The Effect of Sodium Silicate to NaOH Ratio on Strength Development of Fly Ash Geopolymer Mortar in Marine Environment

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Abstract. This paper presents the effect of sodium silicate to NaOH ratio on the strength performance of fly ash geopolymer mortar subjected to continuous immersion in a simulated marine environment during 1-year observation. The geopolymer mortar specimens were prepared using class C fly ash activated with sodium silicate and NaOH 15 Molar combination. The sodium silicate to NaOH ratio varied from 1.4 to 2.7 to keep the water-to-solid ratio and Na2O content at 0.37 and 10, respectively. The strength properties were measured based on compressive strength test, weight, and porosity changes. The compressive strength was investigated at 90, 180, and 360 days after immersion. The results showed that the sodium silicate to NaOH ratio significantly affected the long-term performance of geopolymers in simulated marine environments. A ratio between 1.6 to 2.3 provides better durability by reducing the deterioration rate, i.e., strength, weight, and porosity, of geopolymer specimens in simulated marine environments. However, increasing the ratio by more than 2.30 tends to decrease the performance of the geopolymer. It can be concluded that geopolymer can be used as an alternative construction material in marine environments in a specific sodium silicate to NaOH ratio.

1 Introduction

As an archipelagic country, Indonesia's marine area reaches more than 70% of Indonesia's total area [1]. This has an impact on some of the construction work that will be in contact with the marine environment. The marine environment itself has a negative impact on the concrete material [2, 3]. It is necessary to develop a material that has better resistance to marine environment exposure conditions. One alternative is the use of fly ash-based geopolymer which has better resistance than concrete in marine environments [4]. Apart from that, the use of geopolymer will reduce global warming as a result of the cement production process as the main material for traditional concrete [5].

Under conditions of exposure to the marine environment, concrete experiences various chemical reactions involving sulfate and chloride ions where several reaction mechanisms

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that occur can result in damage to the concrete, in particular the formation of ettringite, as the result of the reactions with CH and unreacted C3A components, which causes loss of concrete constituents [6]. This condition causes loss of concrete constituents and brings concrete deterioration such as damage to the concrete cover in the form of mortar and the formation of salt crystallization [7-9]. Previous research shows that the use of fly ash-based geopolymer has better resistance in marine environments [4]. This is because the Si-O-Al geopolymer matrix formation is polymeric compared to the C-S-H matrix in normal concrete. The geopolymer matrix itself is greatly influenced by the main component that makes up the geopolymer, namely fly ash that reacted with an alkaline activator, a combination of sodium silicate and sodium hydroxide (NaOH) [10].

This research reports the effect of the sodium silicate to sodium hydroxide (NaOH) ratio on the strength development of fly ash geopolymer mortar in a 3 wt% NaCl simulated marine environment. High ferrite class C fly ash was used as the source material of the geopolymer mortar specimen. The variation of sodium silicate to NaOH ratio ranging from 1.41 to 2.70 was applied to investigate the role of sodium silicate to NaOH ratio of geopolymer specimens in simulated marine environments. The strength developments were investigated by compressive strength, oven dry weight, and porosity throughout 1-year observation. All specimens were tested at 90, 180, and 360 days after being immersed in a simulated marine environment.

2 Research Methods

2.1 Materials

The geopolymer material was fly ash from a coal power plant in Indonesia. It had high calcium (Ca) and ferrite (Fe) content. It is classified as class C fly ash with a total SiO2, Al2O3, and Fe2O3 content of 67.94% and Ca content of 22.61% conforming to ASTM C618 standard [11]. However, it has a low aluminate (Si) and silicate (Si) of 12.97% and 4.73%, respectively. The X-Ray Fluorescence (XRF) test was used to obtain fly ash's chemical compositions as shown in Table 1.

Table 1. The main composition of class C fly ash (%).

Materials	SiO_2	Al_2O_3	Fe_2O_3	CaO
Fly ash	12.97	4.73	50.24	22.61

The alkali activator solution was mixed with 15 Molar sodium hydroxide (NaOH) and sodium silicate. The 15 Molar NaOH solution was prepared by dissolving a 600-grams NaOH pellet in 1 liter of water. The sodium silicate was supplied by a local chemical supplier with Na_2O and SiO_2 contents of 9.25% and 30.52%, respectively. The fine aggregate was provided by a local supplier. It has a specific gravity and fineness modulus (FM) of 2.52 kg/m^3 and 2.05, respectively.

2.2 Mix Design

Mix design of control and geopolymer mortars (GPM) specimens are listed in Table 2. The mix control specimen was Ordinary Portland Cement (OPC) conforming to ASTM C109 standard [12]. The design strength of OPC was 20 MPa at 28 days. The mix design of the geopolymer specimen (GPM) was determined by 100% replacing Portland Cement with fly ash as the primary material. The water to binder ratio of GPM varied from 0.60-0.80 based on trial to maintain the workability.

Table 2. The mix design ratio of fly ash geopolymer mortar (GPM).

Mixture	Portland Cement	Fly ash	Fine aggregate	Sodium silicate	NaOH 15 M	Water	Sodium silicate to NaOH (SS/SH) ratio
OPC	1	-	2.75	-	-	0.485	-
GPM-1	-	1	2.75	0.329	0.233	0.107	1.41
GPM-2	-	1	2.75	0.369	0.220	0.091	1.68
GPM-3	-	1	2.75	0.410	0.207	0.080	1.98
GPM-4	-	1	2.75	0.452	0.195	0.070	2.32
GPM-5	-	1	2.75	0.492	0.182	0.057	2.70

The geopolymer mortars were developed by activating fly ash with sodium silicate and NaOH 15 M as activator solution. It has a water-to-solid ratio of 0.37. The Na2O dosage of the geopolymer specimen was kept at 10. The sodium silicate to NaOH 15 M (SS/SH) ratio varied from 1.41 to 2.70 for GPM-1 to GPM-5, respectively, as shown in Table 2. All specimens have a cementitious material to-fine aggregate ratio of 1:2.75 by ASTM C109 [12].

2.3 Specimen Preparation and Testing

All specimens were made using a standard 50 mm x 50 mm x 50 mm steel mold by ASTM C109 standards for hydraulic cement mortar [12]. The control specimen (OPC) was cured at a standard curing regime. It was immersed in water for 28 days. The heat curing regime at 100OC for 24 hours was applied for all geopolymer specimens due to the geopolymer matrix requires a heated environment to achieve its structural integrity [13-15]. After curing treatment for each type of specimen, both control and geopolymer mortar specimens were placed at room temperature prior to testing. The simulated marine environment was prepared by dissolving 3 wt% sodium chloride (NaCl) in water. It was replaced every two weeks to maintain the NaCl content. All specimens were immersed in a NaCl-simulated marine environment after 28 days of age.

The strength development of all specimens was carried out by the compressive strength test conforming to ASTM C109 standard [12]. The oven dry weight and porosity tests were performed to support the result of the compressive strength test and to identify the physical properties development of all specimens throughout 360 days or 1-year observation. All specimens were tested at the age of 7, 14, and 28 days before being immersed in a simulated marine environment. Further tests were done at the age of 90, 180, and 360 days after being immersion.

3 Result And Discussions

3.1 Strength Development

The strength developments of all specimens are shown in Table 3 and Figure 1. All specimens demonstrated significant strength development up to 28 days prior to immersion in a simulated marine environment. All GPM specimens exhibited a better strength performance than the control OPC specimen. The highest compressive strength was achieved by GPM-3 (SS/SH ratio of 1.98) and GPM-4 (SS/SH ratio of 2.32) with the strength of 54.4 MPa and 52.3 MPa, respectively, at 28 days. This shows that the ratio of sodium silicate to NaOH has a significant role in the strength development of geopolymer specimens.

Table 3. Compressive strength prior to and after immersion in simulated marine environment (MPa).

Mixture	Prior immersion (days)			After immersion (days)		
	7	14	28	90	180	360
OPC	16.8 ± 2.2	21.6 ± 1.8	22.5 ± 3.4	13.2 ± 2.1	N/A	N/A
GPM-1	31.2 ± 3.7	41.2 ± 2.3	42.9 ± 2.8	37.4 ± 2.5	37.5 ± 3.2	33.8 ± 3.7
GPM-2	46.1 ± 3.1	48.8 ± 2.9	50.4 ± 4.1	47.4 ± 3.3	44.1 ± 4.3	37.1 ± 3.5
GPM-3	50.2 ± 2.2	54.0 ± 3.4	54.4 ± 3.6	52.9 ± 3.8	51.2 ± 4.6	48.5 ± 4.2
GPM-4	41.9 ± 3.4	50.4 ± 3.8	52.3 ± 3.2	49.4 ± 4.1	42.9 ± 3.7	41.6 ± 3.5
GPM-5	39.6 ± 2.5	46.4 ± 3.3	49.8 ± 2.9	43.9 ± 3.5	40.8 ± 3.3	36.3 ± 3.8

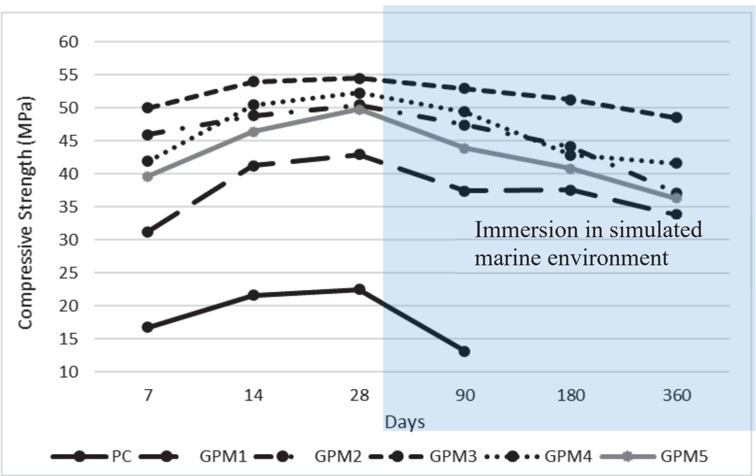

Fig. 1. Compressive strength prior to and after immersion in the simulated marine environment (MPa).

The immersion process in simulated marine environments was carried out after all specimens reached 28 days. The long-term immersion in a 3% NaCl simulated marine environment was performed for 1-year observation. Figure 1 shows that all specimens demonstrated a significant decrease in strength during 1-year immersion in simulated marine environments. The highest deterioration was shown by OPC control mortar specimens. It exhibited a 41.3% strength decrease from 22.5 MPa (28 days) to 13.2 MPa (90 days immersion). and disintegrated at 90 days of age which was unable to identify further. This research is in accordance with previous research which stated that concrete is vulnerable to chloride attack [9, 16].

On the contrary, Figure 1 indicates that geopolymer specimens are more durable than normal concrete. All geopolymer specimens demonstrated a lower rate of strength reduction during the simulated marine environment. The strength reduction rate of all geopolymer specimens ranged from 10%-30% with the lowest reduction rate achieved by GPM-3 (SS/SH ratio of 1.98) at 10.9%. While GPM-5 (SS/SH ratio of 2.70) exhibited the highest strength reduction rate at 27.1% from 49.8 MPa (28 days) to 36.3 MPa (360 days) during 1-year observation. Increasing the ratio of sodium silicate to NaOH by more than 2.00 tends to decrease the durability of geopolymer specimens in the simulated marine environment.

3.2 Weight and Porosity Development

The results of oven-dry weight developments of all specimens are demonstrated in Table 4 and Figure 2. All specimens showed no change in oven-dry weight up to 28 days of age prior to immersion. The oven-dry weight of all mortar specimens ranges between 298-313 grams.

Table 4. Oven dry weight prior to and after immersion in the simulated marine environment (gram).

Mixture	Prior immersion (days)			After immersion (days)		
	7	14	28	90	180	360
OPC	297 ± 2.8	296 ± 2.2	298 ± 2.4	258 ± 2.6	N/A	N/A
GPM-1	302 ± 3.1	301 ± 2.9	302 ± 2.6	298 ± 2.8	297 ± 2.7	283 ± 2.7
GPM-2	314 ± 2.9	313 ± 3.2	313 ± 3.0	311 ± 3.3	310 ± 3.1	309 ± 3.3
GPM-3	304 ± 2.7	303 ± 3.1	305 ± 2.8	304 ± 3.0	303 ± 2.5	301 ± 3.2
GPM-4	303 ± 2.4	302 ± 3.4	305 ± 2.7	303 ± 3.1	302 ± 2.9	300 ± 3.1
GPM-5	313 ± 2.6	312 ± 2.8	313 ± 3.2	307 ± 3.4	298 ± 3.1	293 ± 3.0

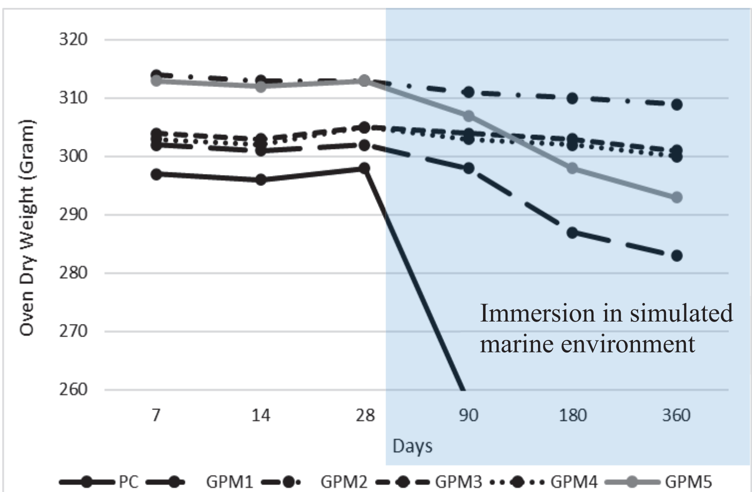

Fig. 2. Oven dry weight prior to and after immersion in a simulated marine environment (gram).

Similar to the previous discussion, the OPC control specimen experienced disintegration at the age of 90 days. It demonstrated a high rate of oven-weight decrease ratio of 13.4% from 28 to 90 days of immersion and disintegrate at 90 days of age. On the other hand, all geopolymer specimens performed better durability in simulated marine environments. GPM-2 (SS/SH ratio of 1.68), GPM-3 (SS/SH ratio of 1.98), and GPM-4 (SS/SH ratio of 2.32) demonstrated a slightly decreased ratio of oven-dry weight under the simulated marine environment with the decrease ratio of 1.3%, 1.3%, and 1.6%, respectively, during 1-year observation. However, a low sodium silicate to NaOH ratio, as well as a sodium silicate to NaOH ratio of more than 2.32 significantly affect the durability of geopolymer specimens as shown in GPM-1 (SS/SH ratio of 1.41) and GPM-5 (SS/SH ratio of 2.70) with the oven-dry weight decrease ratio of 6.3% and 6.4%, respectively. This finding is consistent with the previous finding on concrete deterioration such as damage to the concrete cover due to chloride attack on the cement matrix [9]. It also corroborated the previous finding on the strength reduction in simulated marine environment immersion.

In addition, the finding on the porosity development of geopolymer specimens as shown in Table 5 shows that despite the strength and oven-dry development being reduced, the porosity of geopolymer specimens was slightly consistent along with the duration of simulated marine environments immersion. The porosity ranged between 3.7% - 4.4% prior to immersion, and still in the range of 3.1% - 3.7% after the immersion in simulated marine environments.

Table 5. Porosity prior to and after immersion in simulated marine environment (%)

Mixture	Prior immersion (days)			After immersion (days)		
	7	14	28	90	180	360
OPC	11.2 ± 1.2	10.1 ± 1.1	9.8 ± 0.9	N/A	N/A	N/A
GPM-1	4.0 ± 0.4	3.9 ± 0.4	3.7 ± 0.5	3.6 ± 0.5	3.6 ± 0.4	3.5 ± 0.4
GPM-2	3.9 ± 0.5	3.8 ± 0.4	3.5 ± 0.4	3.5 ± 0.4	3.4 ± 0.4	3.2 ± 0.3
GPM-3	3.6 ± 0.3	3.5 ± 0.3	3.4 ± 0.4	3.2 ± 0.3	3.1 ± 0.3	3.1 ± 0.3
GPM-4	4.2 ± 0.3	4.2 ± 0.4	4.1 ± 0.3	4.0 ± 0.4	3.7 ± 0.4	3.4 ± 0.4
GPM-5	4.6 ± 0.4	4.5 ± 0.5	4.4 ± 0.4	3.8 ± 0.4	3.8 ± 0.5	3.7 ± 0.4

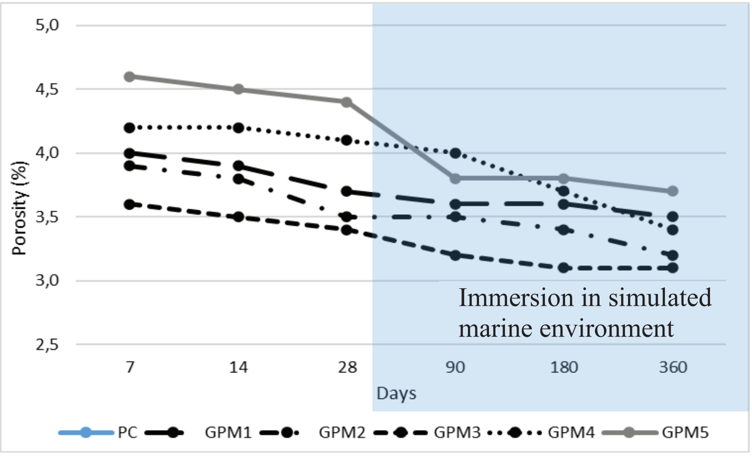

Fig 3. Porosity development prior to and after immersion in simulated marine environment (%).

The porosity development of geopolymer specimens was improved during 1-year observation as shown in Figure 3. This indicated that the chloride attack only damaged the surface of the geopolymer mortar specimens. This is possibly caused by the better permeability of geopolymer compared to cement-based concrete. In addition, this also showed that the geopolymer matrix has better resistance compared to the normal concrete matrix.

4 Conclusions

This research works on the effect of the sodium silicate to NaOH ratio on the strength development of fly ash geopolymer mortar in a simulated marine environment. It can be concluded that:

- The long-term performance of fly ash geopolymer in simulated marine environments was significantly affected by the sodium silicate to NaOH ratio.
- A ratio of sodium silicate to NaOH between 1.6 to 2.3 provides better durability by reducing the deterioration rate as shown in the strength, weight, and porosity performance, of geopolymer specimens in simulated marine environments.

- Increasing the ratio of sodium silicate to NaOH by more than 2.30 tends to decrease the performance of the fly ash geopolymer in simulated marine environments.
- Fly ash geopolymer can be used as an alternative construction material in marine environments in a specific sodium silicate to NaOH ratio.

The authors would like to thank Universitas Negeri Surabaya for the support and research funding.

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