The Influence of Salt Water on Chloride Penetration in Geopolymer Concrete

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Abstract. This paper presents the influence of chloride ion penetration in geopolymer concrete. Fly ash as based material for geopolymer concrete was used in this mixture. Fly ash was mixed with sodium hydroxide (NaOH) 8 M and sodium silicate (Na2SiO3) as the alkali solution. The sizes of cylindrical specimens were prepared with a diameter of 100 mm and 200 mm high. Some specimens were immersed in salt water at a concentration of 3.5%, and other control specimens were cured in tap water for 30, 60, 90, and 120 days. The mechanical properties were determined with compressive test which was conducted at 28, 30, 60, 90 and 120 days. Some durability tests were performed for porosity, chloride penetration, and pH measurement. It was found that geopolymer concrete has higher compressive strength than concrete made with Ordinary Portland cement (OPC). However, chloride penetration in geopolymer concrete is higher than OPC. The pH measurement showed that geopolymer concrete has less pH than OPC concrete. The porosity of concrete has been found to influence chloride penetration and pH of concrete.

1 Introduction

Concrete is one of the most widely used construction materials in the world. In addition, ordinary Portland cement (OPC) is the main binding material in concrete. The consumption of energy during manufacturing of Portland cement releases a large amount of greenhouse gases into the atmosphere causing global warming. The cement industry is responsible for about 6-8% of all CO2 emissions, since the production of one ton of Portland cement emits approximately one ton of CO2 into the atmosphere [1, 2].

The previous studies showed geopolymer cement is one of the solutions to replace the Portland cement in construction [3, 4]. Fly ash is one of the construction materials, which is used commonly to produce geopolymer concrete [5]. Fly ash-based geopolymer concrete has many significant benefits such as environmental friendly, high-performance material solution, and economic benefits. Fly ash-based geopolymer concrete is also resistant to corrosion [6].

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Durability of geopolymer concrete in salt water is affected by its permeability. It is the major factor for determining the long-term durability of concrete in marine environment. Denser concrete will lead against destructive agents to penetrate and flow through the pores [7]. However, the chloride environment sometimes can increase the compressive strength of the geopolymer concrete [8]. According to some previous research, fly ash-based geopolymer concrete has better durability than Portland-based concrete in aggressive environment such as sulphate, acid, and fire [9-13]. Nevertheless, there are only few literatures discussing about the influence of salt water on chloride penetration in geopolymer concrete. This paper discusses factors affecting the strength geopolymer concrete in salt water.

2 Materials

2.1 Fly ash

Class F fly ash was obtained from the fertilizer factory, PT. Petrokimia Gresik Indonesia. The composition of fly ash is listed in Table 1.

Table 1. Chemical composition of fly ash (%) by XRF.

| Chemical | SiO2 | Al2O3 | Fe2O3 | TiO2 | CaO | MgO | Cr2O3 | K2O | Na2O | SO3 | Mn2O3 |
|----------|------|-------|-------|------|-----|-----|-------|-----|------|-----|-------|
| SiO2     | 48.47| 26.05 | 12.54 | 0.92 | 5.18| 2.77| 0.02  | 1.66| 0.47 | 1.05| 0.19  |

2.2 Alkaline activator

Activators used in the mixture are NaOH and Na₂SiO₃. NaOH solution was prepared by dissolving flakes form in distilled water. Concentration of NaOH used is 8M. Sodium silicate was obtained from PT. Kasmaji Inti Utama (PTKIU), Indonesia. Sodium silicate contains 18.5% of Na₂O, 36.4% of SiO₂, and 45.1% of H₂O. The mass ratio of Na₂SiO₃ to NaOH was kept at 2.5.

2.3 Aggregates

Coarse aggregate and fine aggregate were collected from PT. Surya Beton Indonesia. The densities of coarse aggregate and fine aggregate are 2.6 g/cm³ and 2.7 g/cm³ respectively.

2.4 Superplasticizer

Polycarboinic Acid Salts used in the mixture was obtained from PT. Sika Indonesia. It was applied to the mixture to ensure the workability of fresh concrete. The dosage of SP was 2% by weight of fly ash.

3 Methods

The fresh concrete was cast in cylindrical molds with a diameter of 100 and 200 mm high. One day after casting, the concrete was demolded and cured at room temperature for one day before immersing into tap water for 28 days. After that, the immersion was continued in two conditions which were tap water and salt water. All specimens were cured for 30, 60, 90, and 120 days. Fig. 1 shows the sequence of treatment and testing.
The specimens were immersed in tap water

The specimens were immersed in salt water

| Treatment                          | Mixing | Open the mold and immersed the specimen in normal water | Three specimens were kept at room temperature | Test of concrete compressive strength at 28 days | Some specimens were immersed into salt water | Compressive strength test | Compressive strength test | Compressive strength test |
|-----------------------------------|--------|-------------------------------------------------------|-----------------------------------------------|-----------------------------------------------|----------------------------------------------|--------------------------|--------------------------|--------------------------|
| Days                              | 0      | 1                                                     | 27                                            | 28                                            | 30                                           | 60                      | 90                      | 120                      | 180                      |
| Cylinder concrete                  |        |                                                       |                                               |                                               |                                               |  ✓                      |  ✓                      |  ✓                      |  ✓                      |

Fig. 1. The treatment and testing of cylindrical concrete specimens.

4 Test procedures

The mechanical properties of concrete were determined by compressive strength test according to ASTM C 39 [15]. Porosity test for the specimens at 28 days (initial condition) and those which were cured in salt water for 30, 60, 90, and 120 days. The tests for chloride penetration and pH were only measured for geopolymer concrete and OPC, which were immersed in salt water, containing 3.5% of NaCl solution. Chloride ion penetration test and pH measurement were selected from samples at three points as described in Fig. 2. Three points are determined with some distance from a concrete surface at a depth of 0 cm, 4 cm, and 8 cm.

Fig. 2. The model of sample for chloride penetration and pH measurement.
5 Results and discussions

5.1 Compressive strength

OPC concrete was used as a control specimen to compare its compressive strength with geopolymer concrete. Table 2 and Fig. 3 showed that geopolymer concrete has higher compressive strength than OPC in salt water. It is proved that salt water influences the strength of geopolymer concrete. In addition, geopolymer concrete has also higher compressive strength in tap water than OPC.

Fig. 3 shows that the compressive strength of geopolymer and OPC concrete in tap water were decreased at 90 and 120 days. However, the compressive strength of geopolymer concrete decreases less significant than OPC concrete. Compressive strength of OPC specimen which was immersed in salt water reduces drastically from 59.99 MPa at 90 days to 45.21 MPa at 120 days. This proves that the geopolymer concrete is more resistant than OPC concrete in aggressive environment. It has a good agreement with Ekaputri [14]. The durability of structure was decreased from the first year (2005) when research was conducted and after 20 years of investigation. Ekaputri [14] calculated the safety factor to obtain the structure performance in sea water and it was found that the protection of structure has been declined year by year. Bayuaji, et al [8] found that geopolymer concrete cured in sea water provides higher compressive strength than the other curing system using fresh water and room temperature. Giasuddin [16] explained that there is abundance of Na⁺ in the surrounding medium in salt water curing. It is very likely that Na⁺ as well as other cations (Ca²⁺) in the sample are less prone to leaching. These excess cations in the surrounding curing solution and in the sample will help to promote reaction mechanism and geopolymer formation.

Table 2. The comparison for compressive strength in geopolymer concrete and OPC concrete.

| Type of Concrete | Compressive Strength |
|-----------------|----------------------|
|                 | Curing (days) | 0 | 30 | 60 | 90 | 120 |
| Geopolymer      | Age (days)    | 28 | 58 | 88 | 118 | 148 |
| Salt water      | 51.42 | 65.49 | 68.33 | 70.39 | 65.19 |
| Tap water       | 51.42 | 57.76 | 68.07 | 66.27 | 65.66 |
| OPC             | Salt water    | 46.61 | 52.28 | 60.14 | 59.99 | 45.21 |
| Tap water       | 46.61 | 48.35 | 57.76 | 55.69 | 52.64 |

Fig. 3. The comparison for compressive strength in geopolymer and OPC concrete.
Another investigation showed that geopolymer concrete has a good development of compressive strength in aggressive environment for a long term [9]. During the geopolymerisation process, silica and alumina in fly ash dissolve with NaOH to form sodium-alumina-silicate, which contributes to the strength of geopolymer concrete. Salt water which containing sodium ions from NaCl keeps the ions in geopolymer concrete during geopolymerization [12]. It causes the compressive strength of geopolymer concrete higher than OPC concrete. The compressive strength on OPC was decreased because portlandite (Ca(OH)_2) leaks out from OPC concrete. Then, this compound bonds with NaCl to form calcium chloride (CaCl_2) which then reacts with aluminate in the cement. As a result, this reaction forms Friedel salt (3CaO.Al_2O_3.CaCl_2.10H_2O) which fills the pores. Chloride in salt water can cause cracks and accumulation of salt crystal as well [17]. It also happened on the compressive strength of geopolymer concrete which was immersed in salt water. The strength was decreased at the age of 118 to 148 of days for 0.61 MPa because calcium oxide in the fly ash will react with NaCl to form calcium silicate chloride (Ca_2SiO_3Cl_2). In addition, the calcium content in the fly ash is not as much as in the cement and this compound is very easy to react with other compounds.

5.2 Porosity

Porosity measurement on the cylindrical specimen was obtained from total porosity (Pt). The measurement of porosity test was conducted after the specimens were immersed in salt water and tap water at specific age.

Table 3 shows that OPC concrete has better durability in tap water than in salt water. It is caused by the porosity of OPC concrete in salt water is greater than in tap water. If it is compared to geopolymer concrete, it shows that total porosity of OPC concrete is less than geopolymer in salt water.

In wet curing, sodium leaks out of concrete to the water. It causes the geopolymer concrete become more porous. It was proved by the result of pH measurement listed in Table 4. Before the concretes were soak in the water, the pH of immersion water was 7.9 with a concentration of solution was 266 ppm. The pH and concentration increased day by day until 10.4 and 1283 ppm respectively at 10 days. It is likely can be proposed that moist curing may be more recommendable than wet curing.

Table 3. Porosity test of geopolymer concrete and OPC concrete

| Type of Concrete | Curing (days) | Total Porosity Pt (%) |
|------------------|--------------|-----------------------|
|                  | 0            | 30                    | 60 | 90 | 120 |
|                  | Age (days)   |                       |
| Geopolymer       | 28           | 58                    | 88 | 118| 148 |
| Salt water       | 20.10        | 20.56                 | 21.71| 21.19| 20.67|
| Tap water        | 20.10        | 20.40                 | 23.94| 22.38| 23.58|
| OPC              | 14.20        | 18.27                 | 22.38| 20.00| 21.15|
| Salt water       | 14.20        | 22.83                 | 20.42| 22.28| 20.48|
| Tap water        | 14.20        |                       |     |     |     |
Table 4. The result of pH measurement and concentration of immersion water

| Days of immersion | pH   | Concentration of solution Ppm |
|-------------------|------|-------------------------------|
| 1                 | 7.9  | 266                           |
| 2                 | 9.6  | 383                           |
| 3                 | 9.7  | 461                           |
| 4                 | 10.1 | 593                           |
| 5                 | 10.0 | 685                           |
| 6                 | 10.1 | 763                           |
| 7                 | 10.1 | 801                           |
| 8                 | 10.2 | 958                           |
| 9                 | 10.4 | 1096                          |
| 10                | 10.4 | 1283                          |

5.3 Chloride penetration

The measurement of chloride penetration was intended to determine the depth of concrete that has been damaged by chloride ions. Fig. 4 illustrates that the chloride penetration of geopolymer concrete is larger than OPC. For instance, geopolymer concrete which was immersed in salt water for 30 days contained chloride penetration at 0 cm, 4 cm, and 8 cm from the surface were 0.15%, 0.13%, and 0.12% respectively. Whereas, OPC concrete has 0.10% at 0 cm, 0.07% at 4 cm, and 0.03% at 8 cm. This indicates that there is a correlation between porosity and chloride penetration. The greater the total porosity, the more chloride ion penetrate to concrete. In the previous study [9, 18], the geopolymer concrete was kept at room temperature before it was immersed in salt water. In this research, the concrete was directly soaked into normal water for 28 days. It causes the bond of Si-Al in the concrete becomes weaker because its greater pores. Olivia and Nikraz [18] said that the chloride concentration was large in geopolymer concrete because there is no C₃A in fly ash, which could enable a chloride binding mechanism to minimize direct chloride ion penetration of the concrete paste. However, the use of fly ash can slow the effects of chloride and CO₂ into concrete [19].

![Fig. 4. Chloride penetration in geopolymer and OPC concrete.](image)

5.4 pH measurement

The measurement was conducted for geopolymer and OPC concrete in salt water. It was intended to determine the correlation between pH value and chloride penetration. Generally,
geopolymer concrete has a high pH because of the reaction which occurred when fly ash was mixed with alkaline solution. Fig. 5 shows the result of pH measurement for the different of penetration depth at 0 cm, 4 cm, and 8 cm from the concrete surface.

Fig. 5 shows that pH in geopolymer concrete is less than OPC concrete. pH value is influenced by porosity. The greater the total porosity, the higher sodium is leaching. This is proved by the measurement of initial pH on geopolymer concrete is 11.24 before it is cured in normal water for 28 days. After that, the specimens were immersed in salt water. pH value decreases because the leaching of sodium from geopolymer concrete. It is proved with the pH measurement that is shown in Table 4. In addition, pH value of geopolymer concrete and OPC ranged between 10.32 until 11.70. It means that both concrete are in alkaline condition and good for corrosion resistance.

Fig. 5. pH measurement in geopolymer concrete and OPC concrete.

6 Summary

Geopolymer concrete has higher compressive strength than OPC in salt water. It proves that geopolymer concrete is durable in aggressive environment because there is abundance of Na⁺ in salt water. Na⁺ as well as other cations (Ca²⁺) in the sample are less prone to leaching. These excess cations in the surrounding curing solution and in the sample which help to promote reaction mechanism and geopolymer formation. Porosity of OPC concrete in salt water is larger than in tap water. It shows that OPC concrete has a good durability in tap water. If it is compared with geopolymer concrete, it shows that the total porosity of OPC concrete is smaller than geopolymer in salt water. In wet curing, sodium leaks out of concrete to the water. It causes the geopolymer concrete become more porous. The chloride penetration of geopolymer concrete is higher than OPC concrete. This indicates that there is a correlation between porosity and chloride penetration. Greater porosity increases chloride penetration into geopolymer concrete. pH value in geopolymer concrete and OPC ranged between 10.32 until 11.70. It means that both concrete are alkaline and good for corrosion resistance.

References

1. McCaffrey, Climate Change and the Cement Industry (GCL Magazine, London, 2002)
2. J. Davidovits, Rev. Geopolymer Inst., 1 (2013)
3. A.M. Mustafa Al Bakri, H. Kamarudin, M. Binhussain, I. Khairul Nizar, A.R. Rafiza, Y. Zarina, Rev. Adv. Mater. Sci., 30, 90 (2011)
4. Z.F. Farhana, H. Kamarudin, Azmi Rahmat, A.M. Mustafa Al Bakri, Aust. J. Basic Appl. Sci., 7, 230 (2013).
5. Information on http://www.geopolymer.org/applications/global-warming
6. K. Zerfu, J.J Ekaputri, Mater. Sci. Forum, 841, 162 (2016)
7. D.V Reddy, J.B Edouard, K. Sobhan, S.S Rajpathak, J. Mater. Civ. Eng., 25, 1465 (2011)
8. R. Bayuaji, M.S Dharmawan, B. Wibowo, N.A Husin, S. Subekti, J.J Ekaputri, Mech. Mater., 754, 400 (2015)
9. P. Chindaprasirt, W. Chalee, Constr. Build. Mater., 63, 303 (2014)
10. M.M Hossain, M.R Karim, M.K Hussain, M.N Islam, M.F.M Zain, Constr. Build. Mater., 93, 95 (2015)
11. Kupwade-Patil, K. and Allouche, E.N., J. Mater. Civ. Eng., 25, 1465 (2013)
12. F.U.A Shaikh, (2014), Adv. Concr. Constr., 2, 109 (2014)
13. Singh N, Vyass S, Pathak RP, Sharma P, Mahure NV, Gupta SL, Int. J. Eng. Innov. Tech., 3, 2277(2013)
14. J.J. Ekaputri, Proceedings Fourth International Conference on Forensic Engineering, (2008)
15. ASTM C 39 / C 39M-03 (2003), Standard Test Method for Compressive Strength of Cylindrical Concrete Specimens, United Stated.
16. Giasuddin, M. Haider, Sanjayan, G. Jay, P.G. Ranjith, Fuel, 107, 34 (2013)
17. T. Ishida, S. Miyahara, T. Maruya, J. Adv. Concr. Tech., 6, 287(2008)
18. Olivia, Monita, H.R. Nikraz. Proceedings of Concrete Conference, (2011).
19. S. Dhawan, S. Bhalla, B. Bhattacharjee, International Symposium on Advanced Science and Technology in Experimental Mechanics, (2014)