

Seawater as Alkali Activator in Fly Ash Based Geopolymer

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Abstract – Indonesia as a maritime country in the world with 66% of its territory consists of maritime territory. A lot of potential that can be exploited, such as sea water. XRD characterization results indicate that the sea water from Tanjung Priok, North Jakarta, Indonesia has a compound Halite (NaCl) and Bassanite ($\text{CaSO}_4 \cdot 5\text{H}_2\text{O}$) in the salt form. These compounds are alkaline thereby can influence the compressive strength of the geopolymer. Geopolymer is made up of aluminosilicate precursors which are activated by the alkaline activator solution, which usually combines sodium silicate and sodium hydroxide. The precursor material is waste from the coal based power plant called fly ash that produce 219.000 tonne per year and still underutilized but potentially as an alternative to cement. In this study, seawater was used to substitute the sodium hydroxide in alkali activator as an effort to reduce the manufacturing cost of Geopolymer. Geopolymer prepared by mixing fly ash as a precursor, silica sand as aggregates, with activator, then casted and cured by immersion. After 28 days compression test was conducted to measure the strength of resulting geopolymer. The sample consisted of a mixture of fly ash, silica sand, waterglass, and seawater produces strength of 16.60 MPa. X-Ray Diffraction characterization was conducted to study the compound formed from precursors activated with seawater alkali activator. Resulting diffractogram indicate the formation of anorthite compound as proof of Geopolymerization has been successfully occurred.

Keywords: Seawater; Geopolymer; Alkali Activator; Anorthite

I. INTRODUCTION

The construction of residential houses in the coastal area consists of houses on stilts and simple concrete buildings. The construction process with wood materials is more desirable because of the difficulty of access to making houses with concrete materials. One of the materials that is difficult to meet is the use of clean water, which is a component of mortar that is difficult to obtain due to the complex seawater desalination process. The components in the mortar consist of compounds that can be replaced by other materials with similar characteristics. Joseph Davidovits referred Geopolymer as a material resulting from inorganic polycondensation or can also be referred to as Geopolymerization which involves chemical reactions between aluminosilicate materials such as Fly ash or Metakaolin with alkaline activator solutions such as NaOH and KOH. In this reaction Alumina and Silica have an important role in the polymerization bond, so geopolymers can also be referred to as alkali activated materials. Alkaline activator usually consists of sodium hydroxide (NaOH) solution and waterglass (Na_2SiO_3). Geopolymer can be applied to industries that produce large amounts of waste material and support it as a precursor. Geopolymer was synthesized from precursors that have low calcium content and high levels of Silica (SiO_2) and Alumina (Al_2O_3) such as fly ash (Wong, B.Y.F., et al., 2019). So far, a maximum of 40% of fly ash has been utilized to replace cement in concrete mixtures (Van Tran, M., et al., 2021), whereas if it is used as a geopolymer precursor this material can be utilized up to 100%.

Fly ash is then activated using an alkaline activator solution to form an alkaline aluminosilicate material which will experience a high increase in strength at an early age by heat treatment/soft curing. Geopolymer has a difference

with Portland cement, namely in the formation reaction that occurs. Portland cement depends on the presence of calcium silicate hydrate (CSH) for strength formation, whereas the strength of Geopolymer depends on the polycondensation of aluminosilicate precursors and alkaline activator solutions.

The economic feasibility has been the major factors hindering the commercialization of geopolymer (Rintala, A., et al., 2021). Cost of NaOH is one of the problem to be assessed for geopolymer to compete with traditional cement based concrete. In this study, the seawater with abundant available resources in coastal areas used as NaOH substitution in the manufacture of Geopolymer. Seawater is expected to replace the need for NaOH in the activator because seawater has alkaline ions which are useful in helping the reactions that occur in Geopolymer (Do, Q., et al., 2019). With the discovery of an appropriate substituent material, it is hoped that coastal communities will have a positive impact on being able to use this technology to start small and medium-sized businesses producing Geopolymer-based bricks. The production of bricks that is carried out independently by the community can be used as a construction material for people’s houses or by exporting the production of high quality bricks produced to the surrounding areas. This research was conducted to determine the compounds contained in seawater and the effect of its addition on the compressive strength. The compound of resulting Geopolymer was also studied.

II. METHODS

To see the compounds contained in salt from the crystallization process of seawater taken from Tanjung Priok, North Jakarta, Indonesia then it was crystallized by pouring into evaporating dish and heating in 100°C oven and collected in plastic wrap (Figure 1).

X-Ray Diffraction (XRD) characterization was carried out with the Philips Diffractometer PW1710 at the Characterization and Mineralogy Laboratory, Faculty of Mining and Petroleum Engineering, ITB.



Figure 1. Seawater salt for XRD characterization

Figure 2 shown the process step from the beginning, synthesis, characterization, and data analysis used in this study

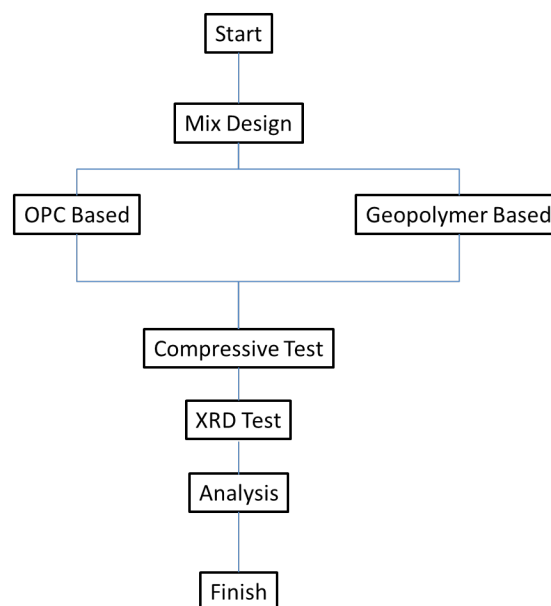


Figure 2 Process Diagram

Table 1 shown the geopolymer mortar mixtures which are prepared to study the addition of seawater as NaOH substitutor in geopolymer. Traditional cement based mortar mixed with seawater are also prepared to compare the resulting compressive strength of samples to geopolymer.

Table 1. Mix Design used in this study

No	Code	Precursor	Activator
1.	OPC-N	OPC	Normal water
2.	OPC-SW	OPC	Seawater
3.	GP-AA	Fly ash	Waterglass+NaOH
4.	GP-SW	Fly ash	Waterglass+Seawater

Note: OPC=Ordinary Portland Cement, GP=Geopolymer

The material used consists of class F fly ash precursor obtained from Suralaya Coal Power Plant, Ordinary Portland Cement (OPC), Silica sand as light aggregate taken from the beach in the Bangka Belitung Islands, Indonesia and is used in a saturated surface dry condition or often referred to as Surface Saturated Dry (SSD). Water Glass is obtained in liquid form through local suppliers. NaOH solution is made by dissolving solid NaOH (with a purity of ± 90%) into distilled water until it reaches 6M, and sea water is obtained from Tanjung Priok, North Jakarta, Indonesia. The oxide composition of fly ash is shown in Table 2.

Table 2. Oxide composition of fly ash

Oxide	Percentage (%)
SiO ₂	52.30
Al ₂ O ₃	26.57
CaO	6.00
Fe ₂ O ₃	7.28
Na ₂ O	1.41
MgO	2.13

Geopolymer is made by mixing Fly Ash and Silica sand which is then mixed with an alkaline activator solution with a ratio of Water Glass and NaOH 2:1 (Harmaji, A., et al., 2016). Mixing was commenced using Hobart™ Mixer to form a slurry then casted with a size of 50 mm x 50 mm x 50

mm , then removed after one day as Figure 3. Samples were cured at room temperature, after removing from mold it was put in a sealed plastic wrap and covered with damp clothes to maintain the moisture and ensure geopolymerization occurred.



Figure 3. Hardened Geopolymer mortar

As a comparison, OPC based mortar was made by mixing cement and water or seawater with a water-cement ratio (w/c) of 0.5 (Figure 4) and paste to sand ratio of 1:2 to form a slurry. The hardened mortar is removed from the mold for a curing process by immersing the entire surface of the sample in water for 28 days to prevent the sample from cracking during the curing process due to an exothermic reaction (Hernández-Bautista, et al., 2017).



Figure 4. Cement based mortar

The compression test was carried out according to ASTM C-109 (Standard Test Method for Compressive Strength of Hydraulic Cement Mortars (Using 2-in. or [50-mm] Cube Specimens) at the Structural Engineering Laboratory of ITB using the Universal Testing Machine (UTM) to determine the compressive strength of geopolymer and cement based mortar at 28 days (Figure 5). Debris from compressive test was collected for XRD purposes.



Figure 5. Compressive test of mortar

III. RESULTS AND DISCUSSION

3.1 Seawater Crystallization XRD analysis

XRD characterization was carried out on seawater salt and then analyzed using X-Powder™ software to determine compounds based on the Joint Committee on Powder Diffraction Standards (JCPDS). The diffractogram shows the presence of Halite (NaCl; JCPDS No. 05-0628) and Bassanite (CaSO₄·5H₂O; JCPDS No. 41-0224) compounds which are shown in Figure 6. Halite and Bassanite identified as strong crystalline form. The percentage of each compound is shown in Table 3 which confirms that the salt has alkaline compounds which can increase the basicity of the mortar. This is one of the important factors for cementitious materials to survive in an acidic environment (Pyatina, T., et al., 2020; Jang, I., et al., 2021).

Table 3. Seawater crystallization compound

Oxide	Percentage (%)
NaCl	16.67
CaSO ₄ ·5H ₂ O	83.33

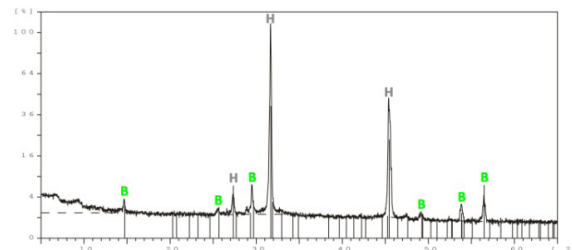


Figure 6. Seawater crystallization diffractogram

3.2 Compressive Test analysis

The compression test is carried out on the entire mix design. The results of each variant can be seen in Figure 7. It can be seen that the OPC-C sample produced a compressive strength of 11.60 MPa, and OPC-SW 14.28 MPa. This increase in compressive strength occurs because Ca²⁺ ions from Bassanite in seawater helps the formation of Calcium Silicate Hydrate (CSH) in the mortar product as the proof of reaction between cement and water or usually called hydration. CSH is crucial in compressive strength of development of material.

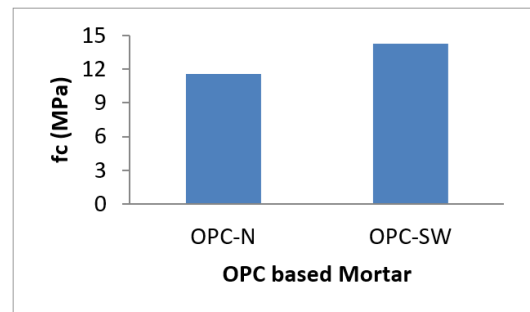


Figure 7. Compressive strength of OPC based mortar

External source of CSH can increase the compressive strength of resulting mortar (Kunther, W., et al., 2017). There are several attempts to increase C-S-H by addition of compound that contains calcium (Ca), silica (Si) such as silica fume and calcium hydroxide nanoparticles (Tavares,

L.R.C. et al., 2020; Camerini, R., et al., 2022), or CSH in various forms such as nano-calcium silicate hydrate, highly crystallized C-S-H Particles, and calcium silicate hydrate seeds (Zhu, S., et al., 2019; Wang, Y., et al., 2020; Alzaza, A., et al., 2022).

Bassanite compound, $\text{CaSO}_4 \cdot 5\text{H}_2\text{O}$ is similar to Gypsum, whether is Anhydrite (CaSO_4), Hemihydrate ($\text{CaSO}_4 \cdot \text{H}_2\text{O}$), or Dihydrate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) which is the raw material of cement manufacture mixed with clinker to produce Portland cement. This means using seawater increase the compound of Calcium Sulfate dihydrate (CSH_2), which if mixed with anhydrous calcium sulfoaluminate ($\text{C}_4\text{A}_3\text{S}$) results in sulphoaluminate cement that has advantage in low-temperature application (Li, M., et al., 2020). Sulfate is adsorbed in calcium silicate hydrate during the acceleration part of the tricalcium silicate (C_3S) peak (Zunino, F., et al., 2020). Sulfate content in Bassanite can react with tricalcium aluminate (C_3A) which influence the rheology, setting time, and hydration of mortar (Kirchheim, A. P., et al., 2018).

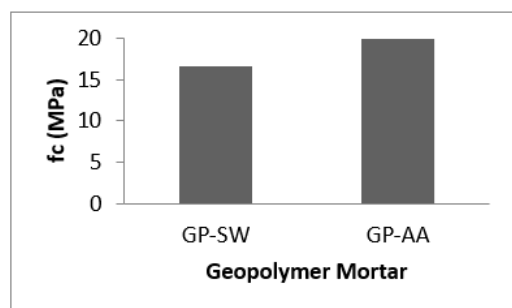


Figure 8. Compressive strength of Geopolymer based mortar

Figure 8 shows the results of the Geopolymer-based mortar sample compression test. GP-SW and GP-AA produces compressive strength of 16.60 and 19.87 MPa, respectively. GP-SW strength was lower because in seawater there is Ca^{2+} ions so that they form anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$) phase in the sample, contrast to GP-AA geopolymer gets additional Na^+ ions from NaOH to form an albite ($\text{NaAlSi}_3\text{O}_8$) phase in the sample. This means aluminosilicate tends to react with Ca^{2+} ion from Bassanite compound faster rather than Na^+ . Viscosity of seawater is higher than NaOH means there are alteration in Geopolymerization since Bassanite has extra H_2O in it, thus affect the compressive strength. There is only slight drop in compressive strength value makes seawater is promising for alkali activator substitutor.

Other research has successfully utilize carbonates such as Na_2CO_3 and K_2CO_3 and silicates such as K_2SiO_3 (Torres-Carrasco, M., et al., 2017; Payá Bernabeu, J., et al., 2022) as alkaline and Si source for alkali activation of geopolymer.

3.3 XRD analysis of GP-AA and GP-SW

Figure 9 shows the resulting diffractogram of GP-AA and GP-SW, the major difference from both diffractogram is the resulting geopolymerization compound. Figure 9b has more amorphous phase than Figure 9a. GP-AA results in albite ($\text{NaAlSi}_3\text{O}_8$; JCPDS No. 19-1184) while GP-SW formed anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$; JCPDS No. 02-0537). Studies reported that anorthite and albite were typical

trademark of geopolymerization (Jamil, N.H., et al., 2021).

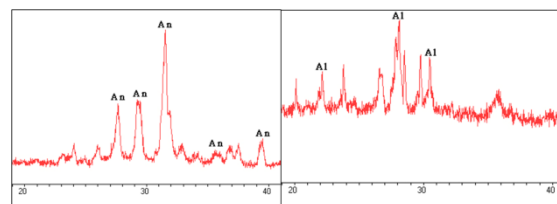


Figure 9. Diffractogram of (a) GP-SW (b) GP-AA

Sodium chloride (NaCl) in seawater results in sodium ions and chloride ions generated new strengthening hydration products (He, W., et al., 2019). Sodium (Na) in albite alter the ratio of $\text{Na}_2\text{O}:\text{Al}_2\text{O}_3$ which affect the compressive strength significantly Huseien, G. F., et al., 2018). Gypsum-like compound in Bassanite can affect the thermal conductivity of Geopolymer (Bumanis, G, et al., 2020).

IV. CONCLUSION

From this study, author can concludes that seawater is a promising substituting material for alkali activator. Bassanite compound from seawater crystallization helps the formation of CSH in OPC based mortar. Geopolymer samples which alkali activator partially substituted with seawater shows slightly lower strength (16.60 MPa) than ordinary alkali activator (19.87 MPa) because anorthite compound in Geopolymer has lower reactivity and higher crystallinity compared to Albite shown in XRD diffractogram.

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