Influence the Addition of Lapindo Mud is Calcined to the Quality of Cement Podzoland by Using Electric Furnace

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Abstract. This research is one of the efforts to reduce the impact of CO2 emissions by cement factory, by making blended cement by mixing Sidoarjo Mud (Lusi) with portland cement. Lusi contains the components of SiO2, Fe2O3, Al2O3, CaO and other components very potential to be utilized as an additive to the cement for the manufacture of concrete and building. The Lusi utilization begins by drying the material in the Oven at 100°C for 1-2 hours and refining to 120 mesh. Furthermore, the calcination process in the furnace at a temperature of 700°C, 800°C, 900°C for 1 hour. Calcined ligands are mixed with 10-60% cement (w/w) to cement blended (cement podzoland). The final cement mixture analyzed the chemical composition and the physical properties test comprising the compressive strength test and the setting time, the cement mixed component analysis with XRD showed calcined Lusi could be added 10-60% in the portland cement, the highest compressive strength achieved from 10 %, 18 kgf/cm2 and 101.97 kgf/cm2 for 3 days and 7 days. While the XRD analysis showed that C2S, C3S, C3A, and C4AF components averaged 79.28% contained in blended cement.

1. Introduction
The increasing demand for cement in development today and in the future will lead to increased cement production. World cement production from 2000 - 2006 increased by 54% and cement production is estimated to increase by 0.8 - 1.2% every year and is estimated to reach 3.7 - 4.4 billion tonnes by 2050 [1]. But on the other hand increased cement production will have an impact on the environment, causing environmental pollution, global warming caused by greenhouse gases CO2 emissions (GHGs) contributed by the cement industry, for every ton of cement generated to produce 900 kg of CO2 emissions [1].

Various efforts have been made by researchers and the cement industry to reduce the impact of these GHGs emissions [1-2]. One of them is making Blended cement that is mixing materials that are podzolanic with cement. This research has been conducted by several researchers such as Gartner (2004), Kolovos (2006), Navia et al (2006), Fairbairn et al (2010) [1].

Indonesia is a resource-rich country that can be used as a source of materials that can be used for cement making, either as raw material or as a mixture of cement for the manufacture of concrete and building. One of them is Sidoarjo mud (Lusi) or Lapindo mud (Lula) which has the potential to become an additional raw material in the manufacture of cement and as a mixture of cement.

Some research by utilizing Lula or Lusi out of the gas well of PT. Lapindo Brantas from 29 May 2006 to the present time, this Lapindo mudflow contains Al2O3, SiO2, Fe2O3 and CaO which can be used as raw material for the manufacture of cement [3-5]. Lapindo mud has been used as well as raw
material for cement manufacturing [6] and is also used as a mixture with cement as cement podzolan [7-10]. Research that utilizes some podzolan materials has also been done by several researchers [11-15].

This research focused on the utilization of sidoarjo mud (Lusi) as a mixture with portland cement, by looking at the effect of adding sidoarjo sludge first in calcination for 1 hour at a temperature of 700°C, 800°C, and 900°C. Furthermore, the mixture of Lusi and cement was analyzed its composition of chemical composition by XRD and tested its compressive strength and setting time according to Indonesian National Standard SNI 0302-2014 [16], the resulting cement is called cement podzoland.

2. Materials and methods
2.1. Materials
Source of podzoland material taken from Sidoarjo Mud (Lusi) in Sidoarjo Regency of East Java Indonesia August 7, 2017. While the portland cement used is Semen Baturaja (PT Semen Baturaja OKU Sumatera Selatan Indonesia).

2.2. Methods
At first, the Sidoarjo Mud (Lusi) from five different locations of the western, northern, eastern, southern and central sections of Lapindo/Sidoarjo mudflow are mixed and homogenized. Further heated in an oven at 110°C for 2 hours to dry the water contained in the material and then dry sludge in the puree, sieved to pass 120 mesh sieve and then analyzed the composition by using XRD. The process is continued wherein the powder is calcined at 700 °C, 800 °C and 900 °C for 1 hour and as much as 10 - 60% is mixed with portland cement (Semen Baturaja). The final mixture analyzed the composite content of the mixture with XRD and performed a compressive strength test and its setting time.

3. Results and discussion
3.1. Chemical Analysis of Lusi with XRD
Data Table 1 was obtained from XRD analysis of Sidoarjo Mud (Lusi) before and after calcination at 700°C (K700), 800°C (K800) to 900°C (K900). From the results of the analysis, it appears that sidoarjo mud before calcination contains 27.25% SiO₂ oxides, 6.73% CaO, 0.64% Fe₂O₃, and 3.89% Al₂O₃. The research ever conducted by [4,6-7,9] total composite of these components reaches 80%.

| Components | Lusi (%) | K700 | K800 | K900 |
|------------|----------|------|------|------|
| SiO₂       | 27.25    | 4.44 | 8.31 | 8.18 |
| Al₂O₃      | 3.89     | -    | 2.29 | 3.11 |
| Fe₂O₃      | 0.64     | 0.91 | 1.36 | 1.33 |
| CaO        | 6.73     | -    | -    | 1.31 |
| CaCO₃      | 11.87    | 3.08 | 4.56 | 4.68 |
| MgO        | 4.45     | -    | 1.79 | 0.52 |
| Na₂O       | 4.66     | 1.30 | 1.82 | 1.14 |
| K₂O        | 7.49     | 0.02 | 2.17 | 2.19 |
| SO₃        | 16.91    | 36.40| 12.80| 5.50 |
| MnO        | 6.87     | -    | -    | -    |
| TiO₂       | 0.87     | 4.44 | 9.39 | 8.10 |
| C₂S        | -        | 1.73 | 6.91 | 10.24|
| C₂F        | -        | 2.35 | -    | -    |
| C₃A        | -        | 1.15 | 2.35 | 2.83 |
Table 1 shows the difference of mud sidoarjo (Lusi) content before and after calcination process. After calcination, there is a difference in the composition of the component content contained by Lusi. The oxide content of $\text{SiO}_2$, $\text{Al}_2\text{O}_3$, $\text{CaO}$, $\text{MnO}$, $\text{MgO}$, $\text{Na}_2\text{O}$, $\text{K}_2\text{O}$, and $\text{CaCO}_3$ tends to decrease while the $\text{Fe}_2\text{O}_3$ content increases with increasing calcination temperature. According to the calcination temperature of 600°C does not give a difference of composition [9], neither does the calcination at 900°C [7], but both expresses activated Lusi as podzoland and calcination cause the crystalline microstructure change to be more amorphous or semi crystalline [7,9].

\[
\begin{array}{lccc}
\text{C}_3\text{S} & - & 12.51 & 25.98 & 25.54 \\
\text{C}_4\text{AF} & - & - & - & - \\
\text{C}_2\text{SH} & - & 62.49 & 24.88 & 26.62 \\
\end{array}
\]
From Figure 1 an analysis with XRD for Lusi before calcination, while Fig. 1 b Lusi after calcination at 800°C, the figure shows the peak number of curves more after calcination. The cement constituent component also looks good at the calcination temperature of 700, 800 and 900°C as C$_2$S, C$_3$A, C$_3$S, and C$_2$SH, whereas C$_2$F and C$_4$AF are not formed, but C$_2$F appears on the calcined samples at 700°C. C$_2$SH Dicalcium silicate hydrate will be more common when the amount of SiO$_2$ reacts with more CaO.

3.2. Influence of Mixed Lusi Calcined with Portland Cement

From chemical analysis with XRD Table 1, calcined Lusi was observed and followed by C$_2$S, C$_3$S, C$_3$A, C$_2$SH forming process starting at a burning temperature of 700°C to 900°C [17-18] next clinkerization process started from temperature 900°C-1300°C [17-18] and can be up to a temperature of 1450°C [6, 19-20]. The chemical composition of the Lusi calcined mixture of 10% (L10) to 60% (L60) with portland cement PC (PT Semen Baturaja OKU) is shown in Table 2, Table 3 and Table 4. Cement Baturaja (PC) is a portland cement type I earmarked in general. The content of portland cement type I contains high C$_2$S and C$_3$A 10-15% [6], or the content of C$_3$S, C$_2$S, C$_3$A, and C$_4$AF ranges from 41.46%, 29.18%, 10.01% and 9.88% [12].

### Table 2. The composition of Cement Podzol with calcination at 700°C

| Components | PC  | L10 | L20 | L30 | L40 | L50 | L60 |
|------------|-----|-----|-----|-----|-----|-----|-----|
| SiO$_2$    | 1.56| -   | -   | -   | 1.63| 1.43| 2.09|
| Al$_2$O$_3$| 0.72| 1.25| -   | -   | -   | -   | -   |
| Fe$_2$O$_3$| -   | 1.34| 2.54| 2.12| 1.85| 1.58| 2.63|
| CaCO$_3$   | 4.80| 7.29| 6.86| 11.50| 12.99| 14.28| 6.77|
| CaSO$_4$   | 5.51| 6.85| 9.32| 11.86| 13.59| 2.23| 10.52|
| C$_2$S     | 20.56| 19.96| 20.28| 15.75| 7.14| 13.75| 16.91|
| C$_2$SH    | -   | 8.09| 17.49| 13.86| 16.69| 25.39| 27.13|
| C$_2$F     | 12.68| 4.04| 1.84| 1.44| 3.09| 2.88| 1.98|
| C$_3$A     | 4.39| 2.15| 4.62| 3.38| 5.43| 5.31| 2.72|
In Table 2, 3 and 4 the content of \( \text{C}_3\text{S}, \text{C}_4\text{AF}, \text{C}_3\text{A}, \text{and C}_2\text{SH} \) at portland cement (PC) amounted to 81.46%. All of the Lusi additions in the three calcining temperature of the main content averaged 79.28%, the lowest of 69.95% in the addition of 40% Lusi (L40) burning temperature of 700 °C and the highest in the addition of 10% Lusi (L10) at a calcination temperature of 900 °C reached 91.24%.

The content dicalcium silicate hydrate \( \text{C}_2\text{SH} \) average decreased when the calcination temperature increased, whereas if the calcination temperature of 900 °C formed tri calcium trisilicate hydrate \( \text{C}_3\text{S}_3\text{H} \). By replacing the amount of cement with podzoland (calcined Lusi) 10-60% there is a \( \text{C}_2\text{S} \) percent reduction, this \( \text{C}_3\text{S} \) can be seen in Table 2 to table 4.

### Table 3. The composition of Cement Podzoland with calcination at 800 °C

| Components (%) | PC | L10 | L20 | L30 | L40 | L50 | L60 |
|----------------|----|-----|-----|-----|-----|-----|-----|
| \( \text{SiO}_2 \) | 1.56 | -   | -   | -   | -   | -   | -   |
| \( \text{Al}_2\text{O}_3 \) | 0.72 | -   | -   | -   | -   | -   | 1.17 |
| \( \text{Fe}_2\text{O}_3 \) | -   | 1.39| 1.24| 1.62| 1.95| 1.33| 2.11 |
| \( \text{CaCO}_3 \) | 4.80| 13.82| 13.85| 7.05| 10.96| 13.97| 14.79 |
| \( \text{CaSO}_4 \) | 5.51| 6.97 | 1.61| 10.48| 11.49| 6.39| 9.31 |
| \( \text{C}_2\text{S} \) | 20.56| 16.06| 20.03| 20.39| 14.18| 15.76| 13.44 |
| \( \text{C}_2\text{SH} \) | -   | 11.41| 15.17| 13.21| 6.01| 19.46| 22.04 |
| \( \text{C}_2\text{F} \) | 12.68| 2.23 | 5.39| 4.88| 1.78| -   | 1.84 |
| \( \text{C}_3\text{A} \) | 4.39 | 5.87 | 3.34| 2.63| 5.92| 3.44| 3.42 |
| \( \text{C}_3\text{S} \) | 41.98| 36.43| 34.25| 33.76| 41.56| 30.24| 30.98 |
| \( \text{C}_3\text{S}_3\text{H} \) | -   | -   | 5.42| 6.00| 6.14| 8.24| 2.08 |
| \( \text{C}_4\text{AF} \) | 1.85 | 5.83 | 5.42| 6.00| 6.14| 8.24| 2.08 |
| \( \text{SO}_3 \) | 3.15 | -   | -   | -   | -   | -   | -   |

### Table 4. The composition of Cement Podzoland with calcination at 900 °C

| Components (%) | PC | L10 | L20 | L30 | L40 | L50 | L60 |
|----------------|----|-----|-----|-----|-----|-----|-----|
| \( \text{SiO}_2 \) | 1.56 | -   | 1.74| -   | -   | -   | 2.60 |
| \( \text{Al}_2\text{O}_3 \) | 0.72 | -   | -   | -   | -   | -   | -   |
| \( \text{Fe}_2\text{O}_3 \) | -   | 4.70| -   | 6.91| 7.05| 4.91| 5.96 |
| \( \text{CaCO}_3 \) | 4.80| 8.99 | 4.72| 9.47| 8.66| 8.3 | 12.46 |
| \( \text{CaSO}_4 \) | 5.51| 4.18 | 2.31| 4.69| 1.81| 4.30| 5.61 |
| \( \text{C}_2\text{S} \) | 20.56| 11.38| 6.74| 4.48| 6.55| 13.63| 7.03 |
| \( \text{C}_2\text{SH} \) | -   | 15.20| 6.79| 12.36| 14.98| -   | -   |
| \( \text{C}_2\text{F} \) | 12.68| 1.76 | 8.68| 3.18| 2.82| 3.41| 9.52 |
| \( \text{C}_3\text{A} \) | 4.39 | 6.21 | 2.16| 6.66| 5.76| 6.12| 4.91 |
| \( \text{C}_3\text{S} \) | 41.98| 26.48| 30.16| 31.27| 29.71| 35.51| 48.58 |
Figure 2 shows the same pattern in which portland PC cement (a) and the addition of calcined Lusi on mixed cement have the same composition of C₃S, C₂S, C₃A, and C₄AF cement compositions see Table 2, Table 3 and Table 4.

|        |     |     |     |     |     |
|--------|-----|-----|-----|-----|-----|
| C₃S₃H | 13.44 | 28.20 | 19.02 | 15.89 | 22.31 |
| C₄AF  | 1.85 | 7.66 | 8.51 | 1.97 | 6.76 | 1.51 | 3.32 |
| SO₃    | 3.15 | -   | -   | -   | -   | -   | -   |

C₃S₃H - 28.20, 19.02, 15.89, 22.31
C₄AF - 1.85, 7.66, 8.51, 1.97, 6.76, 1.51, 3.32
SO₃ - 3.15
Figure 2. XRD results of Portland Cement PC (a) and blended cement L10 at 700 °C (b) (c) L40 at 800 °C and (d) L60 at 900 °C

Figure 2(a) shows the XRD analysis of portland cement as the reference cement product. 2(b) blended cement is blending 10% Calcined lusi at 700°C with portland cement. 2(c) blended cement blended 40% Calcined gum at 800°C, and 2(d) blended cement blending 60% Calcined lusi at 900°C. Figure 2 shows many peaks of one another, which means that the components are also the same. From the composition of PC and Cement mixtures to figure 2 the amount of C\textsubscript{3}S was 41.98% (PC), 44.39% L10 at 700°C, 41.56% L40 at 800°C and 48.58% L60% at 900°C and the overall content of C\textsubscript{2}S, C\textsubscript{3}S, C\textsubscript{3}A, and C\textsubscript{4}AF are only slightly different. This proves that calcined lusi can replace cement up to 60%.

3.3. Compressive Strength Test and setting Time

Table 5 and Table 6 are blended cement test results against the mortar compressive strength made 1: 3 between blended cement and sand and 50% water added from cement quantity printed with size 5 cm x 5 cm x 5 cm on day 3 and 7 whereas Table 7 is the result of the initial and blended bonding assay results.
### Table 5. Compressive Strength of blended cement at the age of 3 day

| Temperature | L10 | L20 | L30 | L40 | L50 | L60 |
|-------------|-----|-----|-----|-----|-----|-----|
| 700°C       | 61.18 | 56.26 | 48.95 | 36.71 | 24.47 | 28.55 |
| 900°C       | 48.95 | 40.79 | 24.47 | 20.39 | 24.47 | 20.39 |

The compressive strength of the blended cement for 3 and 7 days decreases with increasing amount of Lusi composition and will increase on the 7th day of addition of Lusi 10% more reactive on the mortar mixture resulting in higher compressive strength when compared with other samples [9], as well other studies using fly ash in blended cement [21-22]. The compressive strength also falls when the calcination temperature rises from 700 °C to 900°C the same temperature as that of Antoni et al (2013) [7].

### Table 6. Compressive strength of blended cement at the age of 7 day

| Temperature | L10 | L20 | L30 | L40 | L50 | L60 |
|-------------|-----|-----|-----|-----|-----|-----|
| 700°C       | 101.97 | 85.65 | 77.5 | 69.34 | 36.71 | 24.47 |
| 900°C       | 77.5 | 57.10 | 40.79 | 36.71 | 28.55 | 24.47 |

From Table 7, the initial and final setting time of blended cement using the Vicat needle, for calcined Lusi at 700°C Lusi addition causes the initial binding time to decrease while at 900°C the initial setting time decreases from 10% to 30% but occurs increase in the addition of 40% then the initial setting time drops again.

### Table 7. Setting time of blended cement in minutes

| Temperature | Setting time (in minutes) |
|-------------|---------------------------|
|              | L10 | L20 | L30 | L40 | L50 | L60 |
| 700 °C, initial | 35  | 30  | 17  | 8.33 | 8  | 6.38 |
| final         | 93  | 93.75 | 90  | 90  | 75 | 75  |
| 900 °C, initial | 27.5 | 19.3 | 6.4 | 15  | 13.6 | 6.6 |
| final         | 90  | 90  | 90  | 90  | 75 | 75  |

However, when compared to both temperatures, the initial setting time is smaller at 900°C temperature is seen in the addition of 10%-30% Lusi in blended cement, but the addition of 40%-60% increase in the initial setting time. This is not the case at the time of the final setting. For the final setting time at both the calcination temperature, there is not much difference.

### 4. Conclusion

Sidoarjo mud (Lusi) is one of the abundant material sources which can be made as a raw material of cement mixer in making cement podzoland or blended cement. The chemical and physical properties of the podzolan cement produced are also well-matched, almost matching the nature of portland cement type I. The content of C₂S and C₃S in blended cement is slightly smaller than that in portland cement as a controller, but the content of C₂S, C₃S, C₃A, and C₄AF averages 79.28%.

The compressive strength test of the blended cement shows a decrease in compressive strength by increasing the amount of calcined Lusi in the cement mixture and the blended cement strength of the calcined Lusi mixture of 900°C temperature is smaller than at the calcination temperature of 700 °C. The highest compressive strength occurred in a 10% (L10) mixture of 61.18 kgf/cm² for calcination of 700 °C aged 3 days and 101.97 kgf/cm² age of 7 days.
The initial setting time decreases with the increase in the amount of Lusi in the Portland cement mixture while the same final setting time indicates the addition of calcined ligand and the calcination temperature has no impact on the final setting time. The initial and final setting times are slightly less than the required initial and final fastening time standard Cement podzoland SNI 0302: 2014.

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