Manufacturing Unfired Bricks using Coal Fly Ash, Calcium Fluoride and Calcium Silicate

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Abstract— The manufacture of sustainable bricks using waste materials is a topic of ongoing research in many countries. Unfired bricks made from industrial waste materials provide one promising approach. This study examined the potential to manufacture bricks for use in housing applications that are made using coal fly ash (CFA), calcium fluoride and calcium silicate (CFS). Moreover, in practice, the CFS comes from the reaction between calcium hydroxide and sodium fluosilicate. The bricks described in this paper were made at atmospheric pressure and room temperature. The materials were characterized using X-Ray Fluorescence, X-Ray Diffraction and Scanning Electron Microscopy. In addition, the bulk density, the compressive strength and the water absorption were measured and compared with common building bricks. The compressive strength of the brick specimen containing 75% of CFA at 28 day was 6.1 MPa and the water absorption was found to be about 23.8%.

Index Term— Calcium fluoride; calcium silicate; coal fly ash; industrial waste; unfired brick.

1. INTRODUCTION

Cement, calcium silicate and clay have been the primar used as raw materials that have been used to produce brick for construction and building [1].

Cementitious bricks are typically made using ordinary Portland cement (OPC). The production of cement contributes to CO2 emissions due to the combined effects of combustion, calcination and transportation. It is estimated that 0.9 tons of CO2 is produced to obtain 1 ton of clinker [2].

Many cement alternatives have historically been manufactured, while clay bricks manufacturing dates back to 6000 B.C using primarily the soft mud process in which a relatively moist clay is pressed into simple rectangular molds by hands. Modern bricks are produced using the manufacture and the process which all require energy to fire the bricks [3].

Clay brick is generally regarded as the most common brick material due to its high compressive strength and the well-established manufacturing process that enables it to be taken from the laboratory to industrial production [3].

Calcium Silicate (CS) bricks were developed over the past decades and are useful construction and building materials due to the higher compressive strength they provide. They are made from high-grade sand and mixed with high calcium hydroxide in presence of water [3].

Innovative alternatives have also been proposed. For example, bricks containing Calcium Fluoride have been manufactured using patented process developed in 1962 [4]. Since, fluorine might be harmful to health, it was concluded that there is no increase health risk of exposure to bricks containing calcium fluoride as compared with common bricks [5].

Many recent studies have shown the benefits of using alternatives materials to make bricks from industrial waste products [6, 7]. Several studies examined the use of CFA in production of bricks [8]. The preparation and the characterization of lime activated unfired bricks made of CFA were performed [9, 10, 11, 12].

It is well known that CFA, from coal power plant is very useful for the production of building bricks [13]. The long-term performance of compacted-clay industrial waste materials by using CFA has been demonstrated [14] as well as the manufacturing of unfired bricks using CFA, lime and wood aggregates [15].

There is interest in using CFA in terms of resources conservation, environmental protection and low-cost building material [16, 17, 18, 19, 20].

The objective of this study is to manufacture unfired brick at room temperature and atmospheric pressure by combining CFA and CFS which comes from the reaction between calcium hydroxide and sodium fluosilicate.

2. MATERIALS AND METHODS

This section discusses the physical and chemical properties of the raw materials used in this study: coal fly ash (CFA), calcium fluoride and calcium silicate (CFS). In addition, the main steps of the manufacturing process of the bricks and the characterization of the manufactured bricks are outlined.
2.1. Coal Fly Ash (CFA)
A Class F coal fly ash was used in this study with the physical and chemical properties shown in Table I and 2, respectively.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Particle Size (μm)</th>
<th>Moisture (wt%)</th>
<th>Specific Gravity</th>
<th>pH (20% Solids)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Value</td>
<td>6.61</td>
<td>0.27</td>
<td>2.60</td>
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</table>

<table>
<thead>
<tr>
<th>Compound</th>
<th>CaO</th>
<th>SiO2</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>MgO</th>
<th>K₂O</th>
<th>SO₃</th>
<th>Mn₂O₃</th>
<th>ZnO</th>
<th>Cl</th>
<th>TiO₂</th>
<th>Na₂O</th>
<th>P₂O₅</th>
<th>LOI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Content (%)</td>
<td>16.79</td>
<td>44.31</td>
<td>15.5</td>
<td>6.01</td>
<td>5.05</td>
<td>1.56</td>
<td>0.93</td>
<td>0.10</td>
<td>0.02</td>
<td>0.01</td>
<td>0.95</td>
<td>3.45</td>
<td>0.24</td>
<td>5.08</td>
</tr>
</tbody>
</table>

2.2. Mixture of Calcium Fluoride and Calcium Silicate (CFS)
The CFS was produced from the reaction between Sodium Fluosilicate (SF) 95% and Calcium Hydroxide (CH) 95% as shown in the following chemical reaction [21]:

\[ Na_2SiF_6 + 4Ca(OH)_2 \rightarrow 2NaOH + 3CaF_2 + CaSiO_3 + 3H_2O \]  
(Equation 1)

This reaction was previously performed by means of PHREEQC calculations [22]. Experiments were conducted in a 2 L pyrex VWR batch reactor at 50 °C during 2.5h. The homogenization of the reaction mixture was handled by a magnetic stirrer. The products of the reaction were CFS (CaF₂ and CaSiO₃) and an aqueous solution of Sodium Hydroxide.

The typical physical and chemical properties of the CFS are illustrated in Table 3 and 4, respectively.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Particle Size (μm)</th>
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<th>Specific Gravity</th>
<th>pH (20% Solids)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Value</td>
<td>6.82</td>
<td>0.26</td>
<td>2.14</td>
<td>13.55</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Compound</th>
<th>CaO</th>
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<th>Fe₂O₃</th>
<th>MgO</th>
<th>K₂O</th>
<th>SO₃</th>
<th>Mn₂O₃</th>
<th>ZnO</th>
<th>Cl</th>
<th>TiO₂</th>
<th>Na₂O</th>
<th>P₂O₅</th>
<th>LOI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Content (%)</td>
<td>58.04</td>
<td>15.83</td>
<td>0.38</td>
<td>0.08</td>
<td>0.40</td>
<td>0.11</td>
<td>0.11</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.02</td>
<td>6.15</td>
<td>0.03</td>
<td>18.46</td>
</tr>
</tbody>
</table>

2.3. Brick processing
The raw materials CFA and CFS were kept in an oven at 105 °C for 24 h and then crushed with a porcelain mortar and pestle to obtain powder. The two raw materials were mixed in proportions of 25, 40, 50, 60 and 75 % by weight of CFA (BM25, BM40, BM50, BM60 and BM75) using a RENFERT Vacuum Mixer. A paste mixture with a solid-to-liquid ratio (S/L) of 2 was prepared. The solid contains different mixture of CFA with CFS. The liquid contains 1.5 M sodium hydroxide. A total mass of 600 g of solids (CFA+CFS) were prepared for each sample and 300 mL of the aqueous solution of Sodium Hydroxide (1.5 M) was then added to the solid mixture in order to obtain a water-paste (W/P) ratio of about 0.50. A 50×50×50 mm cubic mold was used to cast the samples. The samples were consolidated using a US-M-18×18 VISBO VIBRATOR and then cured inside an environmental chamber at 23 ±1 °C for 7, 14 and 28 days.

2.4. Bricks characterization
The bricks were tested to determine: the bulk density, the compressive strength and the rate of water absorption. The bulk density was measured using ASTM C29/C29M. The compressive strengths at 7, 14 and 28 days after curing inside an environmental chamber at 23 ± 1 °C were determined using the FX 700 testing machine compression (FORNEY LP) in accordance with the ASTM C109/C109-16a [23]. The water absorption was determined in accordance with the ASTM C1585-13 [24]. The characteristics of the bricks were found by means of XRF performed on EPSILON 3 XLE (MALVERN PANALYTICAL Manufacturing), XRD using...
D8-DISCOVER (BRUKER MANUFACTURER) and SEM performed on QUANTA 600 F (FEI COMPAGNY).

3. RESULTS AND DISCUSSIONS
The measurements of physical properties are reported in terms of bulk density, compressive strength and water absorption. The chemical composition and phases identification of the materials were measured.

3.1. Bulk density
The bulk density of the obtained bricks at 28 days is presented in Table 5.

<table>
<thead>
<tr>
<th>Bulk density at 28 days (kg/m$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BM25</td>
</tr>
<tr>
<td>1730</td>
</tr>
</tbody>
</table>

The CFA+CFS bricks have a medium weight because the bulk densities are between 1680 – 2000 kg/m$^3$ [25, 26].

3.2. Compressive strength
The compressive strength of the brick as a function of CFA content after varying curing period is shown in Figure 1.

The experimental results showed an increase of the compressive strength as the proportion of CFA increased to reach maximum values with BM75 (75% of CFA). The CFA is then the primarily factor leading to the compressive strength of the bricks. There was also a reaction between CFA and NaOH leading to geo-polymer formation as illustrated by Equation 2 and 3 [27]:

$$\text{(Si}_2\text{O}_5\text{Al}_2\text{O}_3)n + 3n\text{H}_2\text{O} \xrightarrow{\text{NaOH}} (n(\text{OH})_3 - \text{Si} - \text{O} - \text{Al} - (\text{OH}_3))^−$$

(Equation 2)

$$\text{(n(\text{OH})_3 - Si - O - Al - (OH}_3)^− \xrightarrow{\text{NaOH}} (\text{Na})((\text{SiO} - \text{O} - \text{AlO} - \text{O} - )n + 3\text{H}_2\text{O}}$$

(Equation 3)

The addition of CFS trended to lower the compressive strength due to the content of fluorine. At 28 days, compressive strength of BM75 (6.1 MPa), shown in figure 1, was consistent with the strength of third class of brick [28]. However, BM50 was found interesting as optimum proportion regarding its compressive strength at 28 days (4.8 MPa) and the requirement for some facing bricks (4 MPa) in Senegal. The obtained compressive strengths were lower to common bricks made of coal fly ash [29]. However, the unfired CFA+CFS bricks were carried out at the minimum conditions (23 ±1 °C and 1 atm) which demands no energy consumption from extend source and no pressure during the bricks manufacturing. In fact, pressing and firing the bricks could improve the compressive strength and the dimensional stability.
3.3. Water absorption

Figures 2 and 3 illustrate the rate of water absorption of the bricks specimens in accordance to ASTM C1585-13.

The addition of CFA decreased the water absorption to a minimum of 23.8% for BM75 and 27.8% for BM50 at 28 days cured samples, while the water absorption for solid brick is less than 25% [30].

3.4. Chemical composition

The chemical composition of the bricks specimens BM50 and BM75 was determined by XRF analysis and results are shown in Table 6.
Table VI
Chemical composition of bricks from XRF

<table>
<thead>
<tr>
<th>Content (%)</th>
<th>CaO</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>MgO</th>
<th>K₂O</th>
<th>SO₃</th>
<th>Mn₂O₃</th>
<th>ZnO</th>
<th>TiO₂</th>
<th>Na₂O</th>
<th>P₂O₅</th>
<th>LOI</th>
</tr>
</thead>
<tbody>
<tr>
<td>BM50</td>
<td>35.11</td>
<td>31.49</td>
<td>8.57</td>
<td>3.24</td>
<td>1.00</td>
<td>1.14</td>
<td>0.05</td>
<td>0.02</td>
<td>0.51</td>
<td>7.03</td>
<td>0.11</td>
<td>8.87</td>
<td></td>
</tr>
<tr>
<td>BM75</td>
<td>25.80</td>
<td>36.51</td>
<td>11.62</td>
<td>4.54</td>
<td>3.82</td>
<td>1.38</td>
<td>1.69</td>
<td>0.08</td>
<td>0.02</td>
<td>0.71</td>
<td>6.36</td>
<td>0.15</td>
<td>7.33</td>
</tr>
</tbody>
</table>

The chemical composition highlights interesting cementitious properties of the obtained composites in terms of major oxides contents.

3.5. Solids phases identification
The XRD patterns of the BM50 and BM75 specimens are displayed in Figure 4 and Figure 5.
The patterns revealed a low degree of crystallization of compounds such as aluminum oxide from CFA. Indeed, the microstructure of the CFA activated NaOH is amorphous instead of crystalline [31]. The main phases were Al₂SiO₅, CaF₂, CaCO₃, and CaO characteristically of their peaks. Calcium silicate, which was in amorphous phase also, could not be detected. However, aluminum silicate was formed from the geo-polymerization and the CFS provided cementitious properties due to the system CaO-SiO₂-CaF₂. The SEM images with Fluorine (F) contents are shown in Figure 6 and Figure 7.

The SEM images of bricks after 28 days of curing showed unreacted spherical particles of CFA because of the incomplete geo-polymerization reaction. Heterogeneous phases with some macrospores were also formed. Based on these experimental results, it would be better to improve the performance of the CFA+CFS bricks by changing the S/L.

4. CONCLUSION
This paper examined the potential to manufacture bricks using coal fly ash (CFA), calcium fluoride and calcium silicate (CFS). Experiments showed the feasibility of making bricks using this process at room temperature and atmosphere pressure. The unfired bricks have an average bulk density of 1816.5 kg.m⁻³. The average compressive strength was found to be 4.32 MPa and the water absorption about 26.78% after 28 days curing inside an environmental chamber at 23 ±1 °C. The chemical composition seems suitable for construction and building materials. The results highlighted the potential use of industrial waste materials from phosphoric acid plants in unfired bricks manufacturing. Indeed, calcium fluoride and calcium silicate (CFS) are the solid compounds generated by working-up fluosilic acid which is the main liquid by-product from the manufacturing of phosphoric acid.

5. ACKNOWLEDGEMENTS
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6. REFERENCES


