The effect of alkali concentration on chloride penetration in geopolymer concrete

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Abstract. This paper presents the experimental study on the penetration of chloride ions in fly ash based-geopolymer concrete in the salt-water. To determine the corrosion possibility of reinforcement, lollipop-shape specimens with the size of 10x10x15 cm were prepared with the plain steel bar in the middle of concrete. The specimens were exposed to chloride ion penetration for 30-120 days. The mixtures were varied with alkali concentration of 8M-12M with the mass ratio of Na2SiO3 to NaOH was varied from 1.5 to 2.5. Specimens made with portland cement concrete was also prepared as the control. The best performance was showed by specimens made with 12M of NaOH. Due to ion exchange on the surface of geopolymer concrete, less chloride ion was found in geopolymer made with high alkali concentration. After 90 days, Portland cement concrete showed less performance while geopolymer concrete showed the strength increasing. High binding capacity due to soluble silicate content in geopolymer concrete was one of the reasons why geopolymer specimens are more resistant to chloride ion penetration.

1. Introduction

The application of green concrete technology recently tends to decrease as much as portland cement in the mixture. One of the proposed mixtures is a zero Portland cement so-called geopolymer. This environmental-friendly material is a synthetic of waste materials such as coal ash, rice husk ash and other materials rich in silica-alumina [1, 2]. They are defined as the precursor to form an inorganic silica-alumina [3]. In polymeric process, SiO4- and AlO4- are bound in a skeleton tetrahedral form [4]. In many research studies and application, class F fly ash is one of the most general materials to be used as geopolymer binder. As a waste of burning process from coal power plant, this material is favorable as cement replacement. Natrium hydroxide solution and natrium silicate are commonly used as the alkali activator to mix with fly ash. Phoo-Ngernkham [5] found that the effect of alkali concentration in the mixture influenced the geopolymer concrete strength. The higher the ratio of sodium hydroxide and sodium silicate the higher the strength of concrete. Geopolymer concrete is recognized to show better performance than conventional ones. Besides of its higher mechanical properties, it is recognized that...
geopolymer concrete indicated better durability. It exposes high resistance in fire, sulphate and chloride attack in aggressive environment as compared with Portland cement concrete [6]. Olivia dan Nikraz [7] also emphasized that geopolymer concrete showed more resistant to corrosion as compare to conventional concrete.

Sea water usually contains 2.5-3.5% salts. It can decrease the concrete strength and reduce its durability. The main salts in sea water are chlorides (55%) and sulphates (31%). Ions from salts induces cracks in concrete, dissolve the calcium bond in concrete binder and leave the concrete with its aggregates without cement. Penetration of chloride ions in concrete also causes the steel bars in concrete to corrode with a simple reaction such as $\text{Fe} + 2 \text{Cl}^- \rightarrow \text{Fe}^{2+} + 2\text{Cl}^- + 2e^- \ [8]$. The more electrons are released from the steel, corrosion process becomes progressive and more concrete cracks arise in concrete to cause another corrosion-cracks cycle. Diffusion of this released ions to concrete occurs from high to low concentration eg. from surface of concrete where concrete contact directly to chloride ions to inner part of concrete gradually to form a concentration gradient. Generally, concrete resists to corrosion if it is made with low water to cement ratio, treated with proper curing and low permeability so it has less pores [8]. High pH of concrete which is usually in the range of 12-13 provides protection from aggressive environment for the reinforcement bar with the passive layer. Porous concrete induces chloride ions from concrete surface into the steel-bar. This mechanism decreases the pH, damage of passive film and develop the bars to corrosion stage to lose bond between steel and concrete [9].

This paper presents the corrosion probability of reinforcement bar in geopolymer concrete caused by ion chloride penetration. Different alkali ratio and concentration are the variation to make binders of geopolymer concrete. Salt-water was used for soaking specimens for 90 days. Even though in a very short time, which was less than 100 days, the passive film could not be analyzed, the potential of corrosion was observed with half-cell potential test.

2. Materials

2.1. Fly ash

A class F fly ash [10] with a specific gravity of 2.5 g/cm³ was obtained from the power plant, in Gresik, Indonesia. The composition of fly ash is listed in table 1 and its XRD analysis is presented in figure 1. According to the test, the soluble silicate is 70% of total silicate content.

| SiO₂ | Al₂O₃ | Fe₂O₃ | TiO₂ | CaO | MgO | K₂O | Na₂O | SO₃ | Mn₂O₃ | LOI |
|------|-------|-------|------|-----|-----|-----|------|-----|-------|-----|
| 48.5 | 26.1  | 12.5  | 0.9  | 5.2 | 2.8 | 1.7 | 0.5  | 1.1 | 0.2   | 0.7 |

Table 1. Chemical Composition of Fly Ash (%) by XRF.

![Figure 1. XRD analysis of fly ash.](image-url)
2.2. Activators
Activators used in the mixture were natrium hydroxide (NaOH) and natrium silicate (Na₂SiO₃). NaOH solution was prepared by dissolving its solid form in distilled water. Concentration of NaOH were varied of 8M, 10M and 12M. Natrium silicate contained 19% of Na₂O, 36% of SiO₂, and 45% of H₂O. The mass ratio of Na₂SiO₃ to NaOH was also varied of 1.5, 2.0 and 2.5.

2.3. Aggregates
The densities of coarse aggregate and fine aggregate are 2.6 g/cm³ and 2.7 g/cm³ respectively. The coarse aggregate was collected from crushing river stones. The fine aggregate was from river sand.

2.4. Superplasticizer
Polycarbonic 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 maximum dosage of SP was 2% by fly ash weight.

2.5. Mix design
Material composition and the initial condition of specimens are listed in table 2. Atomic ratio of each binder varies depending on the alkali concentration as well as water to solid ratio.

Silica (Si) content in the mixture is obtained from soluble silica in fly ash and Na₂SiO₃. The aluminum (Al) content is obtained from fly ash only. The content of H₂O obtained from Na₂SiO₃, NaOH (liquid), and NaOH (solid). Therefore, the total solid obtained from Na₂SiO₃ (solid), NaOH (solid), and fly ash.

Table 2. Specimen compositions.

| Code | NaOH (M) | Alkali ratio | Materials (kg/m³) | Slump (mm) | Si | Al | Na₂O | SiO₂ | water solid | 28 day-Strength (MPa) |
|------|----------|--------------|-------------------|-----------|----|----|------|------|-------------|-----------------------|
| 8-1.5 | 8        | 1.5          | 87 131 406 1124   | 80        | 1.41 | 0.27 | 0.263 | 51.0 |
| 8-2.0 | 8        | 2.0          | 73 146 406 1124   | 75        | 1.44 | 0.26 | 0.253 | 52.5 |
| 8-2.5 | 8        | 2.5          | 62 155 406 1124   | 65        | 1.47 | 0.25 | 0.245 | 55.9 |
| 10-1.5 | 10      | 1.5          | 87 131 406 1124   | 75        | 1.41 | 0.29 | 0.253 | 54.5 |
| 10-2.0 | 10      | 2.0          | 73 146 406 1124   | 70        | 1.44 | 0.27 | 0.244 | 56.1 |
| 10-2.5 | 10      | 2.5          | 62 155 406 1124   | 65        | 1.47 | 0.26 | 0.238 | 56.9 |
| 12-1.5 | 12      | 1.5          | 87 131 406 1124   | 60        | 1.41 | 0.32 | 0.243 | 57.3 |
| 12-2.0 | 12      | 2.0          | 73 146 406 1124   | 40        | 1.44 | 0.29 | 0.236 | 60.5 |
| 12-2.5 | 12      | 2.5          | 62 155 406 1124   | 30        | 1.47 | 0.28 | 0.231 | 62.4 |

2.6. Salt-water
Concentration of salt-water of 3.5% was prepared with dissolving pure natrium chloride (NaCl) in solid form to tap water. NaCl of 35 grams was mix with one liter of tap water to simulate the chloride content in sea water. Salt-water was re-new every five days to keep the pH and salt content constant.

3. Methods
Figure 2 (a) shows a mold for lollypop-shape specimens so the steel-bar with a diameter of 16 mm can be fixed in the middle of concrete. The inner size of the mold was set to 100 mm in rectangular and 150 mm in length. The surface of specimens and exposed steel-bar was covered with sealant to prevent from chloride ion penetration during soaking in salt-water as shown in specimen in figure 2(b). The tip of steel-bar was covered with waterproof material that was easily removed for half-cell potential test. Figure 3 describes the specimen’s size (in centimeter) and the re-bar position.
Figure 2. (a) Mold setting up and (b) A lollypop specimen.

Figure 3. Lollypop specimens with 16 mm steel-bar in the center.

The corrosion activity is monitored by measuring the copper/copper sulphate (Cu/CuSO₄) half-cell potential according to ASTM C-876 [11]. The standard provides the interpretation of the HCP data for corrosion probability. The probability of corrosion of the rebars is less than 10% if the potential is greater than -200 mV. Potential values lower than -350 mV indicate a high probability (> 90%) that
corrosion is active. The HCP values between these limits indicate areas where the corrosion activity is uncertain. The setting up of HCP test is shown in figure 4.

After casting, all specimens were cured at a room temperature in the controlled chamber. After the mold was removed, all specimens were subjected to wet curing in tap water for 28 days. After this curing period, all specimens were kept dry in room temperature for two days. At the 30th day after casting, some specimens were immersed in salt-water for 90 days.

![Figure 4. Half-cell potential test for lollypop specimens.](image)

For each variable, three identical concrete cylinders of 10 cm in diameter and 20 cm in height were prepared for some tests, such as compressive strength [12], chloride content, pH, XRD analysis and porosity. Except top and bottom side, the surface of all cylinders was covered with a waterproof coating. Both top and bottom side were expose to salt-water to lead moisture and ion diffusion in one direction. Tests for chloride penetration depth and pH were targeted at some points from concrete surface specimen as illustrated in figure 5.

![Figure 5. (a) Cylindrical specimen and (b) Half part of a cylindrical specimen.](image)
4. Results and discussions

4.1. Compression strength test

Figure 6 shows the compression test results of cylindrical specimen. For all variations, the strength of concrete soaked in the salt-water tends to increase with increasing age of concrete.

The geopolimerization process still occurred to cause the concrete became dense during immersion period for 90 days in salt-water. Higher silicate content provided by natrium silicate in the mixture contributed to increase the concrete strength in every NaOH concentration [13]. This soluble silicate provided the certain ratio of Si/Al which is necessary to build the strength. A specific mol ratio of Si/Al from 1.3 to 1.8 was found as a recommended mix design in fly ash-based geopolymer binder [14]. For 90 days of curing period in salt-water, the chemical reaction of mixture to construct the concrete strength was more dominant than the effect of chemical reaction by NaCl to decrease the concrete strength.

However, the role of higher NaOH concentration is also very important to keep the soluble silicate released from binders to salt-water. Alkali made with 12M of NaOH assure the existing soluble silicate in the mixture preserve the continuous strength development. Specimens made with 8M and 10M of NaOH showed less 120 day-strength than those made with 12M NaOH. This indicated that less alkali concentration is not recommendable to provide good durability against NaCl. In our previous research [15], the strength of geopolymer concrete decreased slightly when it soaked in salt-water for more than 120 days, while the strength of conventional concrete started to decrease significantly at 100 days.

The effect of water to solid ratio was also found to have substantial contribution to the strength. During soaking period, denser concrete provided by less water to solid ratio in the mixture showed higher strength. Figure 7 shows the relation of water in the mixture with the concrete strength. This tendency is similar with the effect of water to cement ratio in the conventional concrete.

![Figure 6. Compressive Strength of specimens during immersion.](image-url)
4.2. Half Cell Potential (HCP) test

The measurement result from HCP test during immersion is listed in table 3 and plotted in figure 8. The initial potential was already more than -350 mV, that indicated the HCP test identified existing negative ion other than electrons. This is not an indication of a high probability corrosion has occurred before concrete was exposed to salt-water. In our previous study [16], where only NaOH solution of 8M and alkali ratio of 2.5 were used, -400 mV was the initial potential value for geopolymer concrete. In figure 8, the higher potential indicates more soluble silicate was involved in the HCP measurement. During immersion for 90 days, the potential values increased due to longer exposure time to chloride ions penetration. At the end of immersion period, it almost reached -700 mV. It is apparently caused by the exchange ions activity with ions in concrete and chloride ions penetration from salt-water. Even though no indication of corrosion was observed during the test, it is interesting to find that the effect of NaOH concentration has responsibility to decrease the potential difference as shown in table 3. Besides increasing the density of concrete, higher NaOH concentration plays a role to refrain the ion exchange between soluble silicate and chloride ion on concrete surface.

### Table 3. HCP measurement.

| Code  | Potential (mV) |  | Potential difference (from initial to final) |
|-------|----------------|----------------|---------------------------------------------|
|       | 30d (initial) | 60d | 90d | 120d (final) |                              |
| 8-1.5 | -401           | -491 | -580 | -665         | -264                           |
| 8-2.0 | -428           | -517 | -576 | -653         | -225                           |
| 8-2.5 | -430           | -516 | -589 | -651         | -221                           |
| 10-1.5| -430           | -510 | -595 | -684         | -254                           |
| 10-2.0| -420           | -498 | -565 | -648         | -228                           |
| 10-2.5| -474           | -559 | -629 | -696         | -222                           |
| 12-1.5| -410           | -493 | -564 | -622         | -212                           |
| 12-2.0| -455           | -538 | -599 | -665         | -210                           |
| 12-2.5| -442           | -514 | -575 | -644         | -202                           |
4.3. Porosity test
Porosity measurement was obtained as a total porosity (Pt) of each variation as shown in figure 9. In addition, a closed porosity is a part of total porosity that express the density of concrete as described in figure 10. The measurement of porosity test was conducted before concrete was soaked in salt-water (initial) and after the specimens were immersed for 30, 60 and 90 days.

Figure 9 shows that the total pore of concrete decrease as longer curing was applied. It is caused by the maturity process where the chemical reaction takes place to make concrete denser. This is related to the compression strength results. Longer curing caused concrete strength increased. Moreover, results shown in figure 10 point out that the denser concrete was also resulted the number of closed pores increased. This represents the size of pores reduced and changed to impermeable pores. Furthermore, as expected, higher alkali concentration plays a part of reducing pore size. Closed pores in specimens with 12M NaOH showed fewer pores but more uniform closed pores. High concentration of NaOH allowed the dissolution of more Si and Al from fly ash, improved the polycondensation and resulted in a decrease of geopolymer concrete porosity. This was also supported by higher Na$_2$SiO$_3$ in the mixture. At lower NaOH concentration, the presence of higher soluble silicate is required to decrease the concrete pores. The contribution of soluble silica is known to prevent interconnection between micropores due to the performance of geopolymorphic gel. This also corresponds to the conclusion that dissolution of silica to form geopolymorphic gel was more influenced by alkali concentration in room temperature [17].

In wet curing, natrium may leak out from concrete surface to the salt-water. This was demonstrated by the pH of salt-water increasing during immersion period. It causes the geopolymer concrete become more porous on the surface and the pore is easily penetrated by chloride ions.

![Figure 8. HCP Test results.](image)

![Figure 9. Total porosity of concrete during immersion.](image)
4.4. Chloride penetration

Figure 11 presents the total chloride content of the specimens at a depth of 0 cm, 4 cm, and 8 cm from concrete surface. The period of salt-water exposure at 90 days, 60 days and 30 days are presented by points in red, blue and black in figure 10. The chloride content at a depth of 8 cm was quite high, which was more than 0.1%. Free chloride was not found in all specimens. The total chloride in this experiment was equal to bound ion in the concrete matrix. According to Indonesian standard for reinforcement concrete structures, the maximum free chloride by cement weight is 0.15% for concrete in aggressive environment. To protect the steel bar, the maximum water to cement ratio is 0.4.

Results from this experiment showed that chloride content in the geopolymer concrete is relatively high. The maximum chloride content on the surface of all specimens were maximum at 0.23. However, the binding capacity of geopolymer concrete was apparently better than conventional concrete. The cation from Na⁺ in the mixture is considered as a shield of Cl⁻ penetration [18].

Reduction of chloride content at a depth of 4 cm and 8 cm was observed in all specimens. Specimens with higher soluble silicate demonstrated better performance to resist chloride penetration. This is an important information since it was found that specimens with 8M NaOH containing alkali ratio of 2.5 exhibited chloride resistance more than specimens with lower alkali ratio. On the other side, higher chloride in specimens with 12M NaOH was found at 8 cm from concrete surface. The application of higher NaOH concentration in the mixture contributed to smaller the pore size in concrete, which is a potential to increase water absorption. A similar result was observed by Olivia [7].
4.5. XRD analysis

Figure 11. Total chloride in concrete.

Figure 12. XRD analysis of concrete.

Figure 12 presents the XRD analysis for geopolymer concrete made with 8M NaOH. As a comparison, concrete with similar age cured in free chloride condition is presented. Chloride was observed to form minerals bound with unreacted compounds such as calcium chloride and magnesium chloride. This proves that the binding capacity of geopolymer to bind to the ion chloride in concrete causes the chloride penetration to not produce free ions in geopolymer concrete.
5. Conclusions
Based on the results and discussions for the high calcium fly ash-based geopolymer concrete, the following conclusions are made.

- During 90 days exposure in salt-water, fly ash-based geopolymer concrete made with 12 M NaOH gain higher strength faster than that with lower concentration. This is because concrete has less pores as curing was prolonged continuously in wet condition.
- The effect of higher alkali ratio represented by soluble Na$_2$SiO$_3$ in the mixture prevented concrete from possibility to corrosion. The participation of soluble silica is believed to decrease pore size because of the formation of better geopolymeric gel.
- Evidently, higher NaOH concentration in fly ash-based geopolymer concrete resulted in better chloride binding capacity. It contributed also to the exchange chloride ion on the surface of concrete.

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