The effect of TiO$_2$ addition on thermal resistance of geopolymer mortar based low alumina fly ash

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Abstract. The utilization of fly ash with low alumina has been carried out. The addition of TiO$_2$ to the base material of fly ash and fly ash added with 20% metakaolin mixed with an alkaline solution has been characterized by heat resistance, compressive strength and porosity. These results indicate that the addition of TiO$_2$ to both fly ash and fly ash with an additional 20% metakaolin shows a reduction in porosity reduction, an increase in the compressive strength value, and an increase in the thermal resistance of the sample. Despite an increase in the compressive strength value, however, the minimum requirement for a fire brick has not been achieved.

1. Introduction

Waste from coal combustion in steam power plants consists of fly ash and bottom ash, categorized as B3 waste by the Government of Indonesia Regulation number 85 of 1999 [1]. The volume of fly ash reaches 75% of the total waste. Fly ash, based on the ASTM 618 standard, is classified into class C and class F. This difference is based on the calcium oxide content contained in it. Class C fly ash contains CaO> 20% while class F contains CaO <10% [2].

The composition of fly ash is highly dependent on the coal input used and the treatment given during the combustion. Therefore, there may be differences in the chemical composition of fly ash in a single generator complex. Research conducted on fly ash originating from coal combustion power plant (PLTU) Asam-Asam reported various studies showing different results, especially the contents between alumina and silicate. Alumina and silicate contents are 45.89% SiO$_2$ and 15.49% Al$_2$O$_3$ [3]. Nevertheless, another research said 74.2% SiO$_2$ and 5.7% Al$_2$O$_3$ [4].

The use of fly ash in cement substitution can reduce concrete conductivity by substituting cement with fly ash. Replacing cement as much as 30% with fly ash can reduce the value of thermal conductivity by 28% [5]. The compressive strength value of concrete produced from the substitution of cement with fly ash is equivalent to standard concrete's compressive strength. Still, it requires a relatively long life span due to the fly ash reaction occurring after the cement hydration reaction [6].
The use of fly ash in the structure world is not only partially substituting cement for fly ash, but fly ash as a whole can replace the function of cement as a binder. The term known today is a geopolymer. Geopolymers are inorganic polymers produced by aluminosilicates' reactions in a high alkaline environment to form a 3-dimensional amorphous polymer structure consisting of Si-O-Al bonds [7]. The widespread application of fly ash is in the structural field, especially as a substitute for cement, which results in a strong and environmentally friendly concrete produced [8].

The geopolymerization reaction that occurs will produce a geopolymer with the best compressive strength, requiring a ratio of 3.3> Si/Al <4.5 [9,10]. Therefore, one of the methods used to achieve the required balance is by mixing fly ash with high alumina materials. Besides, adding TiO₂ nanoparticles will improve the mechanical properties and thermal resistance [11].

The addition of nanoparticle sized TiO₂ resulted in very high production costs; however, the use of TiO₂ microparticle has reduced thermal conductivity. Simultaneously, the addition of Metakaolin can improve the mechanical properties of the geopolymer mortar produced. Additionally, this study aimed to study fly ash's potential application with low alumina content as a geopolymer refractory with adding TiO₂.

2. Methods

The raw materials used are fly ash, kaolin, TiO₂, NaOH, and Na₂SiO₃. Class F fly ash comes from PLTU Asam-asam, South Kalimantan (SiO₂ 50.16%, and Al₂O₃ 4.98%). Kaolin is natural kaolin from South Kalimantan, then calcined at 750°C for 3 hours to form Metakaolin (SiO₂ 72.98% and Al₂O₃ 21.08%) [12]. Sodium hydroxide (NaOH) pellets for analysis grade produced by Merck. Natrium hydroxide (Na₂SiO₃) solution for technical quality made by PT Brataco’s (Na₂O 16.27%, SiO₂ 38.23%).

TiO₂ (0%, 1%, 3%, and 5%) was added to raw material, not only pure fly ash (FA) but also fly ash with the addition of 20% metakaošlin (FM). Then, those mixed until homogeneous. The Alkaline solution was prepared by mixing the Na₂SiO₃ and 5M NaOH in a beaker glass at room temperature until homogeneous. The raw material and alkaline solution mixed, which has formed a paste, is put into the mould and left in the sun for three days and then cured at 60 °C. Sample mould size for heat resistance testing is 15 x 3 x 5 cm, and sample mould size for compressive strength testing is cylindrical mould 3 x 6 cm. Samples were stored until 28 days old and then tested for porosity, compressive strength, and heat resistance. The sample code is presented in Table 1 below.

| Table 1. Raw material and sample code composition |
|-----------------------------------------------|
| TiO₂  | 0% | 1% | 3% | 5% |
| FA + 0% MK | FA0 | FA1 | FA3 | FA5 |
| FA + 20%MK | FM0 | FM1 | FM3 | FM5 |

Porosity testing used the Archimedes method. Compressive strength testing used the Universal Testing Machine (UTM) equipment. The treatment for heat resistance testing is to heat one side of the sample to 957°C for 5 minutes and record the other side’s propagation temperature every 30 seconds.

3. Result and Discussion

3.1 Porosity Characterization

The results of porosity as the function of TiO₂ addition are shown in Figure 1. These results indicate no visible linear relationship between the additional TiO₂ in the samples for each composition. However, from this result, we can see that TiO₂ reduces porosity on the sample with Metakaolin. The presence of porosity is due to trapped air during the moulding process. The trapped air in the sample comes out due to heating and leaves a cavity.
Figure 1. The relationship between the addition of TiO$_2$ to the porosity of samples.

Besides, porosity can also occur due to micro factors that can occur during the geopolymerization process. The accurate calculation between the alkaline solution and the aluminosilicate base material will result in better physical and mechanical characteristics [9]. The presence of porosity in the geopolymer material is caused by a lack or excess of alkaline solution, especially NaOH. In class F fly ash, there was at least 37% inactive SiO$_2$, thus blocking the geopolymerization process. Based on these results, it can be observed that Metakaolin's presence can reduce the amount of inactive SiO$_2$, which then results in a material with better densification.

3.2 Compressive Strength Characterization
The results of the compressive strength test are presented in Figure 2 below. The black line shows the compressive strength characteristics of fly ash as the base material, while the red-coloured line indicates the fly ash added with 20% metakaolin. The compressive strength test results showed that the compressive strength of the sample with the addition of Metakaolin was higher than the sample without Metakaolin's addition. In this study, the contribution made by the addition of TiO$_2$ can also be observed [13].

The highest compressive strength value produced is 12.05 MPa, owned by the FM5 sample. Meanwhile, the lowest compressive strength value of 4.21 MPa is owned by the FA1 sample. This test results do not yet meet the compressive strength requirements for a fire brick, which is specifically 13.9-15 MPa [14]. The compressive strength test results, which have been carried out previously with the same fly ash source, reached 90 MPa [3]. The difference in compressive strength values is believed to be due to Al and Si chemical composition. The previous study's Al and Si content were 15.49% and 45.89%, respectively, while in this study, 4.98% and 50.16%, respectively. The difference in chemical composition possessed by fly ash highly depends on the coal, which is used as the food for the production of energy produced by the PLTU. The geopolymer's high compressive strength will be achieved if the Si: Al ratio is between 3.3 to 4.5 [9,15]. Even though it does not meet the minimum requirements for a fire brick's compressive strength, the addition of TiO$_2$ increases the compressive strength value.
Figure 2. The relationship between the addition of TiO$_2$ to the compressive strength value.

3.3 Heat Resistance Test

On the A-side of the samples, direct heat from the oxy-acetylene ignition source is received constantly at 954°C, and on the B side, the temperature obtained is measured with a thermocouple. The heat transfer to side B for 5 minutes. After 5 minutes, side B's measured temperatures were FA0 71°C, FA1 70°C, FA3 69°C, FA5 55°C, FM0 49°C, FM1 59°C, FM3 61°C, and FM5 43°C. Visually, samples that have undergone heating are presented in Figure 3. Based on this figure, it can be seen that there are sample cracks that occur around the heating point. The addition of Metakaolin as the base material for geopolymer is not only able to provide improvement in the compressive strength, but it is also able to withstand heat from the outside so that the aperture can be reduced.

Figure 3. The visual state of samples (a) FA5 and (b) FM5, after thermal treatment.

The determination of the thermal resistance characteristics, such as the heating rate, is determined by recording the temperature values recorded on side B. The relationship between the temperatures recorded on the thermocouple to the heating time is shown in Figure 3. Each sample shows different characteristics. This pattern indicates the heating rate per unit time received by the sample, as in equation (1) to equation (8).

\[
\begin{align*}
    y_{FA0} &= 0,561x^2 + 1,377x + 49,6 \\
    y_{FA1} &= 1,015x^2 - 2,892x + 57,9 \\
    y_{FA3} &= 1,697x^2 - 2,987x + 40,3
\end{align*}
\]
Based on Figure 4, it can be observed that the use of Metakaolin as a base material can make a positive contribution to temperature resilience. From the two graphs above, it can be seen that the two graphs with a composition of 5% are the samples that have the highest thermal resistance when compared to other samples. Thermal resistance has an inverse relationship to thermal conductivity by entering the values of all the components required for the calculation of thermal conductivity in equation 9. Figure 5 shows that the best thermal resistance value is shown by the sample with the addition of 5% TiO2. This result is per the statement of Timakul et al [13]. The research results' thermal resistance characteristics are better when compared to the results of the study using volcanic ash as a base material, but not better when using fly ash with an Al content greater than 20% [16].

\[ k = \frac{Q \cdot \ell}{A \cdot \Delta T} \]  

Figure 5. The relationship between the addition of TiO2 to the thermal conductivity of samples.
4. Conclusion
The effect of adding TiO2 to low alumina fly ash, which was previously reacted with alkaline activator, has shown results, so it is concluded that TiO2 contributes to improving the compressive strength value, decreasing the porosity value, and increasing the thermal resistance properties of the sample. The addition of 20% metakaolin also contributed the same as the addition of TiO2. The minimum requirement for the compressive strength value for a fire brick has not been fulfilled, but the ability to withstand exposure to the temperature is still reliable.

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