The Study of the Effect of Slag Ferronickel Substitution (FNS) in Portland Concrete on Corrosion Resistance of Reinforced Steel in Chloride Environment with Cyclic Polarization Method

M Ibnu, Rini Riastuti, A S Ashari, I T Aryani
Department of Metallurgical and Materials Engineering, Faculty of Engineering Universitas Indonesia, Kampus Baru UI Depok 16424, Indonesia.

riastuti@metal.ui.ac.id

Abstract. Ferronickel slag is a by-product of the ferronickel extraction process. Smelting process that contain the oxide compounds such as SiO$_2$, CaO, Al$_2$O$_3$, and Fe$_2$O$_3$. The compound content is similar to the content of Portland brand commercial cement (OPC) which is commonly used as raw material for making concrete. Therefore, this research will analyze the effect of using ferronickel slag as a cement mixture on the resistance of reinforced steel in concrete. The author will analyze the corrosion behavior of various mixtures of OPC cement and ferronickel slag with variations in the use of Ferronickel slag as much as 5%, 10%, 15%, 20% with OPC cement in the process of curing concrete for 28 days then it is immersed 3.5% NaCl solution. The concrete will uses cyclic polarization method to analyze pitting behaviour and resistance corrosion of reinforced steel in chloride environment. The results show that the steel in the 20% slag concrete mixture added with OPC cement has resistance compared to other mixed variations.

Keywords: Portland concrete; Corrosion resistance; 3.5% NaCl solution; Cyclic Polarization; Slag ferronickel (FNS)

1. Introduction
Concrete is one of the most widely used construction materials in the world. Concrete is one of the important components in buildings, the life of a building one of which is influenced by the resistance of concrete to any interference both mechanical and environmental. Indonesia, especially as an archipelago country has a large sea area than land area. The condition like this makes a considerable effect on building design. The existence of aggressive ions due to the process of building damage salinity make faster [1]. In fact, the wind can carry chlorides in the air up to distances beyond 3 km [2]. Whereas the concrete structure is generally expected to survive without repair and maintenance in a long time (up to 100 years). Therefore, the 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. Corrosion is defined as damage of a material caused by the reaction between the environment and the material itself. Penetration by chloride ions and carbonation are some of the main causes of corrosion especially in concrete [3]. Controlling of corrosion on materials will increase the service life of the material.
Therefore, it is necessary to innovate the raw material for the concrete constituent material to overcome the existing problems.

Concrete is made of the mixture of cement and aggregate. Basically, the concrete is only made of cement and aggregate such as sands. Currently, the mixture of concrete becomes more varied, for example is the usage of Ground Granulated Blast Furnace Slag (GGBS) such as Ferronickel slag. The one of innovation is using ferronickel slag to substitute cement. Ferronickel slag is a waste or side product from alloying industry of nickel and iron [4]. 1 ton of ferronickel production can produce 14 tons of slag that has composition of SiO$_2$, MgO, CaO, Al$_2$O$_3$, and Fe$_2$O$_3$ [5], so that there is a lot of waste or side product that can be used. The compound content is similar to the content of Portland brand commercial cement (OPC) commonly used as raw material for making concrete.

The method that will be used in this study is Cyclic Polarization which is used to analyze reinforcement steel in concrete which is used OPC cement with mixture some cement of Slag when exposed under a corrosive environment such as chloride solution. The method will give some parameters quantitative such as current density of corrosion, corrosion rate, pitting corrosion tendency and passivation behavior which can be analyzed from the polarization curve presented [6].

2. Experimental method

2.1. Materials

The materials of concrete consist of Cement which is a mixture from Ordinary Portland Cement (OPC) and ferronickel slag cement, coarse aggregate, fine aggregate and water. The ferronickel slag cement used is a waste product from PT Antam Pomaala Tbk which have similar composition with Ordinary Portland Cement which can be shown from the result of X-ray Diffracion of OPC and ferronickel slag as presented following Table 1.

|     | CaO  | SiO$_2$ | Al$_2$O$_3$ | Fe$_2$O$_3$ | SO$_3$ | Basicity | MgO  | T.Ni  | Cr$_2$O$_3$ |
|-----|------|---------|-------------|-------------|-------|----------|------|-------|-------------|
| OPC | 66.00| 21.10   | 5.50        | 3.90        | 2.75  | -        | 5.00 | -     | -           |
| Slag| 2.7  | 52.9    | 2.2         | 7.6         | -     | 0.63     | 30.8 | 0.12  | 1.1         |

2.2. Sample preparation

Initially, the reinforcement steel was ground with a series of abraded paper (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 in order to connect with copper cable for cyclic polarization test. The OPC cement and ferronickel 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 10 cm and a length of 20 cm, meanwhile a single steel bar was symetrically positioned in the mold shown in Fig. 1. The cylindrical concrete was then immersed in water for 28 days for curing. Then, the concrete was exposed with NaCl 3.5% solution consisting of sodium chloride in 1 L of aquadest. After that, the concrete specimens in NaCl 3.5% solution were analysed using cyclic polarization.

The ferronickel slag as raw material was ground using abrasive machine to achieve 200 mesh of partikel size. Then, the reinforcement steel was ground with a type of abraded paper (200,400, 600,800, 100 and 1200) until some oxide scale was removed and the steel was smooth. The steel bar was mounted eith using resin and catalyst. The process of mixture uses 0.5 water/binder (w/c) ratio. After the mixture is complete, the materials will be filled to cylindrical concrete moulds with a diameter of 10 cm and a length of 20 cm. A single steel bar must be symetrically positioned in the mold shown in figure. 1. The cylindrical concrete was then immersed in water for 28 days for curing in order that can get maximum strength. After immersed, the concrete was immersed again in NaCl 3.5% solutions. The concrete in NaCl 3.5% solution were analysed using cyclic polarization in different day variations.
2.3. Concrete composition

The composition of Ordinary Portland Cement and Ferronickel Slag Cement used in this study are shown in Table 2.

Table 2. Formula of OPC and ferronickel slag cement as a raw material in concrete composition.

| Composition of Cement | Ferronickel Slag Cement (wt. %) | Ordinary Portland Cement (wt. %) | w/c Ratio |
|-----------------------|-------------------------------|----------------------------------|-----------|
| OPC95-FNS5            | 5                             | 95                               | 0.50      |
| OPC90-FNS10           | 10                            | 90                               | 0.50      |
| OPC85-FNS15           | 15                            | 85                               | 0.50      |
| OPC80-FNS20           | 20                            | 80                               | 0.50      |

2.4. Cyclic Polarization Test

The Nova Autolab 2.0 with The New Electrochemistry Software from Metrohm Autolab was used for cyclic polarization tests. The electrochemical cell devices consist of the concrete as working electrode, platinum wire as a counter electrode (CE) and Ag/AgCl as reference electrode, the devices are illustrated in Figure 2. The Polarization test is carried out in 4 times test, Namely first, third, sixth, and ten days in immersed NaCl solutions. The polarization curves were determined by setting up time in open circuit determination (OPC) until 120 seconds and the upper and lower vortex potential until ±0.095 V.
2.5. Compressive test
The concrete mixture is poured to make compressive test specimens. The compressive strength test refers to ASTM C39/C39M-18 “Standard Test Method for Compressive Strength of Cylindrical Concrete Specimens” [9]. The loading test is carried out with the position of the specimen as shown in Figure 3.

![Compressive strength test procedure](image)

**Figure 3.** Compressive strength test procedure.

2.6. Carbonation test
The carbonation test was did by dripping the Phenophtalein indicator (PP) on the surfaces of the concrete steel which had been immersed in 3.5% NaCl solutions for 15 days of testing. The colour change in the PP indicator will produce a pink colour if the concrete steel non-carbonated but if the concrete show transparent colour so it is carbonated [3].

3. Results and discussion
3.1. Cyclic polarization curves
The results of reinforcement steel in beton will be shown by the orange polarization curves for OPC85-FNS5, the red curves for OPC90-FNS10, the green curves for OPC85-FNS15 and the blue curves for OPC80-FNS20. All comparison of polarization curve in testing using day variations will be shown from Figure 4.
Figure 4. Comparison of cyclic polarization curve on reinforcement steel in slag and OPC mix in (a) day 1, (b) day 3, (c) day 6 and (d) day 10.
composition tends to 

as shown by positive loop direction which mentioned 

ot 

rosion resistance. The leftmost location and the highest 

IOP Conf. Series: Materials Science and Engineering 553 (2019) 012007 doi:10.1088/1757-899X/553/1/012007

| Code       | Immersion Time (day) | Potential Applied (V) | WE (1). Current (A) | WE (1). Current (A) |
|------------|----------------------|-----------------------|---------------------|---------------------|
| OPC95-FNS5 | 1                    | -0.775                | 2.76x10^-5          | -0.773              |
|            | 3                    | -0.667                | 2.81x10^-5          | -0.666              |
|            | 6                    | -0.727                | 16.31x10^-6         | -0.726              |
|            | 10                   | -0.848                | 17.44x10^-6         | -0.846              |
| OPC90-     | 1                    | -0.203                | 1.18x10^-5          | -0.202              |
| FNS10      | 3                    | -0.512                | 10.93x10^-6         | -0.511              |
|            | 6                    | -0.388                | 10.33x10^-6         | -0.387              |
|            | 10                   | -0.522                | 9.07x10^-6          | -0.520              |
| OPC85-     | 1                    | -0.329                | 8.37x10^-6          | -0.329              |
| FNS15      | 3                    | -0.552                | 10.17x10^-6         | -0.55               |
|            | 6                    | -0.535                | 11.12x10^-6         | -0.534              |
|            | 10                   | -0.509                | 7.76x10^-6          | -0.507              |
| OPC80-     | 1                    | -0.304                | 8.86x10^-6          | -0.305              |
| FNS20      | 3                    | -0.301                | 7.2x10^-6           | -0.302              |
|            | 6                    | -0.128                | 0.923x10^-6         | -0.127              |
|            | 10                   | -0.253                | 6.57x10^-6          | -0.254              |

On the first day of testing, the cyclic polarization curve for the anodic reaction side of the OPC95-FNS5, OPC90-FNS10, OPC85-FNS15, and OPC80-FNS20 concrete steel tends to be in the right-to-left position as shown in Figure 4a. The maximum result of corrosion resistance is the OPC90-FNS10 concrete steel because it has lower current density which is 0.37 μA/cm² and the polarization curve is in the far-left position. Meanwhile, the minimum corrosion resistance is the OPC95-FNS5 because it has the highest current density which is about 0.87 μA/cm² and the polarization curve tend to right. Moreover, the tendency of a passive layer that is stable can be seen from the range potential is very large and the current meeting tends to be stable in each composition, meaning that there is no electron flow, the passive layer can keep from electron (corrosion) attacks.

On the third day of testing, the cyclic polarization curves tend to move to left compared to the others so that current density becomes but the most significant movement shown by the OPC80-FNS20. This movement make the OPC80-FNS20 has highest corrosion resistance because has the lower current density which is 0.092 μA/cm² and the lower corrosion resistance shown by the OPC95-FNS5. The OPC95-FNS5 steel concrete has highest current density which is 0.36 μA/cm² and the polarization curve still tend to right position. In this observation, there was no pitting corrosion formed in each concrete steel composition after 3 days of immersion as shown by positive loop direction which mentioned polarization curves.

On the sixth day of testing, The current density of concrete steel in each composition tends to decrease can be seen from the polarization curve which still tends to move leftward, this shows a decrease in corrosion resistance to 3.5% NaCl solution. The polarization curve OPC80-FNS20 shows the maximum results which is a value of 0.012 μA/cm² and the minimal results are shown by the composition of OPC95-FNS5 which is 0.208 μA/cm². In addition, the polarization curve above shows that the passive layer formed in the composition is still stable enough to resist the penetration of chloride which will enter the concrete. Figure 5c also shows that on the sixth day the pitting corrosion has not been formed in each composition, this is indicated by the polarization curve having a positive loop direction.

On the tenth day of testing, the cyclic polarization curves of OPC80-FNS20 steel concrete has the lowest value which means it has the best corrosion resistance. The leftmost location and the highest corrosion potential make OPC80-FNS20 composition have the highest corrosion resistance. But, the composition of OPC95-FNS5 has the lowest corrosion resistance, this already showed from the first day
of immersion until the tenth day. This showed by Figure 4d if the polarization curve OPC95-FNS5 has the rightmost curve meaning that it has a large current density and OPC80-FNS20 is located on the far left so that the composition of OPC80-FNS20 is the lowest current density compared to other compositions. The current density is proportional to the electron flow. The current density is proportional to the electron flow. If there are more electron flowing can make reaction of anode became faster. So that, corrosion behaviour even easier to occur. Until the tenth day the symptoms of pitting corrosion were still not visible, it could be seen from the movement of the loop that was still positive.

The corrosion rate on third days of immersion for each concrete steel specimen increased as shown in Table 4. The highest corrosion rate was shown by the OPC95-FNS5 steel concrete which was 28.489 mm/year. The corrosion rate has increased because chloride ion between the interface of steel reinforced and concrete pore solution have increased also but the chloride threshold value still has not exceeded so that pitting corrosion still no formed [8]. The lowest corrosion rate of 0.246 mm/year is shown by concrete steel specimens in OPC80-FNS20. These results indicate that addition of 20% ferronickel slag cement will provide a higher and more stable steel reinforced corrosion resistance compared to other concrete steel composition immersed in 3.5% NaCl Solution.

| Code        | Immersion Time (day) | βa (V/decade) | βc (V/decade) | Ecorr (mV) | Icorr (μA/cm²) | Corrosion Rate (mm/year) |
|-------------|----------------------|---------------|---------------|------------|----------------|--------------------------|
| OPC95-FNS5  | 1                    | 1.19          | 3.206         | -0.079     | 0.001617       | 18.875                   |
|             | 3                    | 1.56          | 8.23          | -0.74      | 0.00245        | 28.489                   |
| OPC90-FNS10 | 1                    | 1.16          | -2.97         | -0.69      | 0.001915       | 22.248                   |
|             | 3                    | 1.073         | -2.97         | -0.69      | 0.00168        | 19.474                   |
| OPC85-FNS15 | 1                    | 0.679         | -31.946       | -0.54      | 0.000388       | 4.507                    |
|             | 3                    | 1.142         | -2.33         | -0.65      | 0.00162        | 18.87                    |
| OPC80-FNS20 | 1                    | 0.6283        | -3.29         | -0.597     | 0.00721        | 8.37                     |
|             | 3                    | 0.0915        | 0.0413        | -0.607     | 2.11x10⁻⁵⁻     | 0.246                    |

3.2. Compressive test

![Figure 5. Compressive test result.](image-url)
From Figure 5, it can be observed that the percentage of slag in each composition does not have a significant difference, it can be seen from the pattern. The maximum compressive strength for cement and ferronickel slag mixtures is in the OPC80-FNS20 composition. The difference in strength with OPC 100 is not far. This shows that the addition of slag as a substitute for cement does not significantly affect the mechanical properties of the concrete, because only a reduction in strength about 4 MPa occurs.

3.3. Carbonation test

![Carbonation test images](image)

**Figure 6.** Carbonation test with PP indicator for concrete sample of (a) OPC95-FNS5, (b) OPC90-FNS10, (c) OPC85-FNS15, and (d) OPC80-20.

The discoloration of the concrete specimen into pink after addition of Phenolphthalein indicator (PP) indicates that the carbonation reaction did not occur in the words the alkalinity of the concrete tends to be maintained so that the decreasing pH factor does not happen. The decreasing of pH will indicate breakdown of passive layer which have from concrete steel. If passive layer breakdown, the elements like CO\textsubscript{2} and chloride can penetrate into concrete structure so that can cause concrete corrosion [7].

4. Conclusion
The mixture of cement OPC-FNS20 concrete steel has maximum compressive strength than other composition and also provides best corrosion resistance from embedded steel bars compared to other compositions in 10 days immersion because the OPC80-FNS20 has lower current density that could hindered the movement of the electrons so that the reaction of corrosion is slower than other compositions. But in this research, no pitting corrosion was observed in carbon steel bars embedded in all of concrete steel specimen which immersed in 3.5% NaCl Solution. Otherwise, the reaction of carbonation has not occurred in all of concrete steel specimen.

Acknowledgment
The authors would like to thank University of Indonesia, especially Directorate for Research and Community Engagement (DRPM) division, for the financial support through the 2018 PITTA funding scheme No.2519/UN2.R3.1/HKP.05.00/2018 and PT Antam Pomaala Tbk as the provider of ferronickel slag as the raw material in this research.

References
[1] S. Muthulingam, and B. N. Rao, “Non-uniform time-to-corrosion initiation in steel reinforced concrete under chloride environment”, *Corrosion Science*, vol. 82, pp. 304–315, May 2014, DOI: 10.1016/j.corsci.2014.01.023
[2] A. Neville, “Chloride attack of reinforced concrete: an overview”, *Materials and Structures*, vol.28, pp. 63-70, Mar. 1995, DOI: 10.1007/BF02473172
[3] J. P. Broomfield, *Corrosion of Steel in Concrete, Understanding, Investigation and Repair*, 2nd ed., Jul. 2003, DOI: 10.1201/9781482265491
[4] K. Kokubu, and M. Shoya, “Guidelines for Construction Using Ferronickel Slag Fine Aggregate Concrete”, *Concrete Library of JSCE No. 24*, Dec. 1994

[5] A. K. Saha, and P. K. Sarker, “Expansion due to alkali-silica reaction of ferronickel slag fine aggregate in OPC and blended cement mortars”, *Construction and Building Materials*, vol. 123, pp. 135-142, Oct. 2016, DOI: 10.1016/j.conbuildmat.2016.06.144

[6] R. Riastuti, A. Cahyadi, Y. Pratesa, and S. Siallagan, “The study of corrosion resistance of reinforcement steel embedded in concrete composed of commercial Portland cement and final tin slag against chloride environment”, *IOP Conference Series: Materials Science and Engineering*, vol. 431, pp. 052006, Nov. 2018, DOI: 10.1088/1757-899X/431/5/052006

[7] N. Perez, *Electrochemistry and Corrosion Science*, Jan. 2004, DOI: 10.1007/b118420

[8] R. W. Revie, and H. H. Uhlig, *Corrosion and Corrosion Control: An Introduction to Corrosion Science and Engineering*, 4th ed., Mar. 2008, DOI:10.1002/9780470277270

[9] ASTM C39/C39M-18, “Standard Test Method for Compressive Strength of Cylindrical Concrete Specimens”, ASTM International, West Conshohocken, PA, 2018, DOI: 10.1520/C0039_C0039M-18, www.astm.org