EFFECTS OF POZZOLANIC ADMIXTURE (WASTE BRICKS) ON MECHANICAL RESPONSE OF MORTAR

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Abstract This work presents an experimental study realized at the materials laboratory of the University of M'sila. It consists to vary the percentage of the pozzolanic admixture (waste bricks) in cement by the substitution method (partial replacement of the clinker by the calcined clay). The characteristics of cement at anhydrous state and the hydrated state (chemical composition, specific weight and fineness, consistency of the cement paste, setting times and shrinkage) were studied thus that the mechanical behavior (flexural and compressive strengths) for the mortar was determined. According to the experimental results obtained, it comes that the quantity of pozzolanic admixture (calcined clay) and the chemical composition of cement manufactured are the principal parameters that influence on the variation of the mechanical strengths (flexural and compressive) of the mortars tested.

Keywords Pozzolanic Admixture, Waste Bricks, Cement, Mortar, Mechanical Strength

1. INTRODUCTION

The incorporation of pozzolanic additions (industrial mineral wastes) in the cement manufacturing industry presents two principal interests: an ecological gain (reduction of pollution and environmental protection) and an economic gain (reduction of consumption of clinker and improvement of land conditions).

Research of economic binders through the use of industrial byproducts (blast furnace slag, silica fume, fly-ashes) and natural resources (natural pozzolan, limestone) is a major concern in reducing the deficit recorded during the manufacture of Portland cement [1]. In the cement industry, a large effort is researching the use of supplementary cementitious materials as a partial replacement to Portland cement [2]. A partial replacement of cement by mineral admixture such as fly ash, silica fume or blast furnace slag in cementing materials (mortar or concrete) in mixtures would help to overcome these problems and lead to improvement in the workability, strength and durability of cementing materials [3]. This would also lead to additional benefits in terms of reduction in costs, energy saving, promoting ecological balance and conservation of natural resources, etc. Portland cement with pozzolanic admixture is low in C3S (tricalcium silicate), low in C3A (tricalcium aluminate) and low heat of hydration and high long term strength. The continuing search for partial cement replacement
materials has led the authors to investigate the utilization of waste fired clay bricks as a pozzolan for mortar and concrete.

Clay is a widespread natural material on all continents and in particular in North African countries such as Algeria. It consists of a variety of phyllosilicate minerals rich in silicon and aluminum oxides and hydroxides, which include variable amounts of structural water. Clay is distinguished by its small size, layered shape, affinity for water and tendency toward high plasticity [4]. The Algerian clay industry (bricks, tiles, ceramics, etc.) has particular problems (mineral wastes) with its very high level of mineral waste that remains without being exploited until now. Calcined clay (waste bricks) is an artificial pozzolana which can be hydrated in the presence of Ca(OH)$_2$. The formation of cementitious material by the reaction of free lime (CaO) with the pozzolan admixture (AlO$_3$, SiO$_2$, Fe$_2$O$_3$) in the presence of water is known as hydration. The hydrated calcium silicate gel or calcium aluminate gel (cementitious material) can bind inert material together. Since the lime content of calcined clay is relatively low, with the addition of lime it is necessary for a hydration reaction with the pozzolan of the calcined clay to occur [5]. The pozzolanic reactions are as follows:

\[
\text{Ca(OH)}_2 + \text{SiO}_2 \rightarrow \text{C-S-H} \quad \text{(Calcium Silicate Hydrate)}.
\]

\[
\text{Ca(OH)}_2 \Rightarrow \text{Ca}^{++} + 2[\text{OH}]^-
\]

\[
\text{Ca}^{++} + 2[\text{OH}]^- + \text{SiO}_2 \Rightarrow \text{CSH} \quad \text{(Calcium Silicate Hydrate)}.
\]

(Silica) \quad \text{(Gel)}

\[
\text{Ca}^{++} + 2[\text{OH}]^- + \text{Al}_2\text{O}_3 \Rightarrow \text{CAH} \quad \text{(Calcium Aluminate Hydrate)}.
\]

(Alumina) \quad \text{(Gel)}

The increase rate of the above reaction with various temperatures may be due to an increase of dissolution of Ca(OH)$_2$ in the solution giving more Ca$^{++}$ and OH$^-$ ions [6]. Hydration of tricalcium aluminate in the calcined clay provides one of the primary cementitious products in many types of clay. The hydration chemistry of calcined clay is very complex [7].

This paper presents an investigation of various blended cements produced by replacing 0 %, 5 %, 10 %, 15 % and 20 % of these cements with a calcined clay (pozzolanic additive). The objective of this present experimental work is to evaluate the influence of a pozzolanic admixture (waste bricks) on the physico-chemical properties of cement manufactured with mineral addition (latent hydraulicity) and the mechanical behavior (flexural and compressive strengths) for the mortar.

### 2. CHARACTERISTICS OF USED MATERIALS

#### 2.1. Natural Sand (Fine Aggregates)

The fine aggregate used was dune sand with a maximum diameter of 3 mm. The fineness modulus calculated was $M_f = 1.76$. The information on the physical properties of the natural sand used is given in Table 1. The percentage of oxides (chemical composition) of fine aggregate (dune sand) is: 94.3 % SiO$_2$; 2.96 % CaO; 0.88 % Al$_2$O$_3$; 0.37 % Fe$_2$O$_3$ and 0.11 % MgO.

#### 2.2. Pozzolanic Admixture (Waste Bricks), Gypsum and Clinker

The waste bricks collected from a manufacturing unit (factory of manufacture of bricks) was used for the substitution of clinker. The clinker was partially replaced by 0 %, 5 %, 10 %, 15 % and 20 % of the pozzolanic admixture (calcined clay). The clay used in the present investigation was heated to 900°C with a heating ramp pf 100°C per hour. The chemical compositions (Oxide compositions) of fine aggregate (dune sand) is: 94.3 % SiO$_2$; 2.96 % CaO; 0.88 % Al$_2$O$_3$; 0.37 % Fe$_2$O$_3$ and 0.11 % MgO.

Figures 1 and 2 give the X-ray diffraction (XRD) patterns and the quantitative analysis for the raw clay and calcined clay. The composition of mineral phases of the raw clay and calcined clay were investigated by the X-ray diffraction (XRD). Mineralogy was determined by X-ray diffraction (XRD) analysis using a diffractometer. From Figure 1, it shows that raw clay minerals are mainly composed of quartz, illite, chlorite,

<table>
<thead>
<tr>
<th>Materials</th>
<th>Absolute Density (kg/dm³)</th>
<th>Apparent Density (kg/dm³)</th>
<th>Compactness (%)</th>
<th>Porosity (%)</th>
<th>Sand Equivalent Value (Sight/Test)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dune Sand</td>
<td>02.56</td>
<td>01.64</td>
<td>64.06</td>
<td>35.94</td>
<td>76/78</td>
</tr>
</tbody>
</table>

TABLE 2. Chemical Composition (% by Weight) of Gypsum and Clay (Raw and Calcined).

<table>
<thead>
<tr>
<th>Oxides, %</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>CaO</th>
<th>MgO</th>
<th>K₂O</th>
<th>Na₂O</th>
<th>SO₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gypsum</td>
<td>07.70</td>
<td>03.20</td>
<td>01.44</td>
<td>26.82</td>
<td>01.40</td>
<td>-</td>
<td>-</td>
<td>27.83</td>
</tr>
<tr>
<td>Raw Clay</td>
<td>52.03</td>
<td>16.22</td>
<td>06.30</td>
<td>06.68</td>
<td>02.71</td>
<td>02.38</td>
<td>00.96</td>
<td>00.68</td>
</tr>
<tr>
<td>Calcined Clay</td>
<td>66.52</td>
<td>14.20</td>
<td>05.45</td>
<td>06.06</td>
<td>02.35</td>
<td>02.09</td>
<td>00.67</td>
<td>00.75</td>
</tr>
</tbody>
</table>

Figure 1. Mineralogy (XRD patterns) of raw clay.

Figure 2. Mineralogy (XRD patterns) of calcined clay.
kaolinite, feldspar, and calcite. The main mineral phases for the calcined clay (Figure 2) were quartz, albite and orthoclase.

Table 3 presents the chemical analysis of the clinker and the Bogue composition.

The investigation was performed using the mixture composition for the preparation of the five types of cements containing clinker, gypsum and calcined clay (mineral admixture).

Table 4 presents the mixture composition used in this experimental work as well as their finenesses. The chemical composition of the five cements used in this research has been determined by the testing method “X-ray Fluorescence Spectrometry (XRF)”. The results of the chemical composition of the five cements prepared are presented in Table 5. The incorporation of the pozzolanic additions (industrial mineral wastes) in cement at different percentages (0 %, 5 %, 10 %, 15 % and 20 %) increases the oxides in SiO₂, Al₂O₃ and Fe₂O₃ but decreases the oxide in CaO. The experiments of grinding for the five types of cements (CEM I, CEM II-1, CEM II-2, CEM II-3 and CEM II-4) were performed in vibratory mills. The fineness (specific surface area) of the different cements grinded was determined by the Blaine method (Blaine Air Permeability Apparatus).

In this experimental work, the percentage of the calcined clay (waste bricks) varied in cement prepared (chemical effect) by the method of

<p>| TABLE 3. Chemical Analysis of the Clinker and the Bogue Composition. |
|---------------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|</p>
<table>
<thead>
<tr>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>CaO</th>
<th>MgO</th>
<th>CaOfree</th>
<th>SO₃</th>
<th>C₃S</th>
<th>C₂S</th>
</tr>
</thead>
<tbody>
<tr>
<td>22.10</td>
<td>04.57</td>
<td>03.95</td>
<td>66.34</td>
<td>01.60</td>
<td>00.02</td>
<td>65.70</td>
<td>14.15</td>
<td>5.42</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
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<th></th>
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</thead>
<tbody>
<tr>
<td>Cements</td>
<td>Clinker (%)</td>
<td>Calcined clay (%)</td>
<td>Gypsum (%)</td>
<td>Finenesses S.S.A (cm²/g)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>---------------</td>
<td>-------------</td>
<td>------------------</td>
<td>------------</td>
<td>-------------------------</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CEM I</td>
<td>95</td>
<td>0</td>
<td>5</td>
<td>3310</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CEM II-1</td>
<td>90</td>
<td>5</td>
<td>5</td>
<td>3328</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CEM II-2</td>
<td>85</td>
<td>10</td>
<td>5</td>
<td>3346</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CEM II-3</td>
<td>80</td>
<td>15</td>
<td>5</td>
<td>3332</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CEM II-4</td>
<td>75</td>
<td>20</td>
<td>5</td>
<td>3368</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<p>| TABLE 5. Chemical Composition of the Five Cements Studied |
|---------------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|</p>
<table>
<thead>
<tr>
<th>Types of Cements</th>
<th>SiO₂ (%)</th>
<th>Al₂O₃ (%)</th>
<th>Fe₂O₃ (%)</th>
<th>CaO (%)</th>
<th>MgO (%)</th>
<th>K₂O (%)</th>
<th>Na₂O (%)</th>
<th>SO₃ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CEM I</td>
<td>21.34</td>
<td>5.00</td>
<td>3.38</td>
<td>60.94</td>
<td>1.91</td>
<td>0.54</td>
<td>0.09</td>
<td>2.04</td>
</tr>
<tr>
<td>CEM II-1</td>
<td>26.31</td>
<td>5.95</td>
<td>3.90</td>
<td>56.03</td>
<td>1.95</td>
<td>0.62</td>
<td>0.11</td>
<td>2.01</td>
</tr>
<tr>
<td>CEM II-2</td>
<td>27.89</td>
<td>6.25</td>
<td>3.98</td>
<td>54.49</td>
<td>1.98</td>
<td>0.65</td>
<td>0.14</td>
<td>1.98</td>
</tr>
<tr>
<td>CEM II-3</td>
<td>29.20</td>
<td>6.49</td>
<td>4.19</td>
<td>52.91</td>
<td>2.03</td>
<td>0.68</td>
<td>0.15</td>
<td>1.91</td>
</tr>
<tr>
<td>CEM II-4</td>
<td>31.18</td>
<td>6.91</td>
<td>4.51</td>
<td>50.96</td>
<td>2.07</td>
<td>0.70</td>
<td>0.15</td>
<td>1.80</td>
</tr>
</tbody>
</table>
substitution (partial replacement of the clinker by the calcined clay). Five types of cements manufactured were used with mineral admixture (waste bricks), this was done with the aim of analyzing the influence of a partial replacement of clinker with calcined clay (0 %, 5 %, 10 %, 15 % and 20 %) prepared on the physical and chemical characteristics of hydraulic cements prepared at the anhydrous state and the state hydrated and also on the mechanical behavior (flexural and compressive strengths) for the mortar studied.

The shrinkage is a reduction in length of a test sample caused by desiccation. Three prisms (4 x 4 x 16 cm³) for each test (shrinkage) are cast from the mixed mortar. Measuring pins are cast into the end faces of the prisms. During the hardening and desiccation processes the mortar is exposed to longitudinal changes due to chemical shrinkage and desiccation shrinkage. In order to determine this change the length is measured by the comparator during both the hardening and the desiccation period.

3. MECHANICAL TESTS (FLEXURAL AND COMPRESSION STRENGTHS)

The mortar mixtures had proportions of 1: 3: 0, 5 (binder:sand:xwater). Five different mixtures with various compositions were examined in the present study. Clinker was partially replaced by 0 %, 5 %, 10 %, 15 % and 20 % of the pozzolanic admixture (calcined clay).

The mortar samples were subjected to flexural and compressive mechanical tests. Mechanical strength was determined at 7, 28 and 90 days on 4 x 4 x 16 cm³ prisms specimens with 50 % water-binder ratio and 1:3 binder/sand (By mass). The moulds with fresh mortar test specimens were cured for 24 h at relative humidity of 95 % RH. Three specimens were tested per specimen age.

4. RESULTS AND DISCUSSION

4.1. Effect of the Pozzolanic Admixture (Calcined Clay) on the Grinding Time

The grinding time varies proportionally with the variation of the quantity of the mineral addition (calcined clay) of cement studied (Figure 3). The increase of the quantity of calcined clay added in the cement decreases the time of grinding. This shows the low abrasive property of the calcined clay (the calcined clay is less hard than the clinker). The pozzolanic admixture (calcined clay) plays the role of a grinding agent. It facilitates the process of grinding and decreases the time of grinding. The finenesses of all grinded cements are almost identical.

4.2. Influence of the Pozzolanic Admixture (Calcined Clay) on the Specific Weight of Cement Powder

Figure 4 presents the effect of mineral additions (waste bricks) on the specific weight of cement. From the results obtained (Figure 4), the following conclusions may be drawn:

- A significant difference of the specific weight with the variation of the percentage of calcined clay added in the cement studied.
- A reduction of the specific weight with the increasing of the quantity of calcined clay added in the cement.

According to the results obtained, one notices that the increase in the quantity or percentage of the calcined clay incorporated in the cement has a significant effect on the specific weight of cement. This can be due to the porosity or quality of the replacement level of calcined clay.

4.3. Effect of the Quantity of Calcined Clay Added on the Cement Paste Studied

The experimental results obtained (Figures 5 and 6) present the effect of the content of calcined clay (waste bricks) on the normal consistency of cement paste. The water demand of cement pastes prepared with different percentage of calcined clay (replacement level: 0 %, 5 %, 10 %, 15 % and 20 %) is measured using the Vicat needle test (standart Vicat test). The influence of the quantity of pozzolanic admixture (calcined clay) added on the cement paste is expressed by the changes in normal consistency (water demand ratio). According to the results obtained (Figures 5 and 6), one may notice that the increase of the quantity or percentage of the calcined clay (waste bricks)
incorporated in the cement has a double effect: increase of the quantity of water required to have a normal consistency in the cement paste and a decrease in the setting times.

One also notices that the progressive addition of the pozzolanic addition (calcined clay) influences the water demand, this results in an increase in the quantity of water as a function of the percentage of mineral addition used. This can be due to the porosity of the added calcined clay. In the same way, it is noticed that setting times (initial and final set times) decrease proportionally with the increase the quantity of calcined clay. That is explained by the fact that the chemical reaction is accelerated. It should also be noted that the kinetics of hydration of the binder becomes increasingly rapid according to the increase in the quantity of the pozzolanic admixture added. Consequently the crystals of C-S-H (element responsible for the phenomenon of hardening of the paste) exist in great quantities at the initial period of hardening. The increase of the quantity or percentage of the calcined clay (waste...
bricks) in the cement studied (with or without mineral addition) decreases setting times (shortening of the setting times). Thus the effect of the pozzolanic admixture (waste bricks) on the acceleration of the pozzolanic activity reacts with the calcium hydroxide \([\text{Ca(OH)}_2\), Portlandite\] to form C-S-H gel crystals. The pozzolanic reaction is: \([\text{Ca(OH)}_2 + \text{SiO}_2 + \text{H}_2\text{O} \rightarrow \text{C-S-H}].\)

4.4. Effect of the Quantity of Pozzolanic Admixture (Calcined Clay) Added (Chemical Effect) on the Shrinkage

The variation of the shrinkage as a function of pozzolanic admixture (calcined clay) is shown in Figure 7. According to the results obtained, one can affirm that all the studied cements cause shrinkage on the specimens of normal mortar that one tested. The principal remarks drawn concerning the shrinkage observed for the cements studied are:

- Increase of in shrinkage according to the time of hardening (3, 7 and 28 days).
- Increase of in shrinkage according to the variation of the calcined clay.

The increase in the shrinkage according to the content of calcined clay substituted is essentially due to the presence of an elevated capillary porosity. In this case the kinetics of the hydration reaction speeds up inside the paste of the hydrated cement.

4.5. Effect of the Quantity of Pozzolanic Admixture Added (Chemical Effect) on the Mechanical Behavior (Flexural and Compressive Strengths)

The development of mechanical response (compressive and flexural strengths) of the mortar tested is shown in Figures 8 and 9. In this experimental work, the researchers varied the percentage of the calcined clay (mineral addition) in cement (chemical effect) by the method of substitution (partial replacement of the clinker by the waste bricks). The increase of the pozzolanic admixture (calcined clay) gives a decrease of the mechanical strength at 7 and 28 days (at short and medium-term). That is explained by the decrease of the fast kinetics of hydration of the mineral C\(_3\)S (tricalcium silicate) and C\(_2\)S (dicalcium silicate).

These are the two principal minerals which ensure the development of the resistances to short and medium-term. At 90 days (3 months) the mortars containing up to 10 % of the calcined clay will reach a resistance comparable to those of a witness without calcined clay. Thus, the weakness of strengths to short term can be compensated by the pozzolanic activity of the calcined clay. On the other hand the results obtained at 90 days of the mortars containing 15 % and 20 % of calcined clay...
clay have the mechanical strengths below the 28 days. This reduction is due to the relationships between the chemical process (pozzolanic reactivity) and the mechanical strength development (rate of strength).

The pozzolanic admixture (calcined clay) added in cement clearly improves the mechanical strength of the mortar in the long term process (90 days). This confirms the role of the pozzolanic reaction of the waste bricks in the fast and complete hydration of the cement (pozzolanic activity) by the formation of the Ca(OH)$_2$ released during the hydration of the cement. Calcined clay (waste bricks) is an artificial pozzolana and it can be hydrated in the presence of Ca(OH)$_2$. This pozzolanic reaction gives the second C-S-H supplementary, main responsible for the hardening of the mortar. Therefore the weakness of the strengths during the short-term process can be compensated by the pozzolanic reaction during the long-term process.

5. CONCLUSIONS

The aim of this study was to investigate the effect of the pozzolanic admixture on the strength development of mortar. The pozzolanic activity of calcined clay has mainly been pointed out as well as the possibility to use this industrial waste with a content of 10% for the manufacturing of cement. The calcined clay plays the role of a grinding agent. It facilitates the process of grinding and decreases the time of grinding. The variation of the quantity of the calcined clay (waste bricks) substituted has a significant effect on normal consistency of the cement paste, setting times, shrinkage and mechanical strength.

6. REFERENCES