the form of passive layer which will be damaged cause the penetration of aggressive ion such as chloride ion [4]. Replacing component is a challenge for negative effects resulting from material substitution associated with strength improvement in concretes [5]. Therefore, it is critical to use proper mixture of concrete aggregates which reduces porosity in order to impede corrosion process and mitigate its impact on a building construction.

Application of waste materials including slag, glass, calcium carbide residues, and so on as material substitution is trending recently and studies had been conducted on its application for years [6]. Processing result of tin ore or slag is abundant in Indonesia; however, its utilization is still not widely accepted and this study was expected to improve the prudent use of existing resources. Final tin slag is a byproduct of smelting which contains various oxide compounds including SiO$_2$, CaO, Al$_2$O$_3$, and Fe$_2$O$_3$ all of which are similar to materials found in Portland cement (OPC) that is commonly used in mixing a concrete [7]. Final tin slag possesses a potential to be used as raw material in preparing a concrete due to its common compounds.

This study aimed to identify characteristics of OPC and mixture of cement and final tin slag on corrosiveness of reinforcement steel in concrete by using Linear Polarization that served to analyze corrosion resistance property of reinforcement steel evaluated by corrosion rate of each concrete.

2. Experimental method

2.1 Materials
Materials for concrete included a mixture between Ordinary Portland Cement (OPC) produced by Semen Gresik Manufacturer, Final Tin Slag (FTS) the byproduct of tin processing in PT. Timah Tbk in Bangka, coarse aggregates such as gravel sized 20-40 mm, and fine aggregates such as sand. Table 1 described observation result by X-Ray Fluorescent (XRF) which indicated oxide compounds of both OPC and Final Tin Slag (FTS) cement:

|        | CaO  | SiO$_2$ | Al$_2$O$_3$ | Fe$_2$O$_3$ | SO$_3$ | TiO$_2$ | P$_2$O$_5$ | MgO | SnO$_2$ | Na$_2$O |
|--------|------|---------|-------------|-------------|--------|---------|-----------|-----|---------|---------|
| OPC    | 66.00| 21.50   | 5.50        | 3.90        | 2.75   | -       | -         | 5.00| -       | -       |
| Slag   | 5.65 | 39.66   | 13.18       | 8.77        | -      | 6.84    | 5.26      | 1.91| 4.00    | 3.75    |

Material of reinforcing steel was AISI 1045 medium carbon steel with diameter 10 mm and length 140 mm. Chemical compounds of AISI 1045 are outlined in table 2 below:

|        | C    | Fe   | Mn   | P    | S     |
|--------|------|------|------|------|-------|
|        | 0.420–0.50 % | 98.51-98.98 % | 0.60–0.90 % | ≤ 0.040 % | ≤ 0.050 % |

2.2 Sample Preparation
First, AISI 1045 reinforcing steel was sliced into 5 parts with size 140 mm and diameter 10 mm for each sample. The steels were then polished by angle grinder to remove dirt from its surface. Both ends of steel were then mounted by hardener-mixed-resin with mounting height 20 mm respectively thus left 100 mm of steel unmounted. One end of mounted steel was affixed with copper wire that served to conduct the current during polarization test.
Concrete containing final tin slag was destroyed by ball mill till it reduced to particle size of 100 Mesh. Final tin slag was then mixed with OPC, coarse aggregates sized 20-40 mm, and fine aggregates i.e. sand. All of materials were mixed with water by 0.5 water/binder ration and stirred afterward. The mixture was then poured in cylinder-shaped concrete mold with diameter 100 mm and length 200 mm. Mounted steel was implanted in the middle of concrete mold as illustrated by Figure 1 below.

![Figure 1. Concrete specimen’s dimension.](image1)

The concrete was immersed with water for 28 days in order to achieve its maximum strength. Afterwards, it was soaked with 3.5 % NaCl solution with interval of 0, 3, and 6 days and corrosion behavior were evaluated by Linear Polarization within each interval.

### 2.3 Concrete Composition

The composition of OPC and Final Tin Slag (FTS) in the concrete is shown by Table 3 below:

| Concrete Sample | OPC (wt %) | Final Tin Slag/FTS (wt %) | w/b ratio |
|-----------------|------------|----------------------------|-----------|
| OPC100          | 100        | 0                          | 0.5       |
| OPC90-FTS10     | 90         | 10                         | 0.5       |
| OPC80-FTS20     | 80         | 20                         | 0.5       |
| OPC70-FTS30     | 70         | 30                         | 0.5       |
| OPC60-FTS40     | 60         | 40                         | 0.5       |
2.4 Linear Polarization Test
Gamry Instrument Potentiostat PCI4G750 with Global software was used to analyze corrosion rate in reinforcing steel by Linear Polarization method. Linear Polarization test was conducted regularly based on immersion period of concrete in 3.5% NaCl i.e. in day 0, 3, and 6. The initial and final potentials used to determine the curve of Linear Polarization test result were -0.5V and 0.1V. The test result used in this study was corrosion rate which derived from analysis by comparing potential curve (V) and Current (A). Corrosion rate of each sample was then compared to identify corrosion resistance of each concrete.

![Figure 3. a) Linear Polarization Test Circuit b) Scheme of Linear Polarization Test Circuit [4].](image)

2.5 Compressive Strength Test
The compressive strength test was conducted at Structures and Materials Laboratory, Department of Civil Engineering, Universitas Indonesia. The machine press was used to determine the compressive strength subjected to the given load of each concrete after 28 days of curing.

3. Results and Discussion

3.1 Linear Polarization Test
In the 0 day of immersion, Linear Polarization curve suggested concrete with the highest to the lowest current density were in following order: and OPC60-FTS40, OPC80-FTS20, OPC100, OPC90, and OPC70-FTS30. OPC60-FTS40 concrete had the highest current density i.e. 0.95255 μA/cm² and OPC70-FTS30 concrete had the lowest current density i.e. 0.48551 μA/cm². The graphic also indicated that OPC60-FTS40 concrete was located at the rightmost of the curve and OPC70-FTS30 concrete was at the leftmost.

The third day of immersion revealed that the graphic moved closer to the right end than in previous day for all samples excluding the OPC 80-FTS20 concrete which was located at the leftmost. Graphic movement to the right side indicated greater penetration by chloride ion into the concrete that resulted in greater rates of electron transfer from catodic to anodic. Linear Polarization graphic in Figure 4b) suggested that OPC60-FTS40 concrete had the highest current density than the rest of concretes (2.65830 μA/cm²) while OPC80-FTS20 concrete had the lowest current density (0.00008 μA/cm²).
Figure 4. Comparison of Linear Polarization Curves of Reinforcement Steel in Portland mixed Final Tin Slag (FTS) Concrete Day 0 immersed, b) Day 3 immersed, c) Day 6 immersed.

The sixth day of immersion revealed Linear Polarization graphic at the right side as illustrated in Figure 4c. Concrete with the highest to lowest current density were in following order: OPC60-FTS40, OPC80-FTS20, OPC70-FTS30, OPC100, and OPC90-FTS10. OPC60-FTS40 concrete had the highest current density i.e. 4.32580 \(\mu\text{A/cm}^2\) and OPC90-FTS10 concrete had the lowest current density i.e. 1.74650 \(\mu\text{A/cm}^2\). The current density of all samples increased in comparison with the previous result which suggested greater rates of chloride ion transfer penetrating the concrete which resulted in faster corrosion rate.

Table 4. Quantitative parameter of each steel bar in concrete composition measured in 3.5% of NaCl solution for 6 days from Linear Polarization curve.

| Concrete Sample | Immersion time (day) | \(\beta_a\) (V/decade) | \(\beta_c\) (V/decade) | Ecorr (mV) | Icorr (\(\mu\text{A/cm}^2\)) | Corrosion rate (mpy) |
|-----------------|----------------------|------------------------|------------------------|-----------|-----------------------------|----------------------|
| OPC100          | 0                    | 0.11648                | 0.08565                | -400.020  | 0.49914                     | 0.22852              |
|                 | 3                    | 0.13614                | 0.09506                | -397.430  | 0.53602                     | 0.24540              |
|                 | 6                    | 0.16538                | 0.12249                | -675.480  | 1.75270                     | 0.80242              |
| OPC90-FTS10     | 0                    | 0.16741                | 0.09527                | -496.980  | 0.49490                     | 0.22658              |
|                 | 3                    | 0.32268                | 0.14330                | -625.010  | 1.35360                     | 0.61972              |
|                 | 6                    | 0.18858                | 0.14616                | -733.230  | 1.74650                     | 0.79962              |
| OPC80-FTS20     | 0                    | 0.22239                | 0.17259                | -339.520  | 0.85118                     | 0.38968              |
|                 | 3                    | 0.17347                | 0.16974                | -697.650  | 0.00008                     | 0.00004              |
|                 | 6                    | 0.26096                | 0.17632                | -721.210  | 1.84120                     | 0.84296              |
| OPC70-FTS30     | 0                    | 0.14971                | 0.11546                | -358.390  | 0.48551                     | 0.22227              |
|                 | 3                    | 0.20575                | 0.16826                | -495.650  | 0.93303                     | 0.42717              |
|                 | 6                    | 0.24767                | 0.17864                | -825.110  | 1.76700                     | 0.80900              |
| OPC60-FTS40     | 0                    | 0.18644                | 0.12729                | -319.890  | 0.95255                     | 0.43611              |
|                 | 3                    | 0.25791                | 0.16416                | -592.760  | 2.65830                     | 1.21702              |
|                 | 6                    | 0.25226                | 0.19494                | -716.970  | 4.32580                     | 1.98048              |
Figure 5. Comparison graphic of reinforcement steel corrosion rate in OPC 100, OPC90-FTS10, OPC80-FTS20, OPC70-FTS30, and OPC60-FTS40 concrete.

Comparison of corrosion rate of all five samples were demonstrated in graphic in Figure 5. Corrosion rate was directly proportional with current density. The higher its current density, the faster its corrosion rate would be. It is because current density indicates rates of chloride ion transfer. Corrosion rate in the 0 day revealed OPC60-FTS40 concrete had higher corrosion rate than other samples i.e. 0.43611 mpy, while OPC70-FTS30 concrete had the lowest corrosion rate i.e. 0.22227 mpy.

The third day of immersion indicated an increase in corrosion rate with the exception of OPC80-FTS20 concrete which had a decrease in corrosion rate instead up to 0.38964 mpy. The decrease in corrosion rate was resulted from hydration reaction within NaCl solution. The reaction induces chemical bonding between tricalcium aluminate (C₃A) and chloride ion in pore solution which produced Friedel’s salt and reduced porosity in concrete as well as rate of electron transfer [9,10]. OPC60-FTS40 concrete had the highest corrosion rate i.e. 1.21702 mpy while OPC80-FTS20 concrete had lowest corrosion rate i.e. 0.00004 mpy.

Corrosion rate in the sixth day of immersion suggested a significant improvement in each sample. It was due to greater penetration by chloride ions than in previous days. OPC60-FTS40 concrete had the highest corrosion rate i.e. 1.98048 mpy while OPC90-FTS10 concrete had the lowest corrosion rate i.e. 0.79962 mpy.

The analysis of Linear Polarization curve on corrosion rate revealed that OPC60-FTS40 concrete which was added with 40% of Final Tin Slag (FTS) always had the highest corrosion rate than the other concretes. Meanwhile, OPC90-FTS10 concrete which was added with 10% of Final Tin Slag (FTS) had the lowest corrosion rate after 6 days of immersion.

3.2 Compressive Strength Test
The compressive strength of each concrete sample are shown by Table 5 below:
Table 5. Compressive strength of each concrete.

| Concrete Sample | Compressive Strength (MPa) |
|-----------------|---------------------------|
| OPC100          | 19.220                    |
| OPC90-FTS10     | 4.6988                    |
| OPC80-FTS20     | 12.634                    |
| OPC70-FTS30     | 14.658                    |
| OPC60-FTS40     | 12.346                    |

Figure 6. Compressive strength comparison of each concrete.

The results of the compressive strength test are given by Figure 6 above. It shows that concrete OPC100 had the highest strength with amount of 19.220 MPa and sequentially followed by OPC70-FTS30, OPC80-FTS20, OPC60-FTS40, and OPC90-FTS10 with the amount of 14.658, 12.634, 12.346, and 4.6988 MPa in approximately.

4. Conclusions
The conclusions of the test result are first the reinforcement steel embedded in concrete OPC60-FTS40 was the sufferest towards corrosion since it had the highest corrosion rate in each immersion day among all the concrete samples and followed by reinforcement steel in concrete OPC80-FTS20, OPC70-FTS30, OPC100, and OPC90-FTS10 in six days of immersion. After six days of immersion, OPC90-FTS10 provided the lowest value of corrosion rate. The second is the concrete sample which provided the highest compressive strength was OPC100 while the weakest was OPC90-FTS10. It shows that OPC90-FTS10 gave the highest corrosion resistance, but it was not strong as the other concrete.

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