Effect of Chloride Ions on Concrete with Geopolymer Coatings in Coastal Area

S F Nastiti1* and J J Ekaputri1*
1Departement of Civil Engineering, Institut Teknologi Sepuluh Nopember (ITS), Surabaya 60111, Indonesia
*
Corresponding author’s e-mail: syahfien@gmail.com, januarti@ce.its.ac.id

Abstract. This paper presents the effects of chloride ions on OPC (Ordinary Portland Cement) concrete coated with fly ash-based geopolymer mortar. The coating was applied to protect concrete in coastal areas. The mortar was a mixture of fly ash and alkali activator with a mass ratio of 65:35. The alkali activator was a mixture of Na$_2$SiO$_3$ and NaOH 12M with a mass ratio of 2.5:1. The coating thickness varied at 2.5 cm, 4 cm, and 6 cm. All specimens were exposed to a marine area with seawater curing for 90 days. The mechanical properties of the specimen were determined by compressive strength. Chloride penetration was assessed for durability. A series of tests were carried out after 0, 30, 60, and 90 days of immersion. Compressive strength after a 90-day immersion increased by 34.16%, 39.81% and 31.38% for thickness 2.5 cm, 4 cm, and 6 cm respectively. Compressive strength with a thickness of 4 cm reached 52 MPa, which was the highest strength. The binding capacity of the chloride in geopolymer coatings was more than 80% and could reduce the free chloride content in concrete. Geopolymer mortar coating on OPC concrete showed good results in compressive strength and resistance to chloride attack from sea water. The recommended coating thickness for optimum results suitable for application is 4 cm.

1. Introduction
Concrete durability performance is important during the service life of concrete. Usually, concrete is a durable material that will protect steel reinforcement from corrosion, depending on how good its mixing was [1]. Chloride penetration is some key parameter of reinforced concrete structures in seawater environments. Passive layers, de-passivation of steel reinforcement, can be destroyed by chloride ions ingress, which might cause initiation of corrosion [2, 3]. Several studies [4, 5, 6] state that the penetration of chloride in concrete depends on the composition of the concrete mixture and where the specimens are exposed. In a tidal zone environment, the concentration of aggressive chemical compounds is higher than in an atmospheric zone environment. Chloride penetration content in a tidal zone is much higher than in an atmospheric zone, so durability in these two types of zones could be very different.

Concrete coating methods can protect concrete to extend the service life of concrete structures exposed to a marine environment, especially in the tidal zone by inhibiting corrosive ion intrusion [7]. Geopolymers are mineral polymers resulting from geochemical or geosynthetic processes introduced by Joseph Davidovits. Geopolymers are a potential material for infrastructure protection and retrofitting. Several studies have proved that geopolymer durability showed better performance and it is suitable to be applied as a coating for protection against the chemical attack of chloride [1, 4, 8, 9, 10]. Geopolymers must contain Si and Al (pozzolan) to be involved in the geopolymerization process.
A type of pozzolan which is often used as a binder is fly ash [8]. Some factors that affect the performance of geopolymers are mixture composition, alkaline activator composition, physical and chemical characteristics of fly ash [11, 12]. The ratio of Si/Al contained in fly ash affects the compressive strength of geopolymers. In addition, the fineness of fly ash particles contributes to compressive strength. The finer fly ash particles, the higher the compressive strength of the geopolymer [13].

In addition to the material composition, the thickness of the concrete cover is a factor that affects the durability of reinforced concrete. The concrete cover protects steel reinforcement from direct contact with physical and chemical attacks that have the potential to reduce the performance of the reinforced concrete [14]. Based on previous studies, this research aims to determine the optimum applied thickness of geopolymer coating on reinforced concrete. The results of this research results would be a useful information to utilize waste material to protect the conventional concrete against chloride ion ingress in coastal areas.

2. Materials and Methods

2.1. Materials
Coating was made with mortar using class F fly ash as the base material and sand with a mass ratio of 72:28. Fly ash was obtained from the Suralaya power plant and the chemical composition is shown in Table 1.

| Material | Free Chloride (%) | Bound Chloride (%) | Total Chloride (%) | pH |
|----------|-------------------|--------------------|--------------------|----|
| Fly Ash  | 1.05              | 0.09               | 1.15               | 9.6|
| Seawater | N/A               | N/A                | 1.64               | N/A|

The initial concentrations of free chloride and bound chloride are shown in Table 2. The mass ratio of fly ash with alkali activator was 65:35. The alkali activator was a mixture of Na$_2$SiO$_3$ and NaOH 12M with a mass ratio of 2.5:1. Type BE-52 Na$_2$SiO$_3$ was obtained from PT, Kasmaji Inti Utama and the chemical composition were Na$_2$O 18.5%, SiO$_2$ 36.4%, and H$_2$O 45.1%.

2.2. Methods
All cylinder specimens were prepared with a diameter of 10 cm and a height of 20 cm. The core of the OPC concrete was made with mix design with a compressive strength design of 35 MPa. After 30 days, geopolymer mortar was applied on top of OPC concrete cylinder with 3 variations of thickness as shown in Table 3.
Table 3. Three types of concrete specimen

| Type    | Mortar type | Thickness (mm) | Coding |
|---------|-------------|----------------|--------|
| Type 1  | Geopolymer  | 25             | G-2.5  |
| Type 2  | Geopolymer  | 40             | G-4    |
| Type 3  | Geopolymer  | 60             | G-6    |

The coated concrete was moist cured for 42 days prior to being immersed into the seawater. Some parts of the cylinder surface were coated with epoxy resin to regulate chloride ions ingress in uncoated areas (Figure 1 and Figure 2). All specimens were exposed to tidal area, located ±30 m from the shore of Kenjeran Beach.

Figure 1. Modeling of chloride ions ingress

Figure 2. The specimen being coated with epoxy resin

Figure 3. Three types of cylindrical specimens with a given depth determined
Specimens were tested after 0, 30, 60, and 90 days of immersion in seawater curing. Compressive strength tests according to ASTM C 39 [15] to determine mechanical properties. Chloride penetration was assessed for durability. Test samples were taken every 20 mm of depth as described in Figure 3. Free chloride and bound chloride content were determined from the resulted specimens.

3. Results and Discussion

3.1. Compressive Strength

Compressive strength test data for 0, 30, 60, and 90 days immersion are shown in Table 4. The results indicated that the thickness of coating improved the compressive strength of concrete in seawater. G-4 had higher compressive strength than the other types at 90 days, up to 52.01 MPa. However, the compressive strength of G-2.5 and G-6 were lower from that of G-4, respectively up to 48.09 and 50.99 MPa.

The compressive strength of the concrete increased until 90 days of immersion. According to the results of research conducted by Bayuaji, et al. [16], highly compressive strength of geopolymer in seawater curing was significantly influenced by the ratio of alkaline activator and fly ash. The compressive strength of geopolymer in seawater-curing reached more than 35 MPa. In geopolymerization process, alumino-silicate oxide reacted to alkali polysilicate and produced Si-O-Al polymeric bond. Aluminosilicate polymeric bonds were more stable when submerged in seawater [17].

| Type     | 0 days | 30 days | 60 days | 90 days |
|----------|--------|---------|---------|---------|
| G – 6    | 38.81  | 33.25   | 44.75   | 50.99   |
| G – 4    | 37.20  | 33.32   | 41.41   | 52.01   |
| G – 2.5  | 35.85  | 33.83   | 37.71   | 48.09   |

Figure 4. Compressive strength of concrete immersed in seawater curing
In addition, the compressive strength of all specimens decreased to 33 MPa at 30 days, as shown in Figure 4. In accordance with the results of the research by Albitar, et al. [1], the sulphate attack on OPC concrete reduced the compressive strength from the age of 14 days of immersion. While the compressive strength of geopolymer increased to 60 days. Halim and Ekaputri [18] reported that cations around geopolymers did not interfere with the mechanism and forming of geopolymers. Alhannal, et al. [19] explained that sulphate in seawater would react with Ca(OH)$_2$ to form mineral ettringite. Also, gypsum would react with C$_3$A to form ettringite. The presence of ettringite would cause deep cracks and concrete strength to change.

The collapse mechanism of the specimens is shown in Figure 5 after compressive strength testing. According to ASTM C 39 [15], most of the mechanism patterns are columnar, cone and split, or cone and shear patterns (Figure 6). This shows that the application of coating material on cylindrical concrete satisfied the requirements for carrying out compressive strength testing.

### 3.2. Chloride penetration

Chloride content measurement was done according to the depth described in the model. Free chloride contents of the 3 types of specimens after 90 days are shown in Figure 7. Free chloride content for G-2.5, G-4, and G-6 on the concrete frontage’s surface were 0.12%, 0.13%, and 0.16%, respectively.

![Figure 5. Specimens after testing (immersed in seawater curing)](image)

![Figure 6. Collapse mechanism of the three types of specimens after compressive strength testing (specimens immersed for 90 days)](image)

![Figure 7. Free Chloride at each depth (immersed at 90 days)](image)
For G-2.5 and G-4, the free chloride content decreased from 0.22% to 0.12% (G-2.5) and 0.20% to 0.13% (G-4). The percentage reduction in free chloride content in G-2.5 and G-4 was 45.45% and 35%. Whereas in G-6, free chloride content increased from 0.14% to 0.16%, with the increase percentage of 12.5%. Percentage of free chloride content in G-2.5 and G-4 (frontage's surface) satisfied the requirements for reinforced concrete, which is below 0.15% according to SNI 03-2854-1992 [20].

Figure 7 shows that a layer of concrete with geopolymer mortar could reduce free chloride content ingressed to the concrete. High chloride binding capacity caused a decrease in free chloride content in the concrete. Chloride binding capacity of the three variables are shown in Figure 8 to Figure 10. Based on the pictures, the chloride binding capacity of the concrete front surface were 92.13%, 93.23%, and 86.53% (at a depth of 2.5, 4, and 6 cm). The chloride binding capacity that occurred in 2 cm reached 86.30% after 90 days of immersion, while at a depth of 4 cm it reached 87.61%, and at a depth of 6 cm it was 88.95%. The chloride binding capacity in the geopolymer layer was around 80-88%.

![Figure 8. Chloride Binding Capacity of G-2.5](image-url)
Gunasekara, et al. [21] states that the higher chloride binding capacity occurs in concrete, because of chemical composition and formation of Friedel’s salt (3CaO·Al₂O₃·CaCl₂·10H₂O). Chloride ions are bound to the hydration products of cement, C-S-H and C-A-H gels. However, chloride ions in geopolymer are bound with alumina and calcium oxide to form Friedel’s salt, reducing the chloride ingress to concrete. According to a research by Abd El Fattah, et al. [6], the chloride binding capacity in geopolymers reduces the concentration of free chloride. The lower free chloride content could reduce potential of free chloride to be involved in breaking the passive layer of reinforcement.

4. Conclusion
This study concludes that coating concrete with geopolymer mortar increases the compressive strength in seawater environment. In addition, thickness contributes to the increase of compressive strength of
concrete. High binding capacity of coating material reduced the free chloride content. Free chloride content in concrete at a depth of 2.5–4 cm was found to be less than 0.15%, which is qualified for the limit of chloride content in reinforced concrete. It can be concluded that coating with geopolymer mortar showed good performance on compressive strength. It is proven that the coating can be attached to sound concrete perfectly. The coating bound free chloride ions to ingress into sound concrete. Based on the result of the research, the recommended optimum coating thickness for application is 4 cm.

References
[1] Albitar M, Mohamed Ali M S, Visintin P, and Drechsler M 2017 J. Constr. Build. Mater. 136 pp 374–385
[2] Hájková K, Šmilauer V, Jendele L, and Červenka J 2018 J. Eng. Struct. 174 pp 768–777
[3] Verma S K, Bhadouria S S, and Akhtar S 2013 J. Front. Struct. Civ. Eng 7 379–390
[4] Costa A and Appleton J 1999 J. Materials and Structures 32 pp 252–259
[5] Otieno M, Beushausen H, and Alexander M 2016 J. Cem. Concr. Res. 79 pp 373–385
[6] Abd El Fattah A, Al-Duais I, Riding K, and Thomas M 2018 J. Constr. Build. Mater. 165 pp 663–674
[7] Zhang Z, Yao X, and Wang H, 2012 J. Appl. Clay Sci. 67–68 pp 57–60
[8] Zhang Z, Yao X, and Wang H, 2010 J. Appl. Clay Sci. 49 pp 1–6
[9] Aguirre-Guerrero A M, Robayo-Salazar R A, and de Gutiérrez R M 2017 J. Appl. Clay Sci. 135 pp 437–446
[10] Tittarelli F, Mobili A, Giosuè C, Belli A, and Bellezze T 2018 J. Corros. Sci. 134 pp 64–77
[11] Antoni, Wijaya S W, and Hardjito D 2016 J. Mater. Sci. Forum 841 pp 98–103
[12] Nurwidayati R, Ulum M B, Ekaputri J J, Triwulan, and Suprobo P 2016 J. Mater. Sci. Forum, 841 pp 118–125
[13] Wijaya A L and Ekaputri J J 2017 MATEC Web Conf. 97 01010
[14] Ali M S, Ji C, and Mirza M S 2015 J. Constr. Build. Mater. 93 pp 317–325
[15] ASTM Committee 2001 Annual Book of ASTM Standard (West Conshohocken: ASTM International) 04 pp 1–5
[16] Bayuaji R, Darmawan M S, Wibowo B, Husin N A, Subeki S, and Ekaputri J J 2015 J. Appl. Mech. Mater. 754–755 pp 400–405
[17] Zhang Z, Yao X, and Zhu H, 2010 J. Appl. Clay Sci. 49 pp 7–12
[18] Halim L N, Ekaputri J J, and Triwulan 2017 MATEC Web Conf. 97 01002
[19] Alnahhal M F, Alengaram U J, Jumaat M Z, Alsubari B, Alqedra M A, and Mo K H 2018 J. Constr. Build. Mater. 163 pp 482–495
[20] Badan Standarisasi Nasional 1992 Spesifikasi kadar ion klorida dalam beton (Bandung: Standar Nasional) pp 1-6.
[21] Gunasekara C, Law D, Bhuiyan S, Setunge S, and Ward L 2019 J. Constr. Build. Mater. 200 pp 502–513