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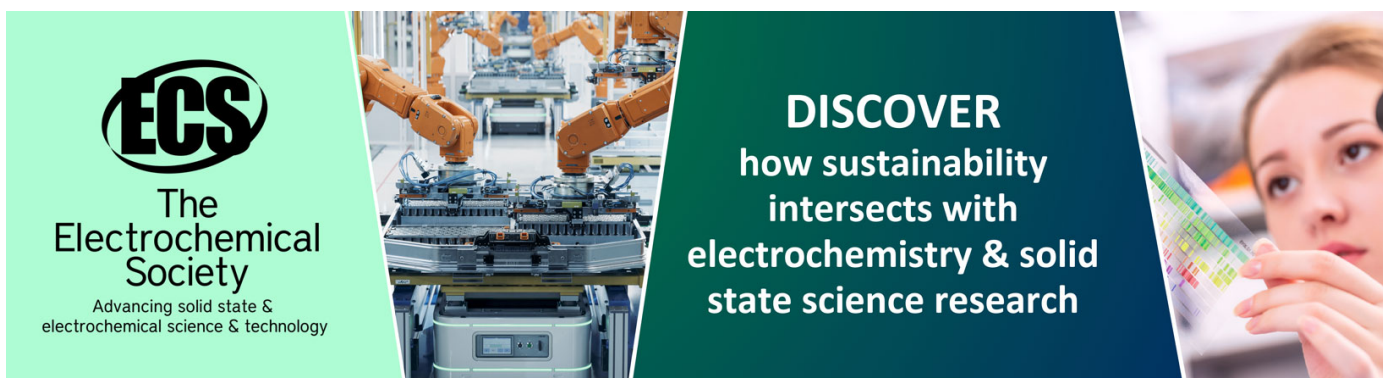
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Synthesis of volcanic ash-based geopolymer with calcium oxide (CaO) addition for building material application

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Abstract. Volcanic ash is a natural pozzolanic material with high mol ratio $\text{SiO}_2/\text{Al}_2\text{O}_3$ but low in CaO. This research aims to study the volcanic ash geopolymer characteristics related to CaO addition. Geopolymers are prepared by mixing volcanic ash, alkali activator solution, sodium silicate, and calcium oxide. Calcium oxide added varies 5–35 g with each interval is 5 g in Solid/Liquid (S/L=1.83) ratio. Geopolymer characteristics investigated include setting time, compressive strength, resistance to sulfuric acid and mineral phase. The results showed that the more CaO was added, the shorter the setting time and the greater the compressive strength until it reached optimum. The amount of optimum CaO that added is 30 g, with the setting time 2.61 hours and the compressive strength 36.26 MP better than the volcanic ash geopolymer without CaO as 103 hours in setting time and 20.34 in compressive strength. Volcanic ash-based geopolymer at the optimum CaO addition proved to be better than cement mortar, which has a shorter setting time, greater compressive strength and greater resistance to sulfuric acid. Mineral phase analysis by XRD shows that the optimum geopolymer containing an amorphous phase with a major mineral is quartz and sodalite.

1. Introduction

Geopolymer is an inorganic material that produced from the reaction between aluminosilicate solid, such as volcanic ash [1,2], with an alkali hydroxide solution and silicate solution [3]. Geopolymer can be used as construction materials [4]. Building construction materials commonly use cement as its main component. Geopolymers are supposed to be first of all an alternative to Portland cement based materials with possible environmental and durability benefits (which are paid by more sensitive mix design and technology, as compared to ordinary Portland cement) [5]. Geopolymer is a prospective technology to replace the function of the cement mortar and concrete in the construction field.

Volcanic ash-based geopolymer is interesting to study because it is cheap and abundant during a volcanic eruption relatively. The use of volcanic ash as the manufacture of geopolymer can also reduce the danger to the body's organs. It is interesting to study further is the fact that the volcanic ash-based geopolymer can not harden at room temperature [2]. This fact happened because volcanic ash is a natural pozzolanic material with a high mole ratio $\text{SiO}_2/\text{Al}_2\text{O}_3$ but low in CaO content.



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Calcium which is in a geopolymer mixture has a positive influence on the setting time and compressive strength of geopolymer product [5, 6, 7]. Ca^{2+} ions in the reaction mixtures of a geopolymer can accelerate pozzolanic reaction in solid aluminosilicate with an alkali solution. The pozzolanic reaction will lead to a faster hardening of geopolymer [6]. In addition, Ca^{2+} ions can react with excess silicate ions to form CASH (Calcium Aluminosilicate Hydrate) [9, 10] and CSH (Calcium Silicate Hydrate) [5, 6, 8]. The gel CSH (Calcium Silicate Hydrate) can help connect the gap between the hydrated phase and its particles, so we get a more dense and homogeneous matrix [6].

This research aims to study the volcanic ash geopolymer characteristics related to CaO addition. Volcanic ash geopolymer characteristics studied include setting time, compressive strength, and geopolymer resistance to sulphuric acid attacks.

2. Methods

The tools that used in this study include Vicat needle apparatus Tatonas, universal testing machine ELE, pH meter Eutech, XRF (X-Ray Fluorescence) BRUKER, AAS (Atomic Spectroscopy Absorption) Agilent Technologies 50 AA, XRD (X-Ray Diffraction) BRUKER. The materials that used in this study include volcanic ash, cement Holcim, aqua dest (H_2O), sodium silicate (Na_2SiO_3) and calcium oxide (CaO , Nofrills) technical, and sodium hydroxide (NaOH) and sulfuric acid (H_2SO_4) grade pro analyst, Merck.

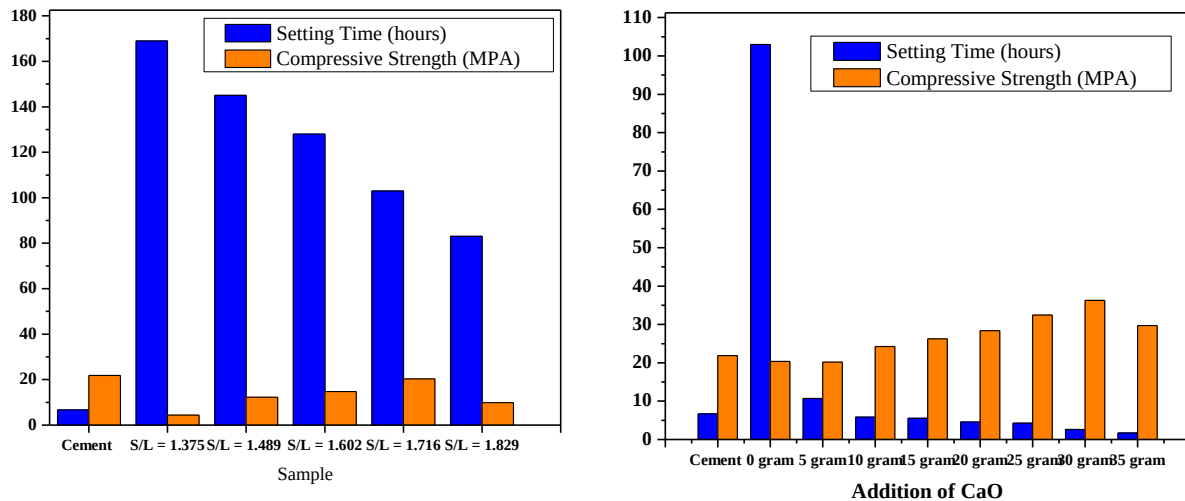
Geopolymer synthesis begins by characterizing the chemical content and mineral phase of volcanic ash, as well as the chemical content of CaO and Na_2SiO_3 technical. Initial research carried out by varying the amount of volcanic ash, to obtain the S/L optimum that used as a reference in geopolymer synthesis by the addition of CaO . Geopolymer synthesis is done by preparing the activating solution, by dissolving NaOH in aqua dest. A gel of Na_2SiO_3 dissolved in the activating solution then poured into volcanic ash and CaO and stirred until homogeneous. The mixture is poured into molds plastic cylinder (diameter: height = 1: 2) [10], then vibrate it for 2 minutes [6]. The setting time of the geopolymer paste is analyzed. A geopolymer paste is left for hardening at room temperature for at least 1 hour [11] and then heated in an oven at 60°C (curing) for 24 hours [7, 8] to stimulate the geopolymerization reaction. Geopolymers were analyzed compressive strength, the resistance of sulphuric acid attack by soaking them in sulfuric acid. The optimum geopolymer was compared to cement mortar. The best geopolymer with excellent characteristics is analyzed with XRD.

3. Result and Discussion

3.1. Volcanic ash-based geopolymer synthesis with Solid/Liquid (S/L) (without CaO addition)

Preliminary research conducted to obtain the optimum ratio S/L in order to obtain, geopolymer with high compressive strength and easy in the process (workability). Characteristics determined include setting time and compressive strength. In this study, geopolymers in the preliminary study can not harden at room temperature, so the curing process was extended. Curing is done at a temperature of 60°C to harden the geopolymers.

Figure 1(a) is a measurement result diagram of the setting time and compressive strength of geopolymer with ratio S/L and compare with cement mortar. The greater ratio S/L will produce a geopolymer with increasingly short setting time. However, a geopolymer with too large ratio S/L will cause difficulties in the process. Setting time of geopolymer with the ratio S/L = 1.8295 is still too long when compared to the setting time of cement mortar. It can be caused due to calcium oxide (CaO) in the geopolymer mixture is relatively small when compared with calcium oxide (CaO) in cement. The rapid hardening process in geopolymer with CaO addition is associated with the rapid formation of a CASH (9) and CSH phase [8].



(a). Variation of the ratio S/L and cement mortar without CaO addition (b). Variation of calcium oxide (CaO) addition at optimum S/L

Figure 1. Setting time and compressive strength of geopolymers

Geopolymer compressive strength increased with increasing the ratio of S/L but decreased at the ratio S/L = 1.8295. The increased of ratio S/L will produce the greater compressive strength of geopolymer [12]. However, the ratio S/L is too large can cause difficulties in the process. Geopolymer with the ratio S/L = 1.7160 has the highest compressive strength of geopolymer when compared with the other of ratio S/L variation. However, the compressive strength of the geopolymer with the ratio S/L = 1.7160 is lower than the compressive strength of cement with a water-cement ratio of 0.4. It can be caused due to calcium oxide (CaO) in the geopolymer mixture is relatively low. Geopolymer with the ratio S/L = 1.7160 is the optimum geopolymer ratio S/L.

3.2. Volcanic ash-based geopolymer synthesis with CaO addition

Figure 1(b) is the measurement result of the setting time and compressive strength of geopolymer hardening with the addition of calcium variations oxide (CaO). The content of calcium oxide (CaO) that relatively high in the mix will react with more excess SiO₂, which can interfere with the dissolution of Si-Al from volcanic ash in the activating solution. Therefore, the amount of excess SiO₂ in the mix will be reduced. Decreasing the number of excess SiO₂ will cause the dissolution of Si-Al from volcanic ash in the activator solution is faster, so that the resulting geopolymer would require a relatively short time to harden. However, the amount of calcium oxide (CaO) in a mixture that is too large will cause the formation of the pores, resulting in a geopolymer with relatively low compressive strength.

Ca²⁺ ions in calcium oxide (CaO) can react with excess aluminosilicate ions to form Calcium Alumino Silicate hydrate (CASH) almost like Portland cement CSH (Calcium Silicate Hydrate) [8, 9, 8]. CASH and CSH which according to [9, 13] can help connect the gap between the hydrated phase and the particles react, so we get a more dense matrix and homogeneous, and obtained the high geopolymer compressive strength [5, 6]. The interaction between Ca²⁺ ions and silicate ions in the geopolymer matrix [3] can be described as Figure 2.

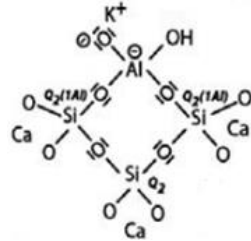


Figure 2. The existence of Ca^{2+} in geopolymer matrix

3.3. Sulphuric acid resistance of volcanic ash geopolymer with CaO addition

Figure 3 is the result of compressive strength testing of cement and geopolymer with the addition of calcium oxide (CaO) variations before and after soaked in sulfuric acid (H_2SO_4) 0.05 M for 7 days and Figure 4 is the reduction percentage of geopolymer compressive strength in sulfuric acid.

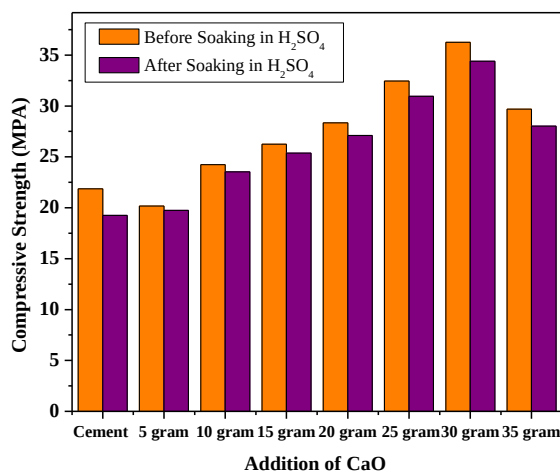


Figure 3. Geopolymer strength before and after soaking in sulfuric acid 0.05 M for 7 days.

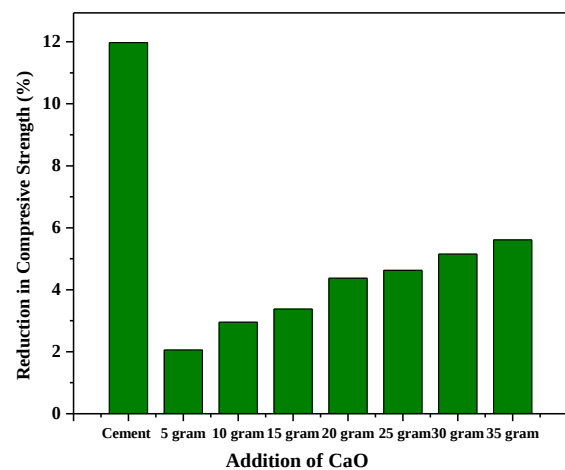
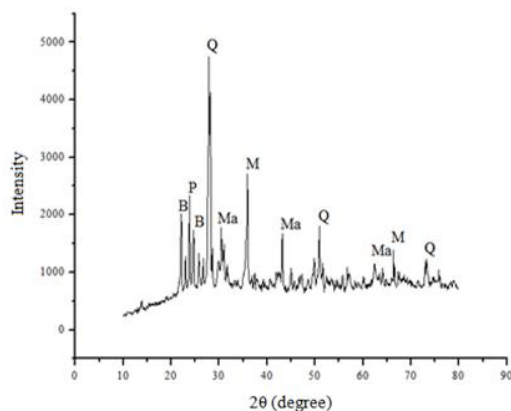


Figure 4. The reduction percentage of geopolymer compressive strength in sulfuric acid.

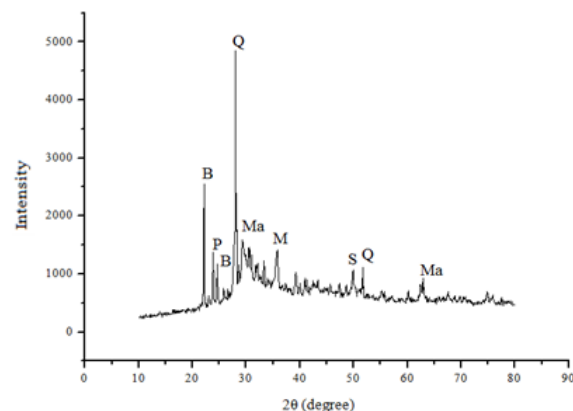
Geopolymer compressive strength decreases with the addition of CaO. According to [14], the improvement in acid resistance was due to a reduction in the CaO/SiO_2 mole ratio of the starting mixture. In this study, the addition of CaO caused a decrease in resistance to sulfuric acid, because CaO addition creates a high CaO/SiO_2 mole ratio. Low calcium content in a cement-based material resulted in lower deterioration by a sulphuric acid solution [15]. Research has been done by [16] explained that the presence of CaO leads to the formation of CSH and $\text{Ca}(\text{OH})_2$ in a geopolymer composite. These calcium-based hydrated products can be easily decomposed by an aggressive solution so resulting in a decrease in compressive strength. Ca^{2+} ions in the geopolymer can react with SO_4^{2-} ions to form gypsum according to the following equation $\text{Ca}^{2+} + \text{SO}_4^{2-} + 2\text{H}_2\text{O} \rightarrow \text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. Gypsum that formed can cause swelling volume so that the compressive strength decreases [15].

3.4. Mineral phase study by XRD on optimum geopolymer

Figure 5 is a diffractogram geopolymer with the highest compressive strength, which is Figure 5(a) is the geopolymer with the addition of 30 g of calcium oxide (CaO), and Figure 5(b) is diffractogram of volcanic ash. The mineral phases content of volcanic ash using XRD (Figure 5(b)) suggest that the volcanic ash has a relatively low amorphous phase, which is signed by a mound at 2θ between 20° - 30° .



(b). Diffractogram volcanic ash



(a). Diffractogram geopolymer with the addition of 30 g of calcium oxide (CaO)

Figure 5. Diffractogram geopolymer compare to volcanic ash. Q = quartz (SiO_2), P = potassium vanadium oxide (KVO_3), M = mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$), S = sodalite ($\text{Al}_6\text{Na}_8(\text{SiO}_4)_6(\text{Cl})_2$), Ma = magnetite (FeFe_2O_4), and B = bassanite ($\text{CaSO}_4 \cdot 5\text{H}_2\text{O}$)

Volcanic ash is dominated by minerals (Q) quartz (SiO_2) which indicated by the peak at 2θ 27.90° ; 50.90° ; and 73.27° (PDF 05-0490). Geopolymer (Figure 5(a)) containing an amorphous phase that signed by a hump at 2θ about 25° - 45° . Geopolymer with the addition of 30 g of calcium oxide (CaO) is dominated by minerals (Q) quartz (SiO_2) which indicated by the peak at 2θ 27.98° and 51.66° (PDF 05-0490). Minerals (P) potassium vanadium oxide (KVO_3) indicated by the peak at 2θ 23.81° (PDF 26-1342), minerals (S) sodalite ($\text{Al}_6\text{Na}_8(\text{SiO}_4)_6(\text{Cl})_2$) is shown by the peak at 2θ 49.82° (PDF 02-0341). The other minerals include (B) bassanite ($\text{CaSO}_4 \cdot 5\text{H}_2\text{O}$) indicated by the peak at 2θ 22.08° and 24.61° (PDF 24-1067), (Ma) magnetite (FeFe_2O_4) indicated by the peak at 2θ 29.35° and 62.50° (PDF 03-0662), and (M) mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) indicated by the peak at 2θ 35.77° (PDF 06-0258). From Figure 5, it can be seen that the mineral phase of geopolymer is more amorphous than volcanic ash signed that there has been formed the geopolymer matrix support its strength.

4. Conclusion

The optimum CaO that added is 30 g, with the setting time 2.61 hours and the compressive strength 36.26 MPa, it is better than the volcanic ash geopolymer without CaO as 103 hours in setting time and 20.34 in compressive strength. Volcanic ash-based geopolymer with the addition of CaO proven has resistance to sulphuric acid. CaO addition is proven to increase the compressive strength and decrease setting time as the formation of amorphous, dense and homogenous matrix Si-O-Si and Si-O-Al.

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