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MICROSTRUCTURE ANALYSIS OF DIFFERENT NaOH MOLARITY TOWARDS FLY ASH GEOPOLYMER FOR UNDERWATER CONCRETING MATERIAL

Geopolymer concrete is a new sustainable and environmentally friendly composite with great potential to replace conventional concrete that is mostly produced by ordinary Portland cement (OPC). Binders used for geopolymer concrete such as fly ash and blast furnaces are mostly industrial wastes or by-products containing high silica and aluminium content that act as stimulants for geopolymerization. Furthermore, geopolymers also exhibit better durability and corrosion resistance than OPCs. However, material subjected to underwater placement method typically exhibit a decrease in properties. While geopolymer has not been widely used as underwater concreting material, this research is purposed to identify the effect of underwater placement method towards geopolymer in terms of microstructure analysis. Using different molarities of sodium hydroxide (NaOH), the optimum compressive strength will be discussed for underwater concrete while correlating with the microstructure result. For alkaline activators, the ratio used is 2.5 and the ratio for solid to liquid is 2.5. The molarities used for alkaline activators were 8 M, 10 M and 12 M. Using the tremie method for underwater concrete, it is possible to measure the leaching loss with respect to the objective of this research. The best compressive strength result is 12 M. The SEM result support with 12 M molarity had less cavities and lowest density.

Keywords: Fly ash, Geopolymer, underwater concreting, concrete

1. Introduction

Underwater geopolymer concrete is a type of building material that is frequently used in structural engineering projects. Underwater concrete should be used in any other structure where the lower levels are expected to remain underwater. Most inshore structures, such as ports and oil refineries, as well as some offshore structures near the seacoast or where the ground water table is high and close to the ground surfaces, require the pouring of concrete underwater. Engineers consider underwater concreting to be a challenge even during design, implementation, and supervision because many precautions must be taken to ensure the casting process's success. If enough attention is paid to the concrete mix itself and the construction methods used, this process can be completed successfully and good quality concrete produced [1].

Geopolymer concrete is a new sustainable and environmentally friendly composite that has the potential to replace traditional Portland cement-based concrete (OPC). Fly ash and blast

furnace slag, for example, are industrial wastes or by-products with high silica and alumina contents that can be used as pozzolanic components for geopolymerization in alkaline environments [2]. When compared to the production of Portland cement, these pozzolanic materials use less energy and emit less CO₂. As a result, in light of sustainable development and environmental concerns, the production of concrete using geopolymer as the binder has stirred up the interest of academics [3].

The properties of geopolymer are highly affected by 3 variable which is solid to liquid ratio, sodium silicate to sodium hydroxide ratio and the molarity of NaOH. These factors contribute to the resulting compressive strength of the geopolymer [4]. Further investigating the effects of the variable can be observed using microstructure analysis where the condition such as microcracks, porosity and unreactive raw material can subjugate the material to a lower compressive strength. Thus, this research is focused on the effect of NaOH molarity towards the microstructure of geopolymer which affects the resulting compressive strength.

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2. Experimental method

2.1. Materials

The raw material fly ash used is attained from Manjung Power Plant, Lumut, Perak which is of low calcium, Class C is used as the base material of geopolymer and is equivalent to ASTM C618. While kaolin used in this study is supplied by Associated Kaolin Industries Malaysia as Si-Al sources materials. The chemical composition of fly ash and kaolin obtained from the analysis as tabulated in TABLE 1. The sodium hydroxide (NaOH) powder was of caustic soda micropearls and 99% purity with the brand name of Formosoda-P. The sodium silicate (Na_2SiO_3) solution with a chemical composition of 30.1% SiO_2 , 9.4% Na_2O and 60.5% H_2O was supplied by South Pacific Chemicals Industries Sdn. Bhd., Malaysia.

TABLE 1

XRF analysis of Fly ash class C and Kaolin powder

Element	SiO_2	Al_2O_3	CaO	Fe_2O_3	TiO_2	K_2O	SrO
Kaolin	54.0	31.7	—	4.89	1.41	6.05	—
Fly Ash	31.4	13.2	23.3	25.44	1.00	1.59	0.177

2.2. Preparation and curing

The effect of NaOH molarity is inspected by varying the molarity by 10 M, 12 M and 14 M while the ratio of sodium silicate to sodium hydroxide and ratio of solid to liquid is kept constant at 2.5 and 2.0 respectively. The TABLE 2 displays the design proportions of the geopolymer mortar.

TABLE 2

Mix design proportions

Mixing designs proportions for geopolymers Molarity of sodium hydroxide	8 M, 10 M, 12 M
Ratio of sodium silicate to sodium hydroxide	2.5
Ratio of alkaline activator to fly ash	2.0
Fly Ash (g)	450
Kaolin (g)	50
Sodium Hydroxide solution (g)	179

This research differentiates between two types of geopolymer where the control geopolymer are poured and cured in room temperature while the underwater geopolymer undergoes underwater concreting placement method during the pouring and is cured in water. The tremie method are choose for the underwater concrete placement method. Following the tremie method, the mixture is poured into 50 mm square mould inside a container of water. The mixture is fed into the mould using a hopper and PVC pipe connecting to the base of the mould until it filled the pipe. Then, the pipe is slowly lifted to let the mixture into the mould. The end of the pipe was ensured to remain inside the mixture until end of feeding to ensure the mixture do not fall and mix with

the surrounding water. The tremie method of pouring concrete prevents cement washout due to water turbulence during the pouring process, resulting in a more reliable strength of product.

3. Experimental testing

3.1. Compressive Strength

The cubic moulds of size 50 mm samples were used for compressive strength testing according to ASTM C109/C109M – 16a by using Instron machine series 5569 Mechanical Tester for sample 10 M, 12 M and 14 M at 7 and 28 days of exposure for both control geopolymer and underwater geopolymer.

3.2. Morphology

Further microstructure analysis was performed using JSM-6460LA model Scanning electron microscope (JEOL) to reveal the microstructure difference between control and underwater geopolymer. The specimens were prepared and coated by gold/palladium (Au/Pd) using Auto Fine Coater JEOL JFC 1600 prior to examination. The microstructure analysis is done for sample 10 M, 12 M and 14 M at 28 curing days for both control geopolymer and underwater geopolymer.

3.3. Density

Density is defined as the mass per unit volume. The density of the geopolymers was determined as per the ASTM C138 using the equation below. Three measurements were taken, and the average value was reported to ensure the repeatability of the measurement. The mass and dimensions were also determined and reported.

$$\text{Density, } \rho = \frac{\text{Mass, } M}{\text{Volume, } V}$$

3.4. Water absorption

The water absorption test was conducted to determine the moisture content of the geopolymer paste. As per instructions in the ASTM C140, the sample was weighed before and dried in an oven. The sample was then immersed in distilled water for another 24 hours before being weighed again. The water absorption was calculated using below.

$$\text{Water absorption} = \frac{W_s - W_d}{W_d} \times 100$$

Where:

W_s – saturated weight of samples (g),

W_d – oven-dry weight of samples (g).

4. Result and discussion

4.1. Compressive strength

Fig. 1 shows the control sample and underwater concrete result for 7 and 28 days. The average compressive strength results are listed at graph below. The result on compression strength of the control geopolymer and underwater geopolymer. By referring the graph in Fig. 1, the highest value of compressive strength of control geopolymer is 37.7 MPa for 7 days and 55.23 MPa for 28 days. For underwater geopolymer, the highest, compressive strength 29.6 MPa for 7 days and for 28 days was 43.4 MPa.

The pattern of compressive strength increases steadily. This can be seen in the graph, the higher molarity of NaOH, the higher compressive strength. The 8 M molarity for control geopolymer and underwater geopolymer had the lowest against 10 M and 12 M. As the result shown, by the sample with higher molarity, the value of compressive strength higher. The increase in compressive strength observed as the NaOH molarity increases was due to the sufficient presence of sodium ion (Na^+) and hydroxide ion (OH^-) provided by NaOH that helps in the dissolution process of Al^{3+} and Si^{4+} in the raw fly ash and kaolin. As the NaOH molarity increases, so does the alkali concentration therefore, further enhance the strength development of the geopolymer. This pattern was noted the same for both control geopolymer and underwater geopolymer. The molarity of NaOH plays an important role for compressive strength. Research by Sathish Kumar et. al (2017), also supports that the increase on NaOH molarity results to an increase in compressive strength [5].

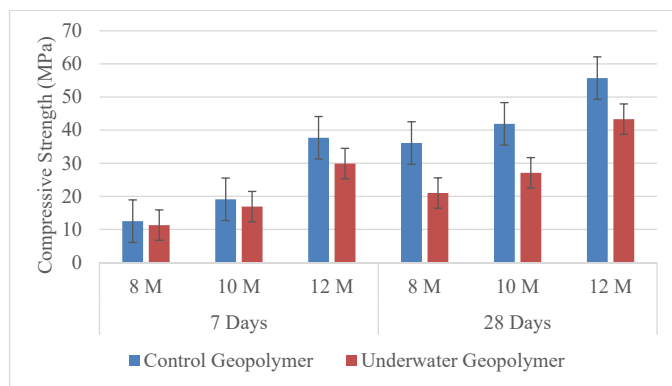


Fig. 1. Compressive strength of geopolymer with different NaOH molarity

However, there was an obvious difference between control geopolymer and underwater geopolymer where for every molarity and curing days, the underwater geopolymer exhibit lower compressive strength compared to the control geopolymer. This was due to the different pouring and curing condition of underwater geopolymer. Research by Grzeszczyk et al. agrees that washout will not only decrease concrete strength; it could also pollute the surrounding water [6]. The surrounding water

of underwater geopolymer obviously affects the properties of underwater geopolymer and is further identified according to the microstructure in the next section.

4.2. Microstructure

The microstructure result at 28 days are shown in Fig. 2. Unreacted fly ash and kaolin particles were clearly visible in sample 8 M presented in Fig. 2(a) and 2(d), which did not participate in the polymerization and resulting in lower compressive strength. Additionally, cavities were discovered, suggesting that the concrete was porous. These microscopic cracks propagate further by branching, resulting in the establishment of weak areas and a significant reduction in strength.

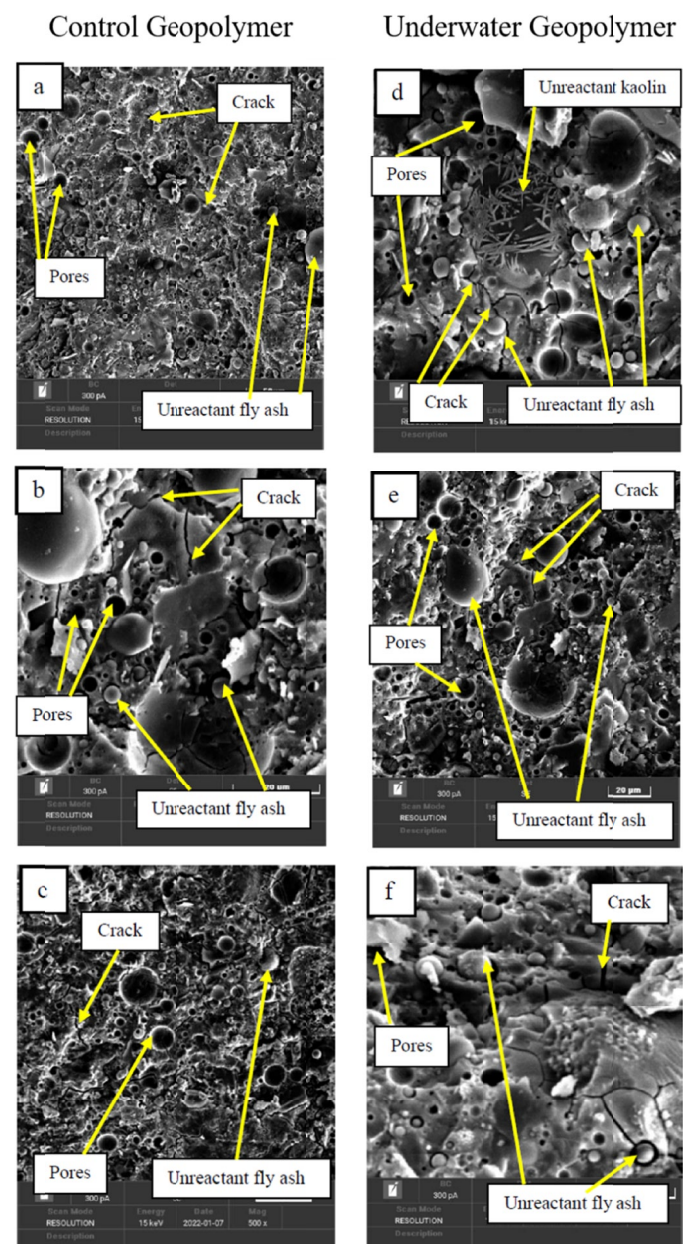


Fig. 2. Microstructure of fly ash based geopolymer for control sample a) 8 M, b) 10 M, c) 12 M and underwater concrete sample d) 8 M, e) 10 M, f) 1 M

As the molarity further increases to 10 M based on the Fig. 2(b) and 2(e), the unreacted particles reduce compared to 8 M. Furthermore, the Fig. 2(c) and 2(f) which used 12 M present the lowest unreacted particles.

Comparison between control geopolymer and underwater geopolymer are observed in Fig. 2(c) and 2(f). Fig. 2(f) which presents the underwater geopolymer shows more visible cracks and unreacted fly ash compared to control geopolymer in Fig. 2(c). This was due to the different of pouring method where underwater geopolymer undergoes underwater placement method and is cured underwater. The presence of surrounding water may cause the dilution of alkali material causing the underwater geopolymer to react inefficiently compared to the control geopolymer. This can be supported by the research from Law & Evans (2015), stated that presence of surrounding water promotes leaching of ion such as calcium, aluminum and sodium which can cause rise in pH water and decrease of strength in the material [7].

4.3. Density

Fig. 3 shows the density properties of control geopolymer and underwater geopolymer for 7 and 28 days. Based on the Fig. 3, the highest density of control geopolymer is 2.3 kg/m^3 which is 12 M for 28 days. For the lowest is 8 M molarity that is 1.68 kg/m^3 from underwater geopolymer. In addition, both control geopolymer and underwater geopolymer exhibit higher density when the NaOH molarity increases from 8 M to 12 M and when curing day increase from 7 to 28 days. While for each molarity, the control geopolymer presents higher density when compared to control geopolymer.

The patterns for control geopolymer and underwater geopolymer show a steady increase as seen in graph. The density is estimated to be between 1.68 kg/m^3 and 2.3 kg/m^3 . This shows that the density was affected by the molarity of NaOH. The result can also be related to the microstructure of the geopolymer sample where the presence of porosity and unreacted fly ash results on lower density of geopolymer. Since underwater geopolymer presents abundant pores in the microstructure result, it is understood that the underwater geopolymer presents lower density compared to the control geopolymer. Due to the underwater method and inability of the concrete to be manually

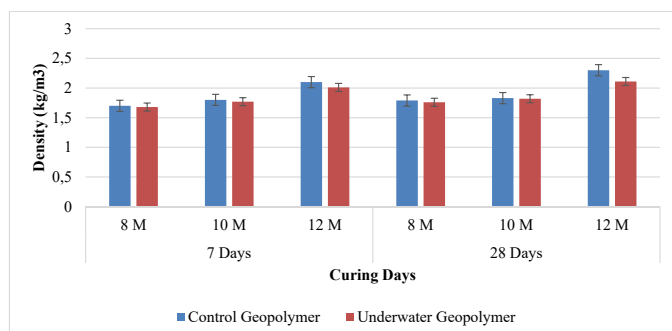


Fig. 3. Density of geopolymer with different NaOH molarity

compacted, more air bubbles are likely to be trapped. Thus, causing the more porous structure of underwater geopolymer compared to control geopolymer. Ng et al., (2019) also stated that the geopolymer concrete with the appearance of air bubbles is said to be weak since the porous structure weaken the structure of geopolymer matrix [8].

4.4. Water absorption

The graph in Fig. 4 identified that the water absorption of control geopolymer is lower than underwater geopolymer. The percentage of the water absorption for the control geopolymer value 3% to 7% while the underwater concrete 4% to 8%. The highest water absorption was observed by underwater geopolymer at 7 days curing using 8 M at 7.6%. While the lowest water absorption was obtained by control geopolymer at 28 days using 12 M at 3.3%. All sample presents a decrease in water absorption as curing days increase from 7 days to 28 days. The increase of NaOH molarity results on the decrease of water absorption for both samples.

Higher water absorb shows that there is higher porosity that will move the water into the concrete. As a result, the reaction increases inside the sample including salt crystallization. This happen because of the cracks and porosity in the concrete sample. This proof by Risdanareni et al. (2017) the open pore is defined as the ability of air and water to pass through the geopolymer combination, making it permeable. Close pore, on the other hand, refers to the fact that air and water cannot pass through the geopolymer combination, making it impermeable. This evidence proved by Yahya et al. (2018) water absorption show good quality of the geopolymer when higher molarity of NaOH [9].

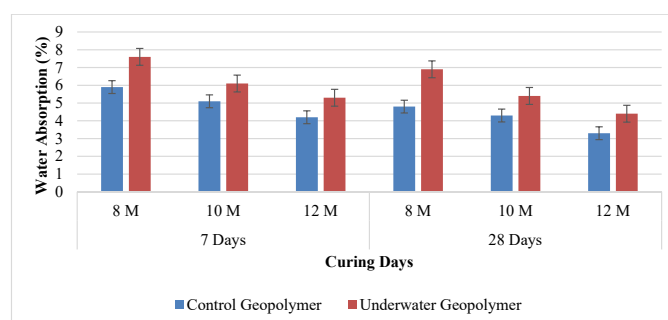


Fig. 4. Water Absorption of geopolymer with different NaOH molarity

Thus, this proves that the microstructure of geopolymer sample plays an important role in the properties of geopolymer. High porosity and unreacted fly ash indicate lower compressive strength, density and higher water absorption. The abundant porosity and unreacted fly ash also provide channels for crack to propagate such illustrated in the Fig. 5. The crack thus will channel higher ion exchange between sample and surrounding atmosphere which lead to further decrease in compressive strength such observed for underwater geopolymer.

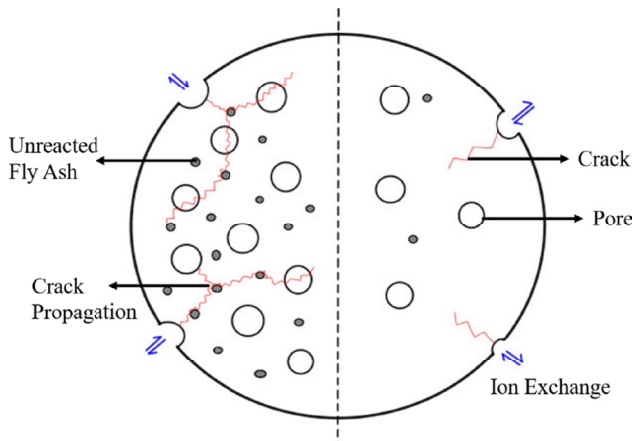


Fig. 5. Crack propagation caused by pore and unreacted fly ash

5. Conclusion

The aim for this research is to produce geopolymer for underwater concreting by identifying the optimum design of sodium hydroxide molarity. The various molarity of NaOH used are 8 M, 10 M and 12 M. The 12 M molarity contributes the highest compressive strength, density, lowest water absorption and the best result for microstructure analysis. For the microstructure analysis, there were less cavities, pores, unreacted fly ash for underwater geopolymer using 12 M compare to 10 M and 8 M molarity of NaOH. This indicates that the 12 M of NaOH provides sufficient presence of sodium ion (Na^+) and hydroxide ion (OH^-) that helps in the dissolution process of Al^{3+} and Si^{4+} in the raw fly ash and kaolin and enhancing the geopolymerization process. However, lower properties of underwater geopolymer compared to control geopolymer are expected due to the factors subjected when using underwater placement method such as force of surrounding water and the inability of material to be manually compacted. Such that more air bubble is likely to be trapped in the geopolymer material, causing higher porosity, higher ion ingress and lower the strength of the underwater geopolymer. Despite that, geopolymer for underwater concreting was successfully produced which leads to the potential of geopolymer to be used as underwater concreting in further studies.

REFERENCE

- [1] H.S. Abdelgader, M.F. Najjar, T.M. Azabi, Study of underwater concrete using two-stage (preplaced aggregate) concrete in Libya. *Struct. Concr.* **11**, 3, 161-165 (2016). DOI: <https://doi.org/10.1680/stco.2010.11.3.161>
- [2] F.H. Ahmad Zaidi et al., Geopolymer as underwater concreting material: A review. *Constr. Build. Mater.* **291**, 123276 (2021). DOI: <https://doi.org/10.1016/j.conbuildmat.2021.123276>
- [3] L. Ahmad Sofri, M. Mustafa Al Bakri Abdullah, M. Rosli Mohd Hasan, Y. Huang, The Influence of Sodium Hydroxide Concentration on Physical Properties and Strength Development of High Calcium Fly Ash Based Geopolymer as Pavement Base Materials. *IOP Conf. Ser. Mater. Sci. Eng.* **864**, 1 (2020). DOI: <https://doi.org/10.1088/1757-899X/864/1/012016>
- [4] Z. Abdollahnejad, F.P. Torgal, Performance of fly ash-based geopolymer mortar. no. January 2015, 1-11 (2017).
- [5] V. Sathish Kumar, N. Ganesan, P.V. Indira, Effect of Molarity of Sodium Hydroxide and Curing Method on the Compressive Strength of Ternary Blend Geopolymer Concrete. *IOP Conf. Ser. Earth Environ. Sci.* **80**, 1 (2017). DOI: <https://doi.org/10.1088/1755-1315/80/1/012011>
- [6] S. Grzeszczyk, K. Jurowski, K. Bosowska, M. Grzymek, The role of nanoparticles in decreased washout of underwater concrete. *Constr. Build. Mater.* **203**, 670-678, Apr. (2019). DOI: <https://doi.org/10.1016/j.conbuildmat.2019.01.118>
- [7] D.W. Law. J. Evans, Effect of Leaching on pH of Surrounding Water. no. May 2013, (2015).
- [8] H.T. Ng, C.Y. Heah, Y.M. Liew, M.M.A.B. Abdullah, The effect of various molarities of NaOH solution on fly ash geopolymer paste The Effect of Various Molarities of NaOH Solution on Fly Ash Geopolymer Paste. **020098**, no. December, 10-15 (2018).
- [9] Z. Yahya, M.M.A.B. Abdullah, N. Mohd Ramli, D.D. Burduhos-Nergis, R. Abd Razak, Influence of Kaolin in Fly Ash Based Geopolymer Concrete: Destructive and Non-Destructive Testing. *IOP Conf. Ser. Mater. Sci. Eng.* **374**, 1 (2018). DOI: <https://doi.org/10.1088/1757-899X/374/1/012068>