The effect of chloride ion diffusion on corrosion activity of kaolin geopolymer paste in artificial seawater

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Abstract. This paper presents the effect of chloride ion diffusion on the corrosion activity of kaolin geopolymer paste in artificial seawater. An aluminosilicate material that rich with aluminium and silicon such as kaolin is selected as a raw material in the geopolymerization of geopolymer. Kaolin then mixed with an alkaline activator that consist mixture of sodium hydroxide (NaOH) solution with sodium silicate (Na2SiO3) solution. Two types of samples are used in this study, which 7 days and 14 days sample. A few testing is conducted in order to test the chloride ion diffusion on the samples such as Rapid Chloride Permeability Test, Rapid Migration Test and Salinity Test. The result shows that sample for 7 days consist the higher penetration of chloride ion compare sample of 14 days. This is proven with the result of salinity. A longer curing time of the sample cause a lesser penetration of Cl− ion.

1 Introduction

Seawater that contains high amount of salt has greatly pretentious the strength, durability and life span of the building and cement for construction especially for offshore building [1, 2]. Corrosion in concrete, mainly occurs due to the chloride ion and carbon dioxide, besides that, the diffusion characteristic of chloride and other corrosion-inducing substances is depending on the porosity and pore of the concrete, indirectly it may influence the initiation and the rate of corrosion [1, 3]. Penetration of chloride ion depends on a single parameter that is the coefficient of diffusion. According to Wang et al. [4], the value of chloride ion diffusion was similar for geopolymer and OPC concrete. Diffusion of chloride occurs when there are differences of mobility of ions or in a simple way there is a different concentration gradient of ion in the pore solution. According to [1] the source chloride ion came from 2 ways that is from internal sources, that chloride exist as contaminant in raw material and another is from external sources such as seawater or de-icing salt.

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Generally, geopolymer has been used as an alternative material to conventional Portland cement and concrete composite [5]. Currently, many studies involve geopolymer grows rapidly and some of it has recorded a good performance of geopolymer that can be obtained by mixing of binder material such as kaolin and fly ash with alkaline activator [6].

2 Materials and Methodology

2.1 Materials and Sample Preparation

Geopolymer paste in this study was made from a mixture of kaolin, sodium hydroxide (NaOH) solution and sodium silicate (Na₂SiO₃) solution. Kaolin is a type of clay that can be found in the nature [7]. It is chemically a hydrous aluminium silicate characterized as very fine powder [8, 9]. The NaOH pellet was used in this research under the brand name of Merck Chemicals by the molar mass of 40.00 g/mol. Distilled water was used to dilute NaOH pellet to produce the NaOH solution. Na₂SiO₃ solution used in this study was obtained from South Pacific Chemicals Industries Sendirian Berhad (SPCI), Malaysia.

An alkaline activator was prepared 24 hrs prior to use. Then, the prepared alkaline activator was mixed with the kaolin. After that, the mixture was placed in molds. The sample in the mold was compacted 25 times by using a rod in three layers of equal weight. The sample remained in the mold until the sample was hardened after 24 hrs, the sample was taken out from the mold and cured at 80°C in the oven for 24 hrs. The sample was then tested after 7 and 14 days. Artificial seawater in this study was prepared by mixing the sodium chloride (NaCl) and distilled water according to ASTM D1141-98 (2013) [10].

2.2 Testing

A few testing is conducted in order to test the chloride ion diffusion on the samples such as Rapid Chloride Permeability Test, Rapid Migration Test and Salinity Test.

3 Results and Discussion

This section will contain all the results and discussion approximately from all the testing that has been conducted to determine the effect of chloride ion diffusion on the geopolymer paste in artificial seawater.

3.1 Rapid Chloride Permeability Test

After 6 hours of testing, the amount of charges passed through the sample was recorded by using a digital multimeter. Based on the results obtained, it shows that most of the samples at 7 days consist range of potential between -170 mV to -190 mV. While for samples at 14 days it consists range of potential between -150 mV to -170 mV. Then the result was compared with the value of ASTM C1202 and AASHTO T277-83 standard in order to determine the rate of chloride permeability of the concrete. It was found out that one joule of energy per coulombs of charge is equal to one volt of potential, in that case for -185.2 mV of potential is equal to -185.2 coulombs of charges. After conversion of the unit, it shows that both samples were categorized for the charge below 100 coulombs. Based on Table 1, if the chloride permeability for the charge below than 100 coulombs the rate of chloride permeability is negligible.
Table 1. Rate chloride of concrete.

| Chloride Permeability | Charge (Coulombs) | Type of Concrete                                                                 |
|-----------------------|-------------------|----------------------------------------------------------------------------------|
| High                  | >4000             | High water-to-cement ratio (>0.6) conventional Portland cement                   |
| Moderate              | 2000-4000         | Moderate water-to-cement ratio (0.4-0.5) conventional Portland cement concrete   |
| Low                   | 1000-2000         | Moderate water-to-cement ratio (<0.4) conventional Portland cement concrete      |
| Very Low              | 100-1000          | Latex modified concrete, internally sealed, concrete                              |
| Negligible            | <100              | Polymer impregnated concrete, polymer concrete                                    |

3.2 Rapid Migration Test

After 8 hours immersion, the sample was split in two, the sample than freshly sprayed using calorimetric indicator (AgNO₃ solution) in order to determine the chloride penetration depth. The calorimetric boundary between the region that contain chloride ion and without chloride ion is shown in Figure 1. The area that contains chloride ion will form a white precipitate that indicates the presences of chloride molecule in the sample while the area that does not contain chloride ion it will form a dark precipitate. This is also being supported by the researcher of Elfmarkova et al. [11], it states that the formation white precipitate in the presence of chloride ion is due to the chemical reaction of of Ag⁺ with Cl⁻ or OH⁻.

![Fig. 1. (a) Before and (b) after geopolymer paste surface being sprayed with AgNO₃ solution.](image)

It also states that the value of non-steady migration state coefficient increase with the increase of penetration depth or when the original colour of the concrete is darker. Based on
Table 2 states that the reading of the non-steady state migration coefficient for sample in 14 days is much lower compared to the sample in 7 days.

Table 2. Reading of non-steady state migration coefficient after 8 hours testing.

| Sample | No. of sample | Applied voltage, (V) | Time (hours) | Average temperature (°C) | Depth penetration, Xd (mm) | Non-steady state migration coefficient (m²/s) |
|--------|---------------|----------------------|--------------|--------------------------|---------------------------|--------------------------------------------|
| 7      | 1             | 30                   | 8            | 20.50                    | 31                        | 53.68 x 10⁻¹²                             |
|        | 2             | 30                   | 8            | 20.05                    | 22                        | 37.27 x 10⁻¹²                             |
|        | 3             | 30                   | 8            | 20.00                    | 23                        | 39.07 x 10⁻¹²                             |
| 14     | 1             | 30                   | 8            | 19.96                    | 13                        | 21.15 x 10⁻¹²                             |
|        | 2             | 30                   | 8            | 20.05                    | 17                        | 28.28 x 10⁻¹²                             |
|        | 3             | 30                   | 8            | 20.45                    | 15                        | 24.74 x 10⁻¹²                             |

3.3 Salinity Test

Through 6 hours of testing, the salinity of the distilled water was measured using a salinity meter every 1 hour and the resulted was shown in Figure 2 and Figure 3 for sample 7 and 14 days. Based on Figure 2, it shows how the salinity permeability of chloride ion from seawater into deionized water was slowly increased from 0.0 ppt to 1.0 ppt. For sample 1 and 2, it only required one hour to reach a transition state while for sample 3 it required two hours to reach a transition state. This indicates that for a kaolin geopolymer paste that samples 7 days required a minimum of two hours for the chloride ion to fully penetrate the sample and in touch or diffuse into the distilled water. It has been reported that the transition state only begins when there is a change in concentration of salinity [12]. In order for transition state alternate into steady state it requires a steady increase of salinity proportional with time [12]. Based on Figure 2, steady state for all the sample starts after 2 hours where the salinity starts to increase proportional to time.
Fig. 2. Salinity test result for samples 7 days.

For samples at 14 days, the salinity result was shown in Figure 3. During the first three hours, the chloride just starts to diffuse into the sample but not yet reach the deionized water this is known as non-steady state where there is no change in concentration of the distilled water [6]. All the sample cured in 14 days start to experience transition state after 3 hours exposed at artificial seawater and change to steady state in the next hour.

Fig. 3. Salinity test result for samples 14 days.
Conclusion

Detailed work has been done to achieve the objectives of this study.

i. Chloride permeability of geopolymer paste is negligible because the charges less than 100 Coulombs.

ii. Sample for 14 days shows a low migration of chloride due to the lower reading of non-steady state migration coefficient after 8 hours testing compare to sample 7 days.

iii. All the sample cured in 14 days start to experience transition state after 3 hours exposed at artificial seawater, while for 7 days sample required a minimum of 2 hours for the chloride ion to fully penetrate.

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References

1. Chindaprasirt, P., W. Chalee. Effect of Sodium Hydroxide Concentration on Chloride Penetration and Steel Corrosion of Fly Ash-Based Geopolymer Concrete under Marine Site. Construction and Building Materials, vol. 63, pp. 303–310 (2014).

2. Rozyanty, A.R., Mohammed, M.M., Musa, L., Shahnaz, S.B.S., Zuliahani, A. The weathering effect in natural environment on hybrid kenaf/glass fiber unsaturated polyester composite (2017) AIP Conference Proceedings, 1835, art. no. 020015.

3. Zainal, F.F., Aml, S.F.M., Hussin, K., Rahmat, A., Abdullah, M.M.A.B. Corrosion Studies of Fly Ash and Fly Ash-Slag Based Geopolymer (2017) IOP Conference Series: Materials Science and Engineering, 209 (1), art. no. 012026.

4. Wang, H, Dai, J., Sun, X. Chloride transport in concrete under sustainable flexural loading. Magazine of Concrete Research, 69(5), 245-254 (2017).

5. Salem, I.A.S., Rozyanty, A.R., Betar, B.O., Adam, T., Mohammed, M., Mohammed, A.M. Study of the effect of surface treatment of kenaf fiber on chemical structure and water absorption of kenaf filled unsaturated polyester composite (2017) Journal of Physics: Conference Series, 908 (1), art. no. 012001.

6. Hashim, M.F.A., Abdullah, M.M.A.B., Sandu, A.V., Puskas, A., Daud, Y.M., Zainal, F.F., Faris, M.A., Hasri, Hartati, Advanced glass reinforced epoxy filled fly ash based geopolymer filler: Preparation and characterization on piping materials (2019) IOP Conference Series: Materials Science and Engineering, 572 (1), art. no. 012037.

7. Zainal, F.F., Hussin, K., Rahmat, A., Abdullah, M.M.A.B., Shamsudin, S.R. A study on hardness behavior of geopolymer paste in different condition (2016), AIP Conference Proceedings, 1756, art. no. 040001.

8. Heah, C., Kamarudin, H., Bakri, A. M., Binhussain, M., Luqman, M., Nizar, I. K. Liew, Y. Effect of Curing Profile on Kaolin-based Geopolymers. Physics Procedia, 22, 305-311 (2011).

9. Mat Daud, Y., Fazlina Osman, A., Farhana Zainal, F., Firdaus Abu Hashim, M., Si, H.M., Si, H.S., Soo Li, N., Arzuria Adnan, S. Effect of Mixing Parameter on Epoxy-Organic Montmorillonite Composites: Flexural and Microscopy Analysis (2019) IOP Conference Series: Materials Science and Engineering, 551 (1), art. no. 012013.
10. ASTM D1141-98 (2013), Standard Practice for the Preparation of Substitute Ocean Water, American Society for Testing and Materials (2013).
11. Elfmarkova, V., Spiesz, P., Brouwers, H. Determination of the chloride diffusion coefficient in blended cement mortars. Cement and Concrete Research, 78, 190-199 (2015).
12. Muntingh, Y. Durability and diffusive behaviour evaluation of geopolymeric material Unpublished Master's Thesis, (2006).