Characteristics of fly ash geopolymer based on alkaline ratio of activators for building materials: A review

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\textbf{A B S T R A C T}

The geopolymer introduced by Davidovits is a new binder for making concrete as an alternative to ordinary Portland cement. One of the materials used to make geopolymers is fly ash. The annual worldwide production of fly ash is estimated to be around 500 Mt. In making geopolymers with fly ash, scientists usually use activators such as silicate and aluminate solutions, as well as with kaolinite. The geopolymerization process is related to the metal oxide ratio of the activator solution. Geopolymers can withstand temperatures up to about 600\degree C, so they are fire/heat resistant. This paper describes the role of the comparison of dominant elements in a mixture of geopolymer paste with fly ash and alkali which produces the best quality based on compressive strength, where there is an effect of the ratio of alkali on the compressive strength of geopolymer paste. Almost all of the highest compressive strength obtained did not follow the Davidovits rule. This is caused by other factors that affect the compressive strength such as the content of elements such as Si and Al in fly ash and the curing temperature. However, the volumetric and mechanical properties of the artificial aggregate (geopolymer fly ash application) meet the requirements as a road material. It's just that the absorption value is above the requirements (>3%). Seeing the properties of these geopolymers, there is hope to be developed into materials for building materials.

\textbf{A B S T R A K}


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1. Introduction

Nowadays, waste is in demand for research as a building material. Research by utilizing mine dust waste in an amount not exceeding 5\% can increase the ability of lateritic soils as subgrade [1]. Another waste, namely fly ash, is currently being studied as a building material in the form of geopolymers to be made into concrete. Fly ash is used as a cement substitute. Although the compressive strength and tensile strength are lower, the workability of concrete

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Fly ash is industrial waste that can be found all over the world. Fly ash is a material that has distinctive properties and is a source of aluminosilicates. Fly ash is an industrial product that is proven to be suitable for producing geopolymer materials. The geopolymer properties of fly ash have been studied extensively in the last decade. A finding indicates that fly ash is suitable for making geopolymers, and the resulting geopolymer presents high mechanical properties and durability [11]. Fly ash has pozzolanic properties and is the result of power plant fuel. Fly ash mainly consists of unburned carbon and aluminosilicate particles as well as mineral constituents of fly ash including the glass phase and the crystalline phase [7]. Table 1 shows that the atomic content in fly ash varies.

<table>
<thead>
<tr>
<th>Source</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>CaO</th>
<th>MgO</th>
<th>Na₂O</th>
<th>K₂O</th>
<th>TiO₂</th>
<th>MnO₂</th>
<th>SO₃</th>
<th>P₂O₅</th>
<th>BaO</th>
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<td>2.50</td>
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<td>0.03</td>
<td>&lt;0.02</td>
<td>0.09</td>
<td>0.05</td>
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<td>&lt;0.03</td>
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<td>0.47</td>
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<td>&lt;0.02</td>
<td>0.07</td>
<td>0.04</td>
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<td>5.21</td>
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<td>0.35</td>
<td>1.75</td>
<td>0.70</td>
<td>0.24</td>
<td>0.885</td>
<td>-</td>
</tr>
<tr>
<td>Pu et al. [11]</td>
<td>29.47</td>
<td>25.56</td>
<td>2.25</td>
<td>5.21</td>
<td>0.15</td>
<td>0.05</td>
<td>0.35</td>
<td>1.75</td>
<td>0.70</td>
<td>0.24</td>
<td>0.885</td>
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<td>Khan et al. [12]</td>
<td>51.11</td>
<td>25.56</td>
<td>12.48</td>
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<td>1.45</td>
<td>0.77</td>
<td>1.32</td>
<td>1.75</td>
<td>0.70</td>
<td>0.24</td>
<td>0.885</td>
<td>-</td>
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<td>R. N. Thakur and S. Ghosh [13]</td>
<td>56.01</td>
<td>29.80</td>
<td>3.58</td>
<td>2.36</td>
<td>0.30</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

2. Fly ash content

Fly ash is industrial waste that can be found all over the world. Fly ash is a material that has distinctive properties and is a source of aluminosilicates. Fly ash is an industrial product that is proven to be suitable for producing geopolymer materials. The geopolymer properties of fly ash have been studied extensively in the last decade. A finding indicates that fly ash is suitable for making geopolymers, and the resulting geopolymer presents high mechanical properties and durability [11]. Fly ash has pozzolanic properties and is the result of power plant fuel. Fly ash mainly consists of unburned carbon and aluminosilicate particles as well as mineral constituents of fly ash including the glass phase and the crystalline phase [7]. Table 1 shows that the atomic content in fly ash varies.
3. The role of alkalils in geopolymer mixture

Geopolymer is a type of cement material with alumino-silicate content. The exact geopolymerization mechanism is not well understood because the process involves rapid chemical reactions [14]. Base activation is a chemical process that gives rapid changes to certain structures [15]. However, the predicted mechanism includes three stages: (1) separation of Si and Al atoms from the material through the action of hydroxide ions, (2) condensation of precursor ions in monomers, (3) arrangement/polymerization of monomers into polymer structures. The atomic ratio of Si:Al in the polysalalgal structure determines the field of application. Low Si:Al ratios 1, 2, and 3 form a very rigid 3D network. The high Si:Al ratio, higher than 15, gives a very dense 3D network. The compressive strength decreases significantly, especially after 7 thermal cycles. The presence of IOT increases the thermal resistance of the geopolymer paste, and did not increase the workability [6].

Alkaline activation of fly ash is different from the hydration of Portland cement. The most widely used alkaline activator is a mixture of sodium or potassium hydroxide (NaOH, KOH) and sodium silicate or potassium silicate. Alkaline liquids can be used to activate silicon (Si) and aluminum (Al) in natural or manufactured materials to produce binders [15]. Sodium hydroxide increases the amount of silicate and aluminate solutions in the geopolymer mixture. Solubility tests on various fly ash samples showed that the solubility increased when the sodium hydroxide concentration in fly ash increased, which also increased the strength of the resulting geopolymer aggregate. The compressive strength of geopolymer aggregates also increases to a maximum before decreasing again when the amount of sodium silicate increases [8]. The geopolymer, introduced by Davidovits in 1970, is synthesized by mixing aluminosilicate reactive materials such as fly ash or iron ore tailings and a strong alkaline solution (such as NaOH or KOH) at room temperature. Alkali activation of waste materials, was first introduced in the 1940s is the origin of geopolymer research [7].

4. Compressive strength of geopolymer paste

Geopolymerization is highly dependent on the physicochemical properties of fly ash, the availability of silicate and aluminate solutions, and the concentration of added sodium hydroxide [8]. This is evidenced by using 6 types of fly ash and 6 variants of alkaline ratios, the paste that produces the highest compressive strength are obtained for Fly ash A = 44.5 MPa, Fly ash B = 13 MPa, Fly ash C = 16.5 MPa, Fly ash D = 13 MPa and Fly ash E = 3.36 MPa. Different fly ash can give different reactivity because the chemical composition varies. The effect of NaOH molarity, fly ash and alkali activator ratio, NaSiO/NaOH ratio, and curing temperature are very important to achieve optimal geopolymer strength [15]. The addition of SP did not cause a significant change in the strength of the alkali activated fly ash paste, and did not increase the workability [6].

The study on geopolymers prepared from iron ore tailings was tested after exposure to 3 and 7 thermal cycles at different heating target temperatures of 200°C, 400°C, and 800°C. Fly ash was replaced in stages from 0% to 30% at intervals of 10% by weight. Under the influence of thermal cycling, the compressive strength decreases significantly, especially after 7 thermal cycles. The presence of IoT increases the thermal resistance of the geopolymer so that there is an increase in compressive strength. The gradual replacement of fly ash up to 30% leads to a reduction in porosity and the microcracks become much denser, resulting in increased compressive strength [7]. The compressive strength for geopolymer specimens with different alkali content shows that the compressive strength increases almost linearly with increasing alkaliinity of the mixture. Increasing the alkali content of the geopolymer mixture, results in a decrease in the number and size of unreacted fly ash particles, indicating the formation of more aluminosilicate gels resulting in an increase in compressive strength [13]. Table 2 shows the compressive strength of the paste from several previous studies.

<table>
<thead>
<tr>
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<th></th>
<th></th>
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</tr>
</thead>
<tbody>
<tr>
<td>Na2O/SiO2</td>
<td>1.016</td>
<td>0.915</td>
<td>2.898</td>
<td>0.363</td>
<td>0.180</td>
<td>0.155</td>
</tr>
<tr>
<td>SiO2/Al2O3</td>
<td>0.845</td>
<td>1.654</td>
<td>2.062</td>
<td>0.299</td>
<td>2.120</td>
<td>4.000</td>
</tr>
<tr>
<td>H2O/Na2O</td>
<td>0.385</td>
<td>12.676</td>
<td>2.969</td>
<td>2.674</td>
<td>10.320</td>
<td>8.170</td>
</tr>
<tr>
<td>Highest Compressive Strength</td>
<td>44.5 Mpa</td>
<td>96.2 MPa</td>
<td>50 MPa</td>
<td>70 MPa</td>
<td>103 MPa</td>
<td>37.27 MPa</td>
</tr>
</tbody>
</table>

5. Discussion

The ratio of Na2O/SiO2, SiO2/Al2O3, and H2O/Na2O in the geopolymer is known by calculating the total weight of the content of each compound. After knowing the content of each in weight, it can be calculated the ratio in moles by dividing the weight of each by the atomic mass. For example, for a mixture of A-1 to find the ratio of Na2O/SiO2, the total weight of Na2O and SiO2 must first be found both from fly ash and from reactants (alkali). The total weight of Na2O = 9.703 grams and SiO2 = 21.563 grams. Then converted into moles by dividing the total weight of each by the mass of each atom. The atomic mass of Na2O = 62 gram/mol and SiO2 = 60.09 gram/mol, then Na2O = 0.0017 gram/62 gram/mol = 0.157 mol and SiO2 = 21.563 gram/60.09 gram/mol = 0.358 mol.
The ratio of Na₂O/SiO₂ = 0.157 mol/0.359 mol = 0.436 is obtained. The ratio of the whole mixture is based on the results of previous studies [8][6][7][11][13].

Figure 1 shows, that with the ratios of Na₂O/SiO₂, SiO₂/Al₂O₃, and H₂O/Na₂O, there are some discrepancies with the intervals given by Davidovits. High compressive strength polarization occurs at more than one interval. At the Na₂O/SiO₂ ratio, it can be seen that the polarization of compressive strength above 50 MPa is concentrated at the interval of 0.321-0.405, partly scattered at the ratio of 0.18 and 0.915. In the SiO₂/Al₂O₃ ratio, it can be seen that the polarization of compressive strength above 50 MPa is concentrated at the interval of 0.162-0.522, partly scattered at the ratio of 1.654, 2.083, and 2.120. At the H₂O/Na₂O ratio, it can be seen that the polarization of compressive strength above 50 MPa is concentrated at intervals of 2.408-3.006, partly scattered at the ratio of 10.320 and 12.676. The results above show that with the same ratio of Na₂O/SiO₂, SiO₂/Al₂O₃, and H₂O/Na₂O, the compressive strength obtained is different. Davidovits limits the geopolymer alkali ratio at the following intervals [8]:

a) 0.2<Na₂O/SiO₂<0.28;
b) 3.5<SiO₂/Al₂O₃<4.5;
c) 15<H₂O/Na₂O<17.5.

Based on the interval above for the Na₂O/SiO₂ ratio, the average compressive strength in that interval is 21.60 MPa, at the SiO₂/Al₂O₃ ratio, the average compressive strength in the interval is 26.715 MPa, and 14.75 MPa is the strength press the average for the interval H₂O/Na₂O ratio. Compressive strength greater than 50 MPa was found at the average ratio of Na₂O/SiO₂ = 0.382, SiO₂/Al₂O₃ = 0.695 and the ratio of H₂O/Na₂O = 3.743. This shows that the alkali ratio is not the only determinant of geopolymer performance. The highest compressive strength of the ratio of Na₂O/SiO₂, SiO₂/Al₂O₃, and H₂O/Na₂O (Table 2). However, it is not necessarily the best ratio that can be used. This is because the compressive strength value is obtained by different methods. The difference in curing temperature and fly ash used can also affect the compressive strength.

In the study of geopolymer pastes with class C fly ash, low water to fly ash (W/F) ratio could satisfy fluidity. Increasing the sodium hydroxide concentration decreases the fluidity of the mixture. In addition to the W/F ratio, the difference in curing temperature also has an effect. With a curing temperature of 70°C for 24 hours, the geopolymer paste experienced a much higher compressive strength. This is because the structure becomes denser, where the density of the paste structure contributes to the increase in compressive strength [16]. Even the composition of lime (Ca) in the geopolymer also has an effect. The addition of lime sand increases the compressive strength of fly ash based geopolymer because it can change the composition of the gel phase in the geopolymer structure and with physical strengthening due to good sand grain bonding. The compressive strength of the geopolymer paste is lower than that of the geopolymer mortar because in the gel phase the geopolymer mortar has a Ca content which is much higher than the Ca content of the geopolymer paste. The value of this parameter increases with an increasing dose of alkali and silicate. At one point, the maximum value is reached and then
it starts to decrease. The compressive strength increases with increasing NaOH concentration and the mass ratio \( \frac{w(Na_2SiO_3)}{w(NaOH)} \), reaches its maximum value at one point and then decreases. Fly ash based geopolymer can be considered as a brittle material based on the maximum compressive strength and minimum flexural strength values. On the other hand, from the increase in compressive strength, there was a slight decrease in the flexural strength of the fly ash geopolymer. In addition, the presence of good physical bonding of the sand grains also contributes to the strength of the fly ash based geopolymer [17].

Artificial aggregate is one application of geopolymer fly ash as a building material (road pavement material). The ratio of alkaline activator between Sodium Silicate and Sodium Hydroxide used is 1.5, 2, 2.5, and 3. Aggregate is made using a granulator. The volumetric and mechanical properties of the aggregate indicate that the aggregate meets the requirements for use as a road pavement material. The weakness found is that the aggregate absorption is greater than 3% (i.e. as low as 6.1% at 2.5% alkali ratio) [5][4].

6. Conclusion

The conclusion of the discussion of the results of several studies on the use of geopolymers as building materials is as follows:

1) There is an influence of the alkali ratio on the compressive strength of geopolymer paste, but the highest compressive strength almost entirely does not follow the Davidovits rule. This is due to other factors that affect the compressive strength such as the content of elements such as Si and Al in fly ash and the curing temperature.

2) The application of geopolymer as an artificial aggregate for road materials, shows weakness in its absorption (>3%), while other characteristics meet the requirements.

Acknowledgements

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REFERENCES