

The study of corrosion resistance of reinforcement steel embedded in concrete composed of commercial Portland cement and final tin slag against chloride environment

R Riastuti^{1*}, A Cahyadi¹, Y Pratesa¹, and S T Siallagan¹

¹Department of Metallurgy and Materials Engineering, Faculty of Engineering, Universitas Indonesia, Depok, 16424, West Java, Indonesia.

*Corresponding email: riastuti@metal.ui.ac.id

Abstract. Final tin slag is a by-product of slag-1 smelting process that contains oxides similar to the oxides in Portland cement (OPC), which are SiO_2 , CaO , Al_2O_3 , and Fe_2O_3 . Therefore, tin slag may be utilized as partial substitute for concrete raw material. The aim of this research is to understand the characteristics of OPC and the slag-2 cement mixture against corrosiveness of the cement and steel material as analysed using the cyclic polarization method. This study uses final tin slag from Bangka Island in Indonesia mixed with OPC of 10%, 20%, and 30% respectively. The molded concrete has a ratio of 0.5 w/c with 28 days curing process and then it is immersed in a 3.5% NaCl solution for 6 days. The result shows that the steel in the 20% slag-2 concrete mixture has the most competitive and stable corrosion resistance compared to original OPC concrete, followed by 10%, and 30% slag mixture respectively.

1. Introduction

Tin slag is a by-product of tin ore smelting process which is rarely utilized. Slag-2 or final tin slag as a by-product of the second smelting process contains only 2-3% of tin content[1]. Recent study shows that final tin slag contains similar oxides as in Ordinary Portland Cement (OPC) such as SiO_2 , CaO , Al_2O_3 , and Fe_2O_3 . Meanwhile, the water absorbance value of Final tin slag is a moderate value of 1.97%[2] compared to 1.08% water absorbance value of OPC. The study from Darshan et. al. shows that the water absorbance mean value should not be more than 5% with none of its particle exceeding 7%[3].

As structural material, concrete which is mainly made of cement and reinforced by steel bar is susceptible to corrosion damage, especially due to salinity in coastal areas[4]. The presence of chloride ion which is very aggressive could initiate corrosion product on reinforcement steel which is embedded in structural concrete. A previous study shows that the presence of sea salt could possibly cause rapid damage within the first 100m from coastal areas[5]. In fact, the wind can carry chlorides in the air up to distances greater than 3 km[6]. Meanwhile, the concrete structure is generally expected to survive without repair and maintenance for a long period (up to 100 years). Therefore, concrete materials constructed as infrastructure in coastal areas should have high corrosion resistance against aggressive ions such as chloride and innovation on the raw material of cement material is required to address the problem of corrosion on reinforcement steel.



This study aims to understand the corrosion resistance behaviour of reinforcement steel embedded in concrete which is made of final tin slag mixed with OPC and tested using the cyclic polarization test under a chloride environment. The quantitative parameters such as the current density (I_{corr}) and the corrosion rate are considered to support the qualitative parameters of corrosion behaviour which is presented by each polarization curve.

2. Materials and Methods

2.1. Materials

The raw materials of concrete consist of Ordinary Portland Cement (OPC) produced by PT. Semen Gresik, and final tin slag as a waste product from Bangka Island. The results from the X-Ray Fluorescent (XRF) test shows the oxide composition of OPC and final tin slag as presented in the following Table 1.

Table 1. Final tin slag and OPC chemical compositions.

	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

The AISI 1022 steel bar with $\varnothing = 10$ mm and length = 150 mm is used as a single concrete reinforcement with chemical composition as exhibited in Table 2.

Table 2. AISI 1022 steel bar compositions.

C	Fe	Mn	P	S
0.21	98.96	0.78	0.022	0.028

2.2. Sample Preparation

Initially, the reinforcement steel was ground with a series of abraded paper (no. 120, 320, 400, 600, 800, 1000, and 1200) until the oxide scale was removed and the steel surface was smooth. The steel bar was then mounted by using resin and catalyst.

The OPC cement and tin slag as concrete raw materials were ground using a grinding machine to achieve 74 micron or 200 mesh of particle size. The raw materials then were mixed with 0.5 water/binder (w/b) ratios to be filled in cylindrical concrete moulds with a diameter of 60 mm and a length of 160 mm, meanwhile a single steel bar was symmetrically positioned in the mould as shown in Fig. 1. The cylindrical concrete was then immersed in water for 28 days for curing. Subsequently the concrete was exposed to NaCl 3.5% solution consisting of 3.5 g sodium chloride in 1 L of aquadest. After that, the concrete specimens in NaCl 3.5% solution were analysed using the cyclic polarization test.

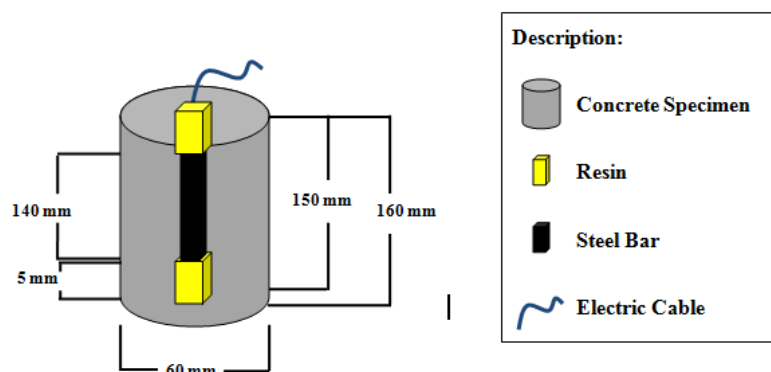


Figure 1. Dimension of concrete specimen for corrosion testing

2.3. Concrete Composition

The compositions of tin slag and OPC used in this study are shown in Table 3.

Table 3. Formula of tin slag and OPC as raw materials in concrete composition.

Code	Tin Slag (wt. %)	OPC (wt. %)	w/b ratio
S10-OPC90	10 %	90 %	0.50
S20-OPC80	20 %	80 %	0.50
S30-OPC90	30 %	70 %	0.50
OPC100	0 %	100 %	0.50

2.4. Cyclic Polarization Test

The Gamry Instrument Potentiostat PCI4G750 with Global Software was used for the cyclic polarization test. The electrochemical cell apparatus consists of steel bar in the concrete specimen as working electrodes (WE), Ag/AgCl reference electrode (RE), and Platinum wire as a counter electrode (CE) as illustrated in Fig. 2. The polarization test was conducted three times namely on the first, third and sixth day of the immersion in NaCl solution. The polarization curve was determined by setting up the initial and final voltage from -0.5 V to 0.1 V with a scanning rate of 5mVs^{-1} versus an open circuit voltage (E_{oc}).

The polarization curves from the test were used by fitting the curves to determine the quantitative parameter. In this study, only the corrosion rate and current density were used as the quantitative parameter to evaluate the corrosion resistance of the steel bar embedded in the concrete.

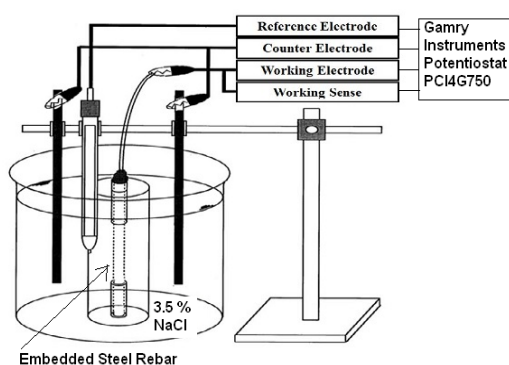


Figure 2. Apparatus of electrochemical measurement cell.

2.5. Carbonation Test

The carbonation test was performed by dripping the Phenophtalein indicator (PP) on the surfaces of each concrete that had been immersed in a sodium chloride solution for 6 days of testing. The colour change in the PP indicator will produce a pink colour on a non-carbonated concrete cross section, while a transparent colour will appear if carbonated[7].

3. Results and Discussions

3.1. Cyclic Polarization Test

The polarization curves of the reinforcement steel in S10-OPC90, S20-OPC80, and S30-OPC70 concrete compared to that in OPC100 immersed in NaCl 3.5% solution obtained from the 3 tests are shown in Fig. 3.

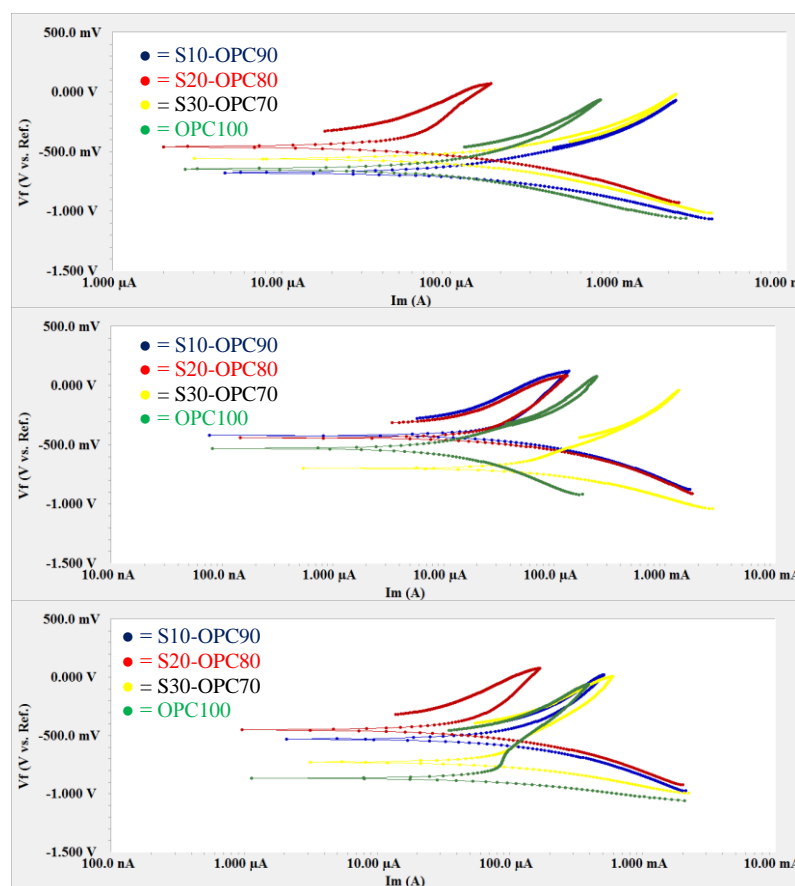


Figure 3. Comparison of *Cyclic polarization curve* on reinforcement steel in slag and OPC mix in (a) day 1, (b) day 3, and (c) day 6.

By conducting a fitting process to each cyclic polarization curve, several quantitative parameters were obtained (Table 4). The quantitative parameters are then plotted into a graph explaining the trend change relationship of the corrosion rate in each data retrieval up to day 6 as illustrated in Fig. 4. This parameter will support the qualitative information derived from the cyclic polarization testing curves of the reinforcing steel for each concrete composition.

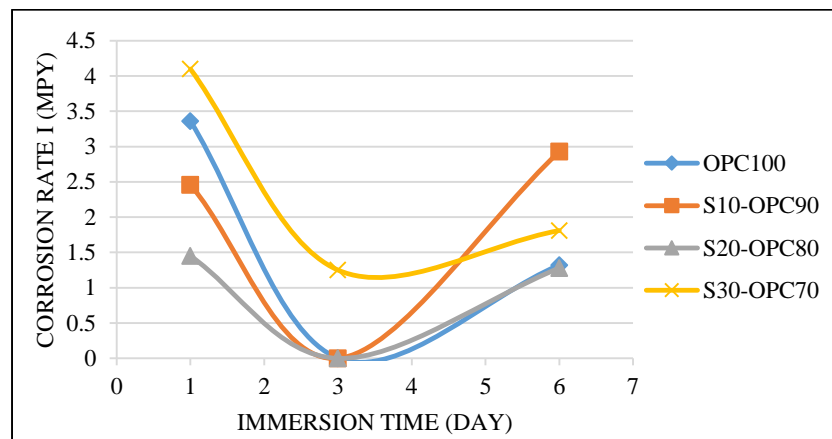


Figure 4. Comparison graphic of reinforcement steel corrosion rate in S10-OPC90, S20-OPC80, S30-OPC70 and OPC100 concrete.

On the first day of immersion, the cyclic polarization curve tends to be in the right-to-left position especially for the anodic reaction side shown on the steel embedded in S10-OPC90, S30-OPC70, OPC100, and S20-OPC80 respectively as pictured in Fig. 3a. The steel sample in S20-OPC80 has the lowest current density value compared to other samples, which is $3.14 \mu\text{A}/\text{cm}^2$, since its polarization curve is in the left-most position especially for the anodic reaction side.

This result shows that S20-OPC80 concrete has the highest corrosion resistance of steel in 3.5% NaCl solution on the first day of immersion. Meanwhile, the highest current density value in the polarization test is approximately $8.87 \mu\text{A}/\text{cm}^2$ achieved by the steel embedded in S30-OPC70 in first day of immersion. This is due to the pitting corrosion behavior as observed from the positive loop direction. Meanwhile, no pitting corrosion was observed on steel embedded in S10-OPC90, S20-OPC80, and OPC100 concrete.

On the third day of immersion, the curve of reinforcement steel in each concrete composition tends to shift to the left side from its position of the first day which means that the rate of the electron transfer from the cathodic and anodic side is slow. This indicates a higher corrosion resistance of steel as illustrated in Fig. 3b. This is due to a hydration process in the concrete which produces *Friedel's salt* that binds free chloride leading to reduced concrete porosity[8]. This phenomenon will keep the alkalinity of the concrete so that the passive layer of steel will remain stable. The reinforcement steel in S30-OPC70 shows a polarization curve with the highest current density value of $2.70 \mu\text{A}/\text{cm}^2$. Based on this polarization curve shown in Fig. 3b, there is no pitting on the third day of immersion for each composition.

On the sixth day of immersion, the current density of reinforcement steel in each concrete composition tends to increase which indicates a decreasing corrosion resistance against 3.5% NaCl solution as shown in Fig. 3c. In this study, the current density value significantly increased in the reinforcement steel in S30-OPC70 concrete which exceeded $3.92 \mu\text{A}/\text{cm}^2$. This result shows that the concentration of chloride ion started to increase around the interface between the steel and the pore solution. Based on the abovementioned polarization curve, no pitting corrosion was observed in each concrete composition especially in S10-OPC90, S20-OPC80, and OPC100 after 6 days of immersion as shown by the positive loop direction.

It also can be inferred that there are similar decreasing tendency on the corrosion rate of reinforcement steel in each concrete composition. After the third day of immersion, the corrosion rate of the reinforcement steel had decreased significantly with the lowest value of 0.354 mpy was shown by the steel specimen embedded in OPC100. The decrease of corrosion rate is due to hydration reaction in NaCl solution, in which *tricalcium aluminate* (C_3A) initiates chemical bonding with chloride ion in the pore solution forming *Friedel's salt* and leading to the decrease of concrete porosity [8].

The corrosion rate on the sixth day of immersion for each concrete specimen increased with the highest corrosion rate shown by the steel bar specimen embedded in S10-OPC90 concrete, which is

2.928 mpy. The corrosion rate may have increased due to the increasing chloride ion between the interface of the steel bar and the concrete's pore solution even though it did not exceed the chloride's threshold value to initiate the pitting corrosion. The lowest corrosion rate of 1.284 mpy was shown by the steel bar specimen in S20-OPC80 which is better than the corrosion rate of the OPC100 mixture. This result shows that the addition of 20% tin slag will give higher and more stable steel bar corrosion resistance compared to other concrete compositions which is immersed in NaCl 3.5% solution.

Table 4. Quantitative parameter extracted from fitting on cyclic polarization curve of steel bar for each concrete composition measured in 3.5% of NaCl solution for 6 days of testing.

Code	Immersion time (day)	β_a (V/decade)	β_c (V/decade)	E_{corr} (mV)	I_{corr} ($\mu A/cm^2$)	Corrosion rate (mpy)
S10-OPC90	1	345×10^{-3}	208×10^{-3}	-674.0	5.33	2.46
	3	392×10^{-3}	134×10^{-3}	-420.9	0.89	413×10^{-3}
	6	921×10^{-3}	298×10^{-3}	-529.4	6.33	2.93
S20-OPC80	1	1517	199.2	-459.1	3.14	1.45
	3	663×10^{-3}	168×10^{-3}	-438.5	1.09	503×10^{-3}
	6	1231	216×10^{-3}	-450.7	2.78	1.28
S30-OPC70	1	421×10^{-3}	370×10^{-3}	-556.7	8.87	4.10
	3	415×10^{-3}	172×10^{-3}	-697.2	2.70	1.25
	6	837×10^{-3}	170×10^{-3}	-729.3	3.92	1.81
OPC100	1	752×10^{-3}	403×10^{-3}	-642.9	7.27	3.36
	3	446×10^{-3}	413×10^{-3}	-529.3	0.76	353×10^{-3}
	6	929×10^{-3}	129×10^{-3}	-860.5	2.85	1.32

3.2. Carbonation Test

Carbonation testing was carried out to determine whether additional reactions such as carbonation were involved in concrete soaked in sodium chloride solution through the environment. The presence of carbonate ions in the concrete could lower the pH of the concrete so that the reinforcement steel inside becomes more vulnerable to corrosion. Phenophtalein indicator was dripped into S10-OPC90, S20-OPC80, S30-OPC70 and OPC100 concrete and the colour changes on its surface are shown in Fig. 5.

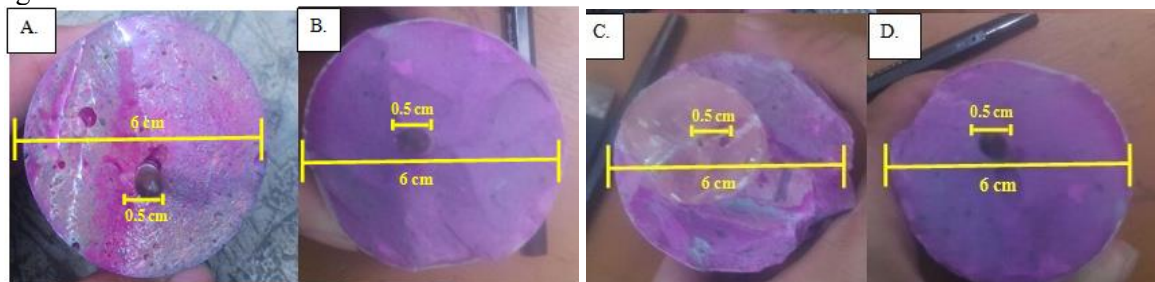


Figure 5. Carbonation test with PP indicator for concrete sample of (a) OPC100, (b) S10-OPC90, (c) S20-OPC80, dan (d) S30-OPC70.

The discoloration of the concrete into pink after the addition of PP indicator indicates that the carbonation reaction did not occur or in other words the alkalinity of the concrete tends to be maintained so that the decreasing pH factor does not play a significant role in observing the behaviour of corrosion resistance of reinforcement steel in the concrete within the chloride environment.

4. Conclusions

Based on the test results, the conclusions are presented as follows:

- The cement materials in S20-OPC80 concrete provided the most competitive and stable corrosion resistance of the embedded steel bar compared to the OPC100 mixture, followed by S10-OPC90, and S30-OPC70 respectively. The polarization curve of S20-OPC80 shows a close approach to the curve of the steel bar in OPC100 condition. The existence of alkali oxide plays an important role in maintaining the pH of the concrete's pore solutions especially in S20-OPC80 so that the passive film of steel tends to be more stable.
- No pitting corrosion was observed on the carbon steel bars embedded in OPC100, S10-OPC90, and S20-OPC80 concrete which were immersed in NaCl 3.5% solution after day 6 of cyclic polarization test. However, potential pitting corrosion on the steel bar in S30-OP70 concrete was indicated by the positive loop and the significant increase of corrosion rate up to 4.1 mpy. As a result, the steel bar in S30-OPC70 concrete is less durable compared to the steel bar embedded in OPC100, S20-OPC80, and S10-OPC90 due to its lower corrosion resistance in chloride environment.
- Similar trends on the corrosion rate of the steel bar for each concrete composition were observed, in which the decrease of the corrosion rate on the third day tends to increase on the sixth day of immersion in 3.5% sodium chloride solution. These trends are a result of the formation of *Friedel's salt* from chemical bond between chloride ion and C_{3A} and C_{4AF} in concrete hydration process until saturation of the pore solution is reached.

Acknowledgement

The authors would like to thank the financial support provided by Universitas Indonesia through the 2018 PITTA funding scheme No. 2519/UN2.R3.1/HKP.05.00/2018 managed by the Directorate for Research and Community Engagement (DRPM-UI).

References

- [1] S. Permana, J. Soedarsono, A. Rustandi, dan A. Maksum, "Other Oxides Pre-removed from Bangka Tin Slag to Produce a High Grade Tantalum and Niobium Oxides Concentrate", IOP Conference Series: Materials Science and Engineering, vol. 131, p. 012006, 2016.
- [2] G. Wang, The utilization of slag in civil infrastructure construction. Amsterdam [etc.]: Woodhead Publishing, 2016.
- [3] Shah, Darshan S., and Jayeshkumar Pitroda. "An Experimental Study On Durability And Water Absorption Properties Of Pervious Concrete". *The Master Builder* (2016): 56-60.
- [4] S. Muthulingam dan B. Rao, "Non-uniform time-to-corrosion initiation in steel reinforced concrete under chloride environment", *Corrosion Science*, vol. 82, pp. 304-315, 2014.
- [5] M. Mustafa dan K. Yusof, "Atmospheric chloride penetration into concrete in semitropical marine environment", *Cement and Concrete Research*, vol. 24, no. 4, pp. 661-670, 1994.
- [6] A. Neville, "Chloride attack of reinforced concrete: an overview", *Materials and Structures*, vol. 28, no. 2, pp. 63-70, 1995.
- [7] J. Broomfield, *Corrosion of steel in concrete*. London: Spon Press, 2003.
- [8] S. Han, "Influence of diffusion coefficient on chloride ion penetration of concrete structure", *Construction and Building Materials*, vol. 21, no. 2, pp. 370-378, 2007.