THE EFFECT OF TEMPERATURE ON CEMENT CLICKER CHARACTERIZATION WITH A 10% SUBSTITUTION OF BASALT STONE ON LIMESTONE MASS

EL EFECTO DE LA TEMPERATURA EN LA CARACTERIZACIÓN DE CLICKER DE CEMENTO CON UNA SUSTITUCIÓN DEL 10% DE LA PIEDRA DE BASALTO EN LA MASA DE PIEDRA CALIZA

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ABSTRACT

This research was conducted to determine the effect of temperature on the chemical content and crystal structure of the cement clinker with 10% substitution of basalt on the mass of limestone. The cement clinker is made from the composition of limestone, basalt stone, clay, silica stone and iron sand. Basalt stone used came from the East Lampung area. The basalt stone has fulfilled ASTM C618 standard with a total compound of SiO₂ + Al₂O₃ + Fe₂O₃ of 79.2%. The raw material was then mixed, milled, formed into pellets with a size of 0.8 - 1.4 cm and continued with combustion at calcination temperatures of 1000 °C, 1100 °C and 1200 with a holding time of 2 hours. Based on the results of the XRF test (X-Ray Fluorescence) of the three cement clinker samples with variations in temperature used, the sample is closer to the standard at a temperature of 1000 °C. For the XRD (X-Ray Diffraction) test results, the three samples have tetragonal, monoclinic, rhombohedral, and orthorhombic crystal structures. As for the MO test results, there was a strong binding between iron sand, limestone, clay, and silica sand characterized by a smooth surface while basalt stones that look like black holes were not completely bound.

Keywords: Basalt Stone; Limestone Mass; Cement; Temperature.

RESUMEN

Esta investigación se realizó para determinar el efecto de la temperatura sobre el contenido químico y la estructura cristalina del clínker de cemento con un 10% de sustitución de basalto sobre la masa de piedra caliza. El clínker de cemento está hecho de la composición de piedra caliza, piedra de basalto, arcilla, piedra de sílice y arena de hierro. La piedra de basalto utilizada vino del área de East Lampung. La piedra de basalto
1. INTRODUCTION

Cement is an important construction material, which is widely used in civil engineering throughout the world (Laibao et al., 2013; Marzuki, 2009). As infrastructure development in Indonesia increases, so does the demand for the cement industry. The need for cement causes the increase of cement consumption level in Indonesia increase by year (Putri & Ramadhani, 2016). In order to improve the quality of cement, building construction continues to be improved including the quality of materials used (Waani & Elisabeth, 2017). According to experts working on observations on global warming, 7% of the production of CO2 emissions in nature is derived from cement production. It is also known that about 1 ton of cement produces 1 ton of CO2 (Uzal, B., Turanli & dan Mehta, 2007), so this encourages experts in the field of building construction engineering to look for alternative materials to replace or substitute cement. In the manufacture of cement preceded in the manufacture of clinker that is the process of changing the physical and chemical raw materials into clinker, where the clinker has undergone a cooling process and then grinding (grinding process). Clinkers are "semi-finished" materials during cement production, produced by burning limestone and alumina-silicate-containing materials such as clay (Rahmawatie & Damayanti, 2017). In making cement, the readiness of the main raw materials such as limestone is very important, where limestone in the formation of cement requires a composition of 80%. So that if their needs are not met, the results will unmet demand and the cessation of the production process (Fitriadi & Utama, 2014; Ishlah, 2008; Kahn, 2002). Therefore an alternative material is needed to prevent the scarcity of raw materials, but it has a composition that is similar to limestone, so it does not affect the quality of cement produced. Pozzolan material such as basalt is a material from the coal industry that can be used as a substitute material in cement (Waani & Elisabeth, 2017). The amount of basalt stone material reserves in Lampung Province is 318,480,000 tons and has not been explored optimally. Based on the analysis of the chemical composition of scoria basalt stone material from Labuhan Maringgai, East Lampung, Indonesia, namely SiO2 + Al2O3 + Fe2O3 is 78.66%. Basuhan scoria Labuhan Maringgai East Lampung, Indonesia fulfills ASTM C618 (American Society for Testing and Materials C168) requiring that the chemical component is a SiO2 + Al2O3 + Fe2O3 minimum of 70% (Ningsih et al., 2012; Oktamuliani et al., 2015; Patty, 2013). So many reserves have only been used as a foundation for housing construction. By optimizing basalt minerals, the economic value will increase, for this reason it is necessary to conduct research on the characteristics of basalt minerals as an alternative raw material for cement clinkers (Amin, 2017). When basalt reacts with other chemicals it does not produce reactions that are harmful to the environment. Therefore basalt is suitable for applications, especially in the field of ceramics (Alisjahbana et al., 2018; Saraya, 2014). Basalt is chemically rich in magnesium oxide, calcium, sodium, potassium, silicon and iron (Benmohamed et al., 2016; Chirikure et al., 2010; Dhand et al., 2014). Basalt stone can be used as an alternative raw material for Portland cement (Andrade et al., 2010), especially as a substitute for clay raw materials in certain areas where clay resources have begun to be scarce. It is recommended that basalt stones can replace clay in 1:1 proportions (Andrade et al., 2010; Ardiantono et al., 2018). According to research by El-Desoky et al., 2017,
clinker furnaces with temperatures around 1200-1450 °C show good combustion (El-Desoky et al., 2017). All samples that have been sintered at 1450 °C have a unique clinker structure. The dominant mineralogical phases such as alit, winding, calcium alminate, ferrite and lime crystallized to produce a peak of 2 Theta (2θ). The levels of various types of reactions in clinkers according to El-Hafiz et al., 1971, the levels of various types of reactions in clinkers that are affected by temperature are as follows (El-Hafiz et al., 2015):

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>100-500</td>
<td>The clinker is dried and the water content evaporates.</td>
</tr>
<tr>
<td>500-600</td>
<td>Dehydroxylation from clay 2SiO2Al2O3.2H2O → 2SiO2 + Al2O3 + 2H2O ↑</td>
</tr>
<tr>
<td>700</td>
<td>Silicate activation and water evaporation</td>
</tr>
<tr>
<td>700-900</td>
<td>Decarboxylation of calcium carbonate with the main combination of alumina, ferric oxide</td>
</tr>
<tr>
<td>900-1200</td>
<td>Belite formation from 2CaCO3 + SiO2 → C2S + CO2 ↑</td>
</tr>
<tr>
<td>&gt;1250</td>
<td>Liquid phase formation (aluminate and ferrite)</td>
</tr>
<tr>
<td>1300</td>
<td>The liquid phase appears and the C2S reaction with CaO forms to form C3S</td>
</tr>
<tr>
<td>1450</td>
<td>As the reaction is complete, alite and belite increase scattered in several small sizes of limestone</td>
</tr>
</tbody>
</table>

Based on the problems and solutions above, a study was carried out on the effect of temperature in the processing of cement clinkers by substituting (10%) of basalt against the mass of limestone in the process of making cement clinkers. Cement clinker was made with the composition of substitution limestone basalt, clay, silica stone, iron sand.

2. RESEARCH METHODOLOGY

Sample preparation (Pellet making), sample preparation was carried out in the following steps:
Raw materials such as limestone, basalt, clay, silica sand and iron sand were prepared with a percentage of mass in 2 kg, namely basalt (8% = 160 g), limestone (72% = 1440 g), clay (9% = 180 g), silica as much (10% = 200 g), and iron sand as much (1% = 20 g). The composition of the raw material was prepared and then ground for 5-6 hours in a ball mill until it becomes a powder mixture. The powder was filtered using 270 mesh sieve, clinker pellet formation using a pelletizing machine with water added to the powder mixture that has been ground with a ball mill and formed into small granules with a size of 0.8-1.4 cm, pellets were dried for 1-2 days at room temperature, the pellet was heated for 5-6 hours at 100 °C (Suryanarayana, 1998).

The reduction process (heat treatment), the reduction process was carried out with the following stages: 12 dried pellets as many as 12 grains on a gravitational disc were inserted into the muffle furnace with room temperature as the initial temperature, the temperature was raised slowly on the muffle furnace until it reaches the specified temperature that was at a temperature of 1000°C, 1100°C, 1200°C, the process of raising the temperature was stopped when the furnace reached the temperature specified number, sintering carried out for 2 hours, the sample was left at temperature room until the temperature in the sample was equivalent to room temperature (Widyawati, 2012).

3. RESULTS AND DISCUSSION

The raw material used in making cement clinker was characterized by using the XRF method, the results of the XRF analysis on the raw material for making cement clinker are shown in Table 1.

<table>
<thead>
<tr>
<th>Component</th>
<th>Basalt Stone</th>
<th>Lime Stone</th>
<th>Silica Stone</th>
<th>Iron-sand</th>
<th>Clay</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>47.3</td>
<td>4,036</td>
<td>95.2</td>
<td>18.7</td>
<td>53.8</td>
<td>%</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>18.9</td>
<td>1,653</td>
<td>3.1</td>
<td>6.3</td>
<td>27.4</td>
<td>%</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>12.9</td>
<td>0.552</td>
<td>0.4</td>
<td>58.0</td>
<td>15.5</td>
<td>%</td>
</tr>
</tbody>
</table>
Based on the XRF analysis data in Table 1, it shows that the chemical content in limestone was dominated by CaO compounds as much as 92.9%, while the remaining compounds were SiO2, Al2O3, MgO, K2O, TiO2, and Fe2O3. For silica stones, the chemical content was dominated by SiO2 compounds of 95.2% and the rest were Al2O3, CaO, TiO2, and Fe2O3 compounds. For iron sand, the highest chemical content was found in Fe2O3 compound at 58.0%, while the rest were MgO, Al2O3, SiO2, SO3, K2O, CaO, TiO2, V2O5, Cr2O3, MnO, and Eu2O3. For the biggest clay compounds, SiO2 was 53.8% and Al2O3 was 27.4%, while the rest were MgO, Fe2O3, K2O, CaO and TiO2 compounds. As for the chemical content in basaltic rocks, the SiO2 compound was dominated by 47.3%, Al2O3 is 18.9%, and Fe2O3 is 12.9%. Based on ASTM C168 pozzolan requirements, the minimum SiO2 + Al2O3 + Fe2O3 compound content was ± 70%.

While basalt stone had all three compounds of 79.2%. Thus basalt had fulfilled the requirements as a raw material for pozzolan for making cement clinker.

Furthermore, an analysis of the cement clinker results from combustion, XRF analysis results of the chemical content of the cement clinker sample to the combustion temperature variation that was sintered for 2 hours with a substitution of 10% basalt stone to the mass of limestone is shown in Table 2.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Combustion Temperature Variations</th>
<th>ASTM C150</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1000°C</td>
<td>1100°C</td>
<td>1200°C</td>
</tr>
<tr>
<td>CaO</td>
<td>60.93</td>
<td>55.64</td>
<td>55.75</td>
</tr>
<tr>
<td>SiO2</td>
<td>21.18</td>
<td>25.38</td>
<td>26.36</td>
</tr>
<tr>
<td>Fe2O3</td>
<td>6.84</td>
<td>7.11</td>
<td>7.45</td>
</tr>
<tr>
<td>Al2O3</td>
<td>8.22</td>
<td>7.57</td>
<td>7.08</td>
</tr>
<tr>
<td>MgO</td>
<td>1.31</td>
<td>1.48</td>
<td>1.86</td>
</tr>
<tr>
<td>SO3</td>
<td>0.27</td>
<td>1.39</td>
<td>-</td>
</tr>
<tr>
<td>TiO2</td>
<td>0.64</td>
<td>0.69</td>
<td>0.67</td>
</tr>
<tr>
<td>MnO</td>
<td>0.12</td>
<td>0.27</td>
<td>0.13</td>
</tr>
<tr>
<td>K2O</td>
<td>0.28</td>
<td>0.26</td>
<td>0.39</td>
</tr>
</tbody>
</table>

Based on the results of the XRF analysis in Table 5.2, the cement clinker sample powder with the treatment temperature closest to the ASTM C150 standard for CaO content was at 1000 °C, SiO2 was at 1000 °C, Fe2O3 was at 1000 °C, Al2O3 was at 1200 °C MgO was at 1000 °C and SO3 was at 1000 °C. So that it can be said that the cement clinker content with temperature variations closer to ASTM C150 was at a temperature of 1000 °C (ASTM C618, 2008; Bendersky, 2001).

Characterization of the crystal structure of cement clinker samples in powder form was carried out using PANRlytical XRD. The cement clinker sample was inserted into the holder then an XRD analysis was performed to see the compounds arranged in the cement clinker sample after the reduction process. The process of reducing the cement clinker was done by heating it in a furnace. In this test using three samples
of cement clinker namely cement clinker heated at temperatures of 1000 °C, 1100 °C, and 1200 °C. Each sample was heated for 2 hours. The results of the cement clinker characterization can be seen in Figure 1, 2 and 3.

XRD test results of cement clinker samples at a temperature of 1000 °C, for cement clinker samples carried out by heating at a temperature of 1000 °C with a holding time of 2 hours and XRD test results obtained as in Figure 1.

![Figure 1](image.png)

Figure 1. The compounds are arranged in a cement clinker sample at a temperature of 1000 °C with a holding time of 2 hours.

The graph in Figure 1 shows the crystalline phase of the cement clinker sample at 1000 °C with a holding time of 2 hours. The formation of monoclinic crystalline structure with the highest peak of Ca at an angle of 37.3784° with the Larnite phase with chemical compound Ca2(SiO4). In addition to the position 37.3784 ° other peaks were at position 20 (23.1018°, 26.6473°, 28.2071°, 32.5529°, 33.1172°, 34.1503°, 41.2621°, 42.4464°, 43.2717°, 44.3655°, 45.818°, 47.3915°, 50.1739°, 58.1511°, and 68.2573°). In addition to the Larnite phase the Gehlenite compound with the Ca2Al(AlSiO7) chemical compound formed a tetragonal crystal structure. In the tetragonal crystal structure with the highest peak was formed with an angle position of 29.3387°. Other peaks are also in the position of 20 (20.8718°, 24.0519°, 31.4276°, 48.4707°, 52.0544°, 53.8732°, 61.0135°, 64°, 1404°, and 67.3556°). Then orthorhombic crystal structure formed with the mineral Forsterite with the chemical compound Mg1.72Fe.28(SiO4) with a peak of 2θ at 29.3387°, and the other peak was also at position 20 (35.5826°, 36.5026°, 39.4885°, 40.2782°, 46.6843°, 56.581°, and 62.6267°).

Cement clinker sample at a temperature of 1100 °C, the cement clinker samples were heated at a temperature of 1100 °C with a holding time of 2 hours and XRD test results are obtained as in Figure 2.
Figure 2. The compounds arranged in a cement clinker sample at 1100 °C with a holding time of 2 hours.

The graph in Figure 2 shows the highest crystalline phase that was a cement clinker sample with a temperature of 1000 °C and a holding time of 2 hours. The formation of a tetragonal crystalline structure with the highest peak belonging to Ca at position 2θ 31.3703° of magnesian gehlenite phase with chemical compounds that was Ca2(Mg0.25Al0.75)(Si1.25Al0.75O7). In addition to the 31.3703° position, the other peaks were also in the position of 2θ (23.1811, 29.0868, 36.6901°, 37.431°, 39.2519°, 39.4928°, 45.8021°, 47.1941°, 50.1135°, 52.0715°, 53.2772°, 56.33382°, 61.1777°, 65.1016°, 67.949°, and 76.0103°). In addition to the magnesian gehlenite phase, Bredigite compounds with the chemical compound Ca1.7Mg0.3SiO4 were also formed, orthorhombic crystal structures. In this crystal structure the highest peak was formed with an angle position of 32.624°. Other peaks were also in position 2θ (25.4684°, 26.3603°, 27.5439°, 30.1388°, 32.1386°, 32.9119°, 33.5333°, 34°, 33.17°, 38.4329°, 40.3272°, 40.7599°, 41.2256°, 43.6143°, 44.4130°, 45.2331°, 47.8456°, 49.5264°, 54.2678°, 57.1423°, 58.6335°, 59.1218°, 68.9647°, and 70.4678°). Then formed a rhombohedral crystal structure such as the mineral Hematite with a chemical compound Fe2O3 had a peak with a position of 2θ at 23.9873°, with another peak at position 2θ (35.5688°, 62.589°).

Sampel klinker semen pada suhu 1200°C, pada sampel klinker semen ini dilakukan pemanasan furnace pada suhu 1200°C dengan waktu tahan selama 2 jam dan diperoleh hasil pengujian XRD seperti pada Figure 3.

Figure 3. The compounds arranged in a cement clinker sample at 1200 °C with a holding time of 2 hours.

The graph in Figure 3 shows the highest crystalline phase in a cement clinker sample at 1200 °C with a holding time of 2 hours. The formation of a tetragonal crystalline structure with the highest peak of Ca at
an angle of 31.3624° phase of the magnesian Gehlenite phase with chemical compounds was \((\text{Mg}0.25\text{Al}0.75)\) \((\text{Si}1.25\text{Al}0.75\text{O}_7)\). In addition to the 31.33624° position, the other peaks were also in the 2θ position (16.1989°, 23.9696°, 29.0925°, 36.6928°, 37.4274°, 50.1295°, 52.0412°, 61.2588°, 62.7966°, 65.0009° and 68.0865°). In addition to the magnesian Gehlenite phase formed Bredigite compounds also had a chemical compound \(\text{Ca}1.7\text{Mg}0.3\text{SiO}_4\) formed orthorhombic crystal structure. In the orthorhombic crystal structure the highest peak was formed with an angle position of 32.6371°. Other peaks were also in the position of 2θ (26.3765°, 33.5475°, 40.3495°, 40.7646°, 42.7593°, 43.6319°, 45.2609°, 47.2165°, 47.8648°, 59.1833°, 68.9610°, 70.4598° and 72.8017°). Then the Larnite \(\text{Ca}2\text{SiO}_4\) mineral formed with monoclinic crystal structure has a score of 33 with the highest peak of 32.9118°. In addition, Larnite minerals had other peaks at position 2θ (27.5745°, 32.1555°, 34.2929°, 35.5609°, 39.2466°, 41.2265°, 44.33657°, 45.6496°, 49.5934°, 54.2816°, 56.4078°, 57.2068°, and 58.6243°).

### 4. CONCLUSION

Based on research that has been done, it can be concluded that the variation of combustion temperature can affect the crystal structure and chemical content of the cement clinker. The element content obtained from the XRF test was dominated by \(\text{CaO}\), \(\text{SiO}_2\), \(\text{Fe}_2\text{O}_3\), and \(\text{Al}_2\text{O}_3\). Based on ASTM C150 results from the three temperature variations used, the cement clinker sample is closer to the standard at 1000 °C. Based on the XRD test results, the three samples had tetragonal, monoclinic, rhombohedral, and orthorhombic crystal structures. The highest peaks were at 1100 °C and 1200 °C with tetragonal crystalline phase. As for the MO test results, there was a strong binding between iron sand, limestone, clay, and silica sand characterized by a smooth surface while basalt stones that look like black holes were not completely bound.

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### REFERENCES


