

The effect of calcium oxide addition from feather clam shells on porosity and water adsorption geopolymer composite bricks

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Abstract

The purpose of this study was to study the effect of adding CaO (calcium oxide) from clam shell ash on physical properties such as density, porosity and water absorption on geopolymer composite bricks. Geopolymer composite bricks are made by mixing sand, geopolymers synthesized from fly ash with NaOH and Na₂SiO₃ and calcium oxide calcined from feather clam shell which is printed in cylinder form. The bricks are then cured for 28 days and physical tests are carried out in the form of density, water absorption and porosity tests. The results showed that the most optimal addition of CaO is 7.5% for the physical properties of geopolymer composite bricks with a density value of 1.80 gr/cm³, a porosity value of 10.30% and a water absorption capacity of 4.68%. The value has filled the quality standard 1st for bricks set by Indonesian National Standard (SNI).

Introduction

Indonesia is an archipelagic country, with an area of water reaching 5.8 million km² and a coastline reaching 81,000 km². It has great potential in terms of managing marine resources, one of which is shellfish (Haryanto, 2016). Shellfish belong to the phylum Mollusca and class Bivalves (by other names Pelecypoda or Lamellibranchiata). Scallops have a bilaterally symmetrical body, with two symmetrical limestone shells of various shapes and sizes. In general, clams can live in fresh water, on the seabed, lakes, ponds or rivers which contain a lot of lime. This lime substance will be used to make clam shells. Many types of shellfish are easy to find on the coast of Indonesia, one of which is the feather clam. Shell Feathers have the Latin name *Anadara antiquata*. This type of shellfish is often used as a food ingredient, but the shell waste itself is rarely used. Usually these shells are thrown away by the community or used as decoration. When discarded, these shells will have a negative impact on the environment. Apart from giving off a foul odor when thrown away, clam shells are also difficult to destroy, so they have the potential to become waste (Silaban et al., 2022). Bharatham et al. (2014) explains, around 95.7% of the shells are composed of Calcium Carbonate (CaCO₃). Shellfish generally consists of about 98.68% Ca with impurities including Manganese (Mn) of 0.059%, Iron (Fe) of 0.11%, Cobalt (Co) of 0.11%, Strontium (Sr) of 0.89%, and Lutetium (Lu) of 0.16% (Insani and Rahmatsyah, 2021). With high levels of CaCO₃, this clam shell has the potential as a source of CaO through the calcination process. CaO itself has many benefits, one of which is as a cement additive.

Brick or concrete brick is a material that is often used as a material for wall pairs. Bricks have many advantages when compared to ordinary bricks such as their larger size, the manufacturing process does not damage the land and does not require heating during manufacture (Budiningrum et al., 2021). On the other hand, the disadvantages of using bricks are the use of cement which has an impact on the CO₂ emissions produced, the manufacturing time is quite long and sometimes many bricks crack or break during transport or transfer due to the poor quality of the bricks (Syamsuddin, 2019).

Geopolymer is an inorganic polymer that was developed in the 1980s is an alternative substitute for Portland cement. Geopolymer, a material that has a binder made from natural ingredients and undergoes a



polymerization reaction when it is made. Geopolymer can be used as an alternative to cement, where the material used as a cement substitute is generally a material that has a high content of silica oxide and high alumina (Davidovits, 1994). Geopolymers have the empirical formula that is $m\text{n}(-(\text{SiO}_2)_z-\text{AlO}_2)_n \cdot w\text{H}_2\text{O}$ where m is alkaline cations used, and n is the polycondensation degree and the z value varies between 1 to 32 (Adisty, 2008). Geopolymer production is very different from Portland, because its processing does not require high temperatures or temperatures so it is very environmentally friendly. Geopolymers can be synthesized from materials containing silicate and alumina or aluminosilicate such as fly ash (Samadhi and Pratama, 2018). According to SNI 03-6414-2002 fly ash is a waste product of coal combustion and is dangerous in nature. Fly Ash is generally used as an expansive soil stabilizer and a cement additive.

The geopolymer itself when reacted with CaO can improve the quality of the geopolymer. When reacted with geopolymer, CaO will react with water to produce $\text{Ca}(\text{OH})_2$. Then $\text{Ca}(\text{OH})_2$ will react with sodium silicate and replace sodium cations as the center of the geopolymer to form hydrated calcium silicate (C-S-H). But in excess $\text{Ca}(\text{OH})_2$ conditions, it will have a bad impact on the geopolymer structure. At the condition of $\text{Ca}(\text{OH})_2$ increase, $\text{Ca}(\text{OH})_2$ will bind more aluminasilicate or silicate to form Calcium aluminasilicate hydrated. Due to the lack of aluminasilicate, the geopolymerization reaction will stop, the geopolymer will dry quickly and will cracks appear on the surface of the geopolymer due to the breaking of the bonds between the geopolymers (Khater, 2012). The cracks that arise will have an impact on the physical properties of the geopolymer and reduce the mechanical properties of the geopolymer. Malik (2016) explains that the maximum addition of CaO to geopolymer is 5%, after that the compressive strength of the geopolymer will decrease because the emergence of many cracks caused by broken bonds during the geopolymerization process. According to Khater (2012), the addition of CaO above 10% will causing the geopolymer structure to deteriorate.

Composite bricks can be made with the basic ingredients in the form of aggregate consisting of sand and shell ash as a filler with geopolymer as a binder. Composite material is a combination of several types of materials that have different characteristics from each other (Nurfajriani et al., 2022). Geopolymer is a polymer resulting from a geopolymerization reaction between silica and aluminosilicate solutions. Geopolymers can be made by reacting an alkaline activator in the form of NaOH and Na_2SiO_3 with materials containing alumina and silicates. Fly Ash, in which the main constituent materials are SiO_2 and Al_2O_3 , can be used as a raw material for making geopolymers. The addition of shells containing CaCO_3 can help harden the geopolymer and cement and can be used as a filler. What distinguishes this research from previous studies is the composite brick made from a binder in the form of a geopolymer made from fly ash, sand CaO from the ashes of clam shells as a filler. The purpose of this study was to study the effect of adding CaO from clam shell ash on physical properties such as density, porosity and water absorption on geopolymer composite bricks.

Method

Tools and Materials

The tools used in this study were glassware, furnace, analytical balance with a capacity of 500 g, large size buckets, sieves (200 mesh and 20 mesh), cylindrical molds (4 cm in diameter and height 10 cm), hammer, gloves, cement spoon. The materials used include type F fly ash, sand, sea shells, 8M NaOH solution, 99% Na_2SiO_3 solution.

Calcium Oxide Preparation

The scallop shells are washed clean and dried in the sun for a long time 3-5 days. The shells are then crushed to facilitate the calcination process in the furnace. The shells were then furnace for 2 hours at 800°C. The purpose of this process is to obtain CaO compounds from the shells of seashells (Husain et al., 2019). Furthermore, the clam shells that have been in the furnace are aerated at room temperature. The clam shells were then crushed using a blender and sieved until they passed 200 mesh sieve. Until we get CaO from the shells of feather clams with a dark gray color.

Making Geopolymer Paste

Fly Ash is put into the mixing container, then added alkaline activator in the form of 8M NaOH and 99% Na_2SiO_3 with a ratio of 62% Fly Ash and 38% Alkali Activator and a ratio between 8M NaOH and 99% Na_2SiO_3 is 1:2. The mixture is then stirred until all the ingredients are mixed and paste formed (Puspitasari et al., 2018; Budiningrum et al., 2021).

Composite Brick Making

The geopolymer paste that has been made before is mixed with aggregate in the form of sand and shells with a ratio of 35% geopolymer cement, 57.5% sand; 60%; 62.5%; 64%; 65%, 0% mussel shells; 1%; 2.5%; 5%; 7.5%. The mixture is then stirred until mixed, then poured into a mold measuring (4cm in diameter and 10cm in height). The sample is then allowed to stand until it hardens (Budiningrum et al., 2021; Tilik et al., 2022).

Density Test

Density testing was carried out on bricks that were 28 days old. The brick samples were first baked in the oven for 1 hour to remove the water content on the surface of the bricks. The bricks are then weighed to determine the dry mass of the bricks. Furthermore, the density measurement of the brick is carried out by weighing the brick in water. The brick samples are hung using wire or rope, then put into a container filled with water. The container filled with water and the suspended samples are then weighed and the volume weight of the bricks is calculated using the equation:

$$\rho_s = \left(\frac{md}{ms - (mss - mw)} \right) \times \rho_{\text{water}}$$

where ρ_s = Density of sample (g/cm^3), md = Mass of dry sample (g), ms = Mass of soaked sample (g), mss = Mass of suspended sample (g), mw = Mass of wire or hanging rope (g), ρ_{water} = Density of Water (1 g/cm^3) (Sebayang et al., 2012).

Porosity and Water Absorption Test

Porosity measurement is carried out simultaneously with the water absorption test. The test object was put into the oven for 24 hours at 100°C . After that the test object is cooled by means of aerated at room temperature room 25°C and then weighed to obtain the weight of the test object in a dry state. After the dry weight of the specimen is obtained, the specimen is then immersed in a tub filled with water for 24 hours. After that the test object is removed and the surface of the test object is wiped. Then weighed to get the after weight. Next, the calculation is carried out using the equation:

$$\%P = \left(\frac{ms - md}{\rho_w \times V} \right) \times 100\% \text{ and Water absorption} = \left(\frac{mss - ms}{mss} \right) \times 100\%$$

Where: ms = saturated mass after immersion (g), md = dry mass after oven (g), $\%P$ = porosity, mss = saturated mass after soaking (g), ρ_w = density of water (1 g/cm^3), V = volume of test object (cm^3) (ASTM C 642-90, 1991; Syamsuddin, 2019).

Results and Discussion

Physical test for bricks is a fairly important test to determine the classification of bricks made. Physical tests include density tests, porosity tests and water absorption tests. This physical test is carried out on bricks that have passed the curing period for 28 days. The results of the brick physical test can be seen in Table 1.

Table 1. The result of density, porosity and water absorption test

CaO Percentage	Density (g/cm^3)			Porosity (%)			Water Absorption (%)		
	1	2	3	1	2	3	1	2	3
0%	1.8132	1.8157	1.8129	13.06	13.30	13.06	6.05	6.17	6.04
1%	1.8089	1.8198	1.8046	12.34	12.58	12.26	5.72	5.85	5.66
2.5%	1.8109	1.8077	1.8093	11.46	11.62	11.70	5.24	5.30	5.32
5%	1.8089	1.8059	1.8045	10.59	10.67	10.67	4.75	4.78	4.76
7.5%	1.8057	1.7963	1.8050	10.19	10.43	10.27	4.65	4.74	4.67

Density is a unit of ratio between mass and volume of an object. Density values in composite bricks are generally influenced by the empty space in the bricks, density, pores and recession cracks in the bricks. From Table 1 it can be seen that there is a decrease in density value as the addition of CaO presented in Fig.-1.

From Fig.-1 it can be seen that the average density value of bricks decreases with the addition of CaO. When the bricks have not been added CaO (CaO 0%), the average density value of bricks is 1.8139 g/cm^3 . This value decreases with the addition of CaO starting from 1% which is 1.8111 g/cm^3 to the addition of 7.5% CaO which is

1.8023 g/cm³. The value of the decrease in density is not too large. Generally, concrete itself has a density of 2.2 g/cm³. When compared with the density value according to SNI, composite bricks made can be categorized as lightweight bricks, because the average density value is < 2.0 g/cm³ (SNI 03-0348-1989).

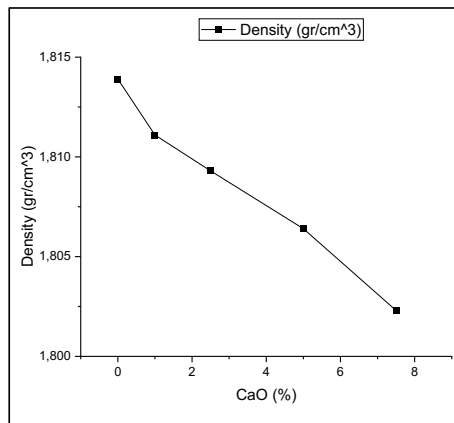


Fig. -1 Geopolymer brick density test graph with CaO addition 0%, 1%, 2.5%, 5%, and 7.5%

Porosity is a measure of the empty space between materials, and is the fraction of the volume of empty space to the total volume, which is valued between 0 and 1, or as a percentage between 0-100%. From Table 1. It can be seen that CaO has a significant influence on the porosity value of bricks geopolymer composite. It can be seen that the porosity value decreased with the CaO addition.

In Fig.-2 is a graph of the relationship between the percentage of the amount of CaO and the porosity value. From the chart can be seen when CaO has not been added, the porosity value is very high which is 13.14%. However, at the time of CaO addition from 1% to 7.5%, there was a significant decrease in porosity value up to 10.27% with the addition of 7.5% CaO. This is caused by the large pores that are formed due to hydration of H₂O. This is also influenced by the appearance of cracks caused by broken bonds during the polymerization process and the number of gaps due to the rough geopolymer structure. When CaO was added, the porosity and water absorption values began to decrease this is caused by Ca₂⁺ ions reacting with silicates to form hydrated calcium silicates (Ca₅Si₆O₁₆(OH)₂ · 4H₂O or C-S-H). This C-S-H formation will later make the geopolymer mixture more homogeneous and smoother. This causes the percentage value of porosity to decrease with the addition of CaO. The pores formed in the sample with the addition of 0% CaO have a larger size and more number when compared to the sample with CaO 5% (Khater, 2012). Malik (2016) also explained that the size and number of pores formed affect the porosity value. Where is the presence of pores with. The larger size of the geopolymer will cause the capacity to absorb water to increase.

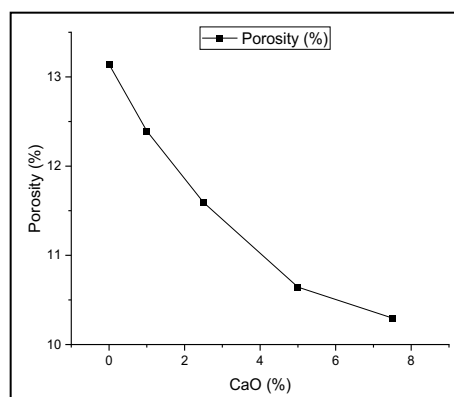


Fig.-2. Geopolymer brick porosity test graph with CaO addition 0%, 1%, 2.5%, 5%, and 7.5%

Water absorption is water absorbed per unit area in g/cm². Water absorption has a close relationship with porosity. Water absorption is the ability of an object to absorb water under normal conditions (Syamsuddin, 2019). If it is connected with porosity, the higher the porosity value have the higher water absorption value.

The graph in Fig.-3 shows the relationship between the average value of water absorption to CaO. The highest water absorption value was the sample without CaO addition, which was around 6.09%. Then when CaO

was added 1%, the porosity value decreased to 5.74% and when CaO was 2.5% it became 5.29%. When CaO is added by 5%, the porosity value decreases to 4.76%. The most optimal condition is when the CaO is 7.5%, which is the porosity value of 4.68%. When CaO is 7.5%, the difference in decreasing porosity value is less. This can be seen in the graph of Fig.-3 where the graph looks sloping.

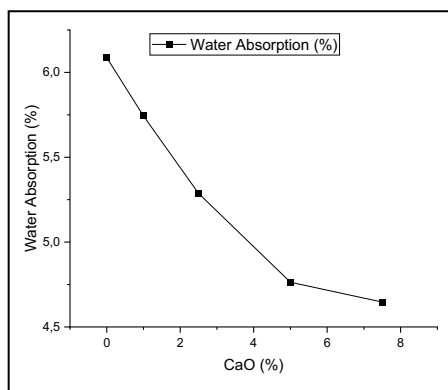


Fig.-3. Geopolymer brick water absorption test graph with CaO addition 0%, 1%, 2.5%, 5%, and 7.5%

In general, the decrease in the value of the physical properties of geopolymers is influenced by the large number of pores, the appearance of cracks and size pore. This crack and pore size will later become a place for water to be accommodated. While the emergence of pores and cracks in geopolymers is generally influenced by factors such as addition of CaO. The addition of CaO can inhibit the geopolymerization reaction. The geopolymer gel or geopolymer paste that is formed decreases due to the disruption of the geopolymerization reaction. This causes the bonds to break and causes clumps to form, all of these factors make CaO affect the physical properties of the bricks has made.

Conclusion

The addition of CaO from the ashes of shells affects the value of the physical properties of geopolymer bricks. Porosity values and water absorption decreased with the addition of CaO. This is influenced by the reaction between CaO and geopolymers that produce C-S-H which will later fill the pores in the brick which has an impact on decreasing the value of porosity and water absorption.

Conflict of Interests

The author (s) declares that there is no conflict of interest in this research and manuscript.

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