A Low Temperature Manufactured Portland Cement Clinker from Pulverized Waste of Fly Ash

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Abstract: The possibility to produce both environmentally and friendly cement exclusively or solely from industrial byproducts such as pulverized fly ash (PFa) was investigated. A low clinkering temperature was attained or acquired to produce cement. It is capable to gain high early and late strength on hydration. The optimum quantities of PFa and clinkering temperature were detected. The results indicated that the higher the clinkering temperature, the higher hydration reactivity of the cement. The optimum PFa content and clinkering temperature for synthesizing cement were found to be 35 wt. % and 1350°C, respectively. The production of cement with PFa at a low clinkering temperature can save energy and natural resources consumption, landfills disposal cost and also can reduce CO₂↑ emission. The formed major phases in presence of PFa are more or less the same as those of the blank as experimentally achieved and approved by the compressive strength. As the PFa content increased, the free lime contents decreased, and also the firing or clinkering temperature decreased. The optimum PFa content must not exceed than 35 wt. %, and any further increase of Pfα resulted in adverse effects on all characteristics of the produced clinker.

Keywords: Cement, Fly Ash, Clinkering Temperature, Phases, Hydration, Free Lime, Strength, XRF

1. Introduction

1.1. Scope of the Study

There is no doubt that the problem of solid wastes is spreading all over the world so that this creates the need to exploit and/or reutilize these solid wastes in useful applications. The pulverized fly ash (PFa) from coal combustion that fired in the thermal power plants is one of such solid wastes. PFa could be obtained by the electrostatic or mechanical precipitation of dust-like particles from the flue gases inside furnaces using coal or lignite at 1100-1400°C. PFa is a fine powder that is mainly composed of spherical glassy particles of silica and depending upon the types of boiler and coal, siliceous, silico-calcareous and calcareous fly ashes with pozzolanic reactivity are produced [1-3]. Fly ash is mostly used as a pozzolanic additive in the cement and/or concrete. However, fly ash may be used for other purposes such as traditional ceramics, glass ceramics [4], as the material for land consolidation in road construction [4-8], land stabilization in mining areas [6], sorbents for the flue gas desulphurization [7], a filling material in making various products [8], and synthesis of zeolites [6-10].

Many authors investigated fly ash to determine its suitability for application in the cement and concrete industry [11–14], as lightweight aggregate [15, 16], as a replacement for cement, mortar and/or concrete [17-21]. Each of these applications requires a complete characterization of the fly ash involved. Although application of fly ash as the cement raw material has been reported, only few articles refer to it as a cement raw feed component [1, 4, 6, 10].

1.2. Environmental Impacts

The manufacture of Portland cement can cause environmental impacts at all stages of the process including emissions of airborne pollution in the form of dust, gases, noise and vibration when it is operating machinery and during blasting in quarries, consumption of large quantities of fuel during manufacture, release of carbon dioxide (CO₂↑) from the exposure in Portland cement plants, from the centers for disease control, states that "Workers at Portland cement
facilities, particularly those burning fuel containing sulfur, should be aware of the acute and chronic effects of exposure to \( \text{SO}_2 \uparrow \), and peak and full-shift concentrations of \( \text{SO}_2 \uparrow \) should be periodically measured [1, 7, 9, 16].

Further reduction of energy consumption and \( \text{CO}_2 \uparrow \) emissions could be achieved by using waste materials containing \( \text{CaO} \) more than \( \text{CaCO}_3 \), thereby in turn a further reduction in the environmental impact. Waste materials suitable for achieving these targets include lime dust, fly ash and granulated blast furnace slag for their high \( \text{CaO} \), \( \text{Al}_2\text{O}_3 \), and \( \text{SO}_3 \) contents rather than \( \text{CaCO}_3 \) [10, 22–25].

### 1.3. Objectives of the Study

It is well known that the production of Portland cement is now very expensive and therefore the current study aims to determine whether pulverized fly ash (PFa) can be utilized as a component in the raw meal for the production of Portland cement clinker or not. So, it can be used as an alternative component in cement industry. Chemical and mineralogical compositions of the produced Portland fly ash clinkers have been performed to know the possibility of its application as a raw material in the construction industry compared with the pure Portland cement clinker. Primarily in the production of Portland cement clinker, the X-ray florescence (XRF) of the produced clinker were done to identify the synthesis and the formed phases comparing to those of the plank sample.

### 2. Experimental and Methods

#### 2.1. Raw Materials

The raw materials are clay (TCY), limestone (SLS) and pulverized fly ash (PFa). The TCY sample was taken from Toska area that is located on latitude 20° 30’ N and longitude 31° 53’ E at 250 km south of Aswan, Egypt. It was related to the Upper Cretaceous age. The selected TCY deposit is belonging to El-Dakhla Shale Formation. About 20 kg TCY was collected from the 85° km north of Aswan/Abu-sample asphaltic road. It is a dark yellowish grey. The TCY sample was first dried at 105°C for 3 days at a suitable dryer, and then crushed using a suitable crusher, ground and quartered to have a representative sample to pass a 200 mesh sieve. The SLS sample taken from Samalout district, was supplied by the Arab Ceramic Company (Aracemco). The PFa sample was obtained from Egyptian Local plant, which in turn was obtained from abroad has a grain size of about \( \approx 63 \) µm. The clay, limestone and pulverized fly ash are respectively given the symbol TCY, SLS and PFa as shown above. The chemical composition of these raw materials, which was achieved classically by normal chemical analysis according to ASTM Standards [26, 27] is shown in Table 1. The mineral composition of PFa specimen was investigated by X-ray diffraction patterns (XRD) and diffraction thermal analysis (DTA). The XRD analysis was achieved by a Philips X-ray diffractometer (XRD), PW 1710 powder with an anticathode copper radiation and Cu-Kα radiation, wavelength of 1.54178 Å and a graphite monochromator. The tube working voltage was 40 kV and current strength was 30 mA, in the range 5–50° 20 with a step of 0.02 and 0.5 seconds retention time for each step, while the DTA analysis was carried out using NETZSCH Geratobau Selb, Bestell-Nr. 348472c at a heating rate 10°C/min up to 1000°C.

### 2.2. Preparation of Cement Pastes

The base batch of PC clinker was prepared from 25 wt. % TCY and 75 wt. % SLS and was given the symbol (F0). The base batch (F0) was replaced by 0, 5, 15, 25, 35 and 45 wt. % of PFa, where the mixes are taken the symbols F0, F1, F2, F3, F4 and F5, respectively as shown in Table 2.

| Table 1. Chemical composition of the starting rea materials, %. |
|-------------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| Oxide Material    | LOI       | SiO₂         | Al₂O₃         | Fe₂O₃         | CaO           | MgO           | Na₂O           | K₂O           | SO₃       |
| TCY               | 9.72      | 53.47        | 26.78         | 3.99          | 0.63          | 1.38          | 1.15            | 1.18          | ---       |
| SLS               | 42.63     | 0.08         | 0.04          | 56.84         | 0.10          | 0.12          | 0.05            | 0.02          | 0.01     |
| PFA               | 2.32      | 60.13        | 21.94         | 5.82          | 6.23          | 0.15          | 0.18            | 0.98          | 1.35     |

| Table 2. Batch composition of Portland cement clinker and its finenesses, wt.% |
|-------------------|----------------|----------------|----------------|----------------|
| Material Batch    | TCY        | SLS           | PFA            | Fineness, cm²/g |
| P0                | 25         | 75            | ----           | 3350           |
| P1                | 25         | 70            | 5              | 3640           |
| P2                | 25         | 65            | 15             | 3850           |
| P3                | 25         | 60            | 25             | 4125           |
| P4                | 25         | 55            | 35             | 4465           |
| P5                | 25         | 50            | 45             | 4640           |

#### 2.3. Test Methods

It is well known that the Portland cement clinker (PCC) is always manufactured in a rotary kiln starting from the atmosphere temperature up to 1450°C. The various forms of PC clinkers mixed with PFa (F0-F5) produced at their optimum firing temperatures (1410-1280°C), respectively were subjected to X-ray florescence (XRF) in order to identify their oxide composition. After the formation of the different clinkers, all are subjected to chemical analysis to identify the free lime and the insoluble residue in each clinker to detect the unreacted silica and other materials during firing [26]. Then, the phase compositions of each clinker could be calculated from Bogue equations [21, 24, 28] as follows:

\[
C_3S, \% = 4.07 \times (\text{CaO}) - 7.60 \times (\text{SiO}_2) - 6.72 \times (\text{Al}_2\text{O}_3) -1.43 \times (\text{Fe}_2\text{O}_3) - 2.85 \times (\text{SO}_3) \tag{1}
\]
In order to compare the quality of each type of the prepared clinkers, each of the prepared clinkers were mixed with 4 wt. % raw gypsum (CaSO$_4$.2 H$_2$O) to prepare Ordinary Portland cement (OPC). Then, they were let to hydrate for 1, 3, 7, 28 and 90 days at which the compressive strength were measured to compare and select the optimum content of PFa in the cement. The compressive strength [29] was measured by using a hydraulic testing machine of the Type LPM 600 M1 SEIDNER (Germany) having a full capacity of 600 KN and the loading was applied perpendicular to the direction of the upper surface of the cubes as follows:

$$CS = \frac{L \text{ (KN)}}{Sa \text{ (cm}^2\text{)} \times 102 \text{ (Kg/cm}^2\text{)/10.2 (MPa)}}$$

(5)

Where, CS: Compressive strength (MPa), L: load (KN), Sa: surface area (cm$^2$).

### 3. Results and Discussion

#### 3.1. Composition of the Used Raw Materials

Table 1 indicates the chemical oxide composition of TCY and P PFa samples. The most important and basic oxides in the chemical composition of TCY and PFa samples are SiO$_2$, Al$_2$O$_3$, Fe$_2$O$_3$ and CaO while the minor and less important oxides are MgO, MnO, Na$_2$O, K$_2$O and SO$_3$. Due to ASTM C618-05, 2005 [27], which is based on the sum of SiO$_2$, Al$_2$O$_3$ and Fe$_2$O$_3$, the used PFa can be classified as a high calcium Fa. The sum of SiO$_2$, Al$_2$O$_3$ and Fe$_2$O$_3$ in the used Fa sample is 85.66%.

On the other side, the oxides of Si, Al, Fe and Ca are the vital and more important constituents of the raw mixture used for Portland cement clinker production. During firing or sintering of these oxides in the kiln, the clinker minerals are formed. These are calcium silicates (C$_3$S and β–C$_2$S), calcium aluminates (C$_3$A) and calcium aluminoferrites (C$_4$AF). The CaO in the cement mixture is usually obtained from calcareous compound, such as limestone (CaCO$_3$), while the oxides of Si, Al and Fe are obtained from an argillaceous compound such as clay. By its chemical composition of Fa sample is similar to TCY to a large extent, so it could be successfully used as a raw component in the raw meal during the manufacture of Portland cement clinker. According to the content of SiO$_2$ in the used Fa sample, it can therefore lead to minimize the need to use other SiO$_2$ carriers like sand or quartz. The chemical composition of the used Fa sample indicates the existence of all oxides we need in the main raw mixture components to produce Portland cement clinker. Table 1 also illustrates the analysis of the limestone which contains essentially CaO (56.84 %) and traces from other oxides, while its loss on ignition was 42.63 %.

#### 3.2. XRD, DTA Analyses and SEM Image of PFa

The XRD diffraction patterns of the used PFa sample are shown in Figure 1. Crystalline and amorphous phases are detected and also the differences in the amounts of amorphous phases. The crystalline phases were identified according to JCPDS standards. The content of any individual mineral phases cannot be easily identified. The PFa sample contains a significant amount of amorphous matter, but low amounts of crystalline phases, as quartz (Q) and feldspar (F). In most cases, hematite (H), anhydrite (A) and mullite (M) are detected. The amorphous phase minerals are more reactive if it is compared to the crystalline phases. This confirms the exploitation of PFa as an alternative substitute for the normal raw mixture used to produce Portland cement clinker.
reduction of the energy needed for the sintering process [30]. The DTA curve of the studied PFa sample up to 1000°C did not show any other exo- and/or endothermic peaks that could eventually correspond to the formation of new mineral phases during heating and/or sintering. Figure 3 shows the microstructure of the PFa sample. There are several particulates with various shapes and sizes as flocculants or almost globulars.

Figure 3. The SEM image of the used PFa sample.

3.3. The XRF and Major Phases of the Formed Cement Clinkers

Table 3 shows the X-ray fluorescence (XRF) of the resulting cement clinkers containing PFa (F0-F5). As it is clear, there are no significant differences in the amounts of the various oxide compositions. Also, the free lime content of the prepared clinkers (Figure 4) was slightly decreased. This is due to that the addition of PFa was at the expense of other main raw materials. On contrast, the insoluble residue was slightly increased due to the gradual increase of silica from PFa. This means that the addition of PFa does not largely affect the main composition of the resulting cement clinkers if compared with the control (F0). Furthermore, the decrease of free lime content is an advantage because as the free lime increases the specific characteristics of the cement are adversely affected. On the other side, the increase of the insoluble residue in the cement is another advantage due to the improvement in the durability of the cement against several aggressive media [31-33].

Table 3. The XRF analysis of the produced cement clinkers.

<table>
<thead>
<tr>
<th></th>
<th>LOI</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>CaO</th>
<th>MgO</th>
<th>Na₂O</th>
<th>K₂O</th>
<th>SO₃</th>
<th>Free lime</th>
<th>Insol. residue</th>
</tr>
</thead>
<tbody>
<tr>
<td>F0</td>
<td>23.2</td>
<td>21.51</td>
<td>6.03</td>
<td>4.12</td>
<td>64.08</td>
<td>0.68</td>
<td>0.21</td>
<td>0.11</td>
<td>1.39</td>
<td>1.12</td>
<td>1.26</td>
</tr>
<tr>
<td>F1</td>
<td>2.71</td>
<td>21.61</td>
<td>5.22</td>
<td>3.76</td>
<td>63.14</td>
<td>1.22</td>
<td>0.17</td>
<td>0.09</td>
<td>2.39</td>
<td>1.10</td>
<td>1.31</td>
</tr>
<tr>
<td>F2</td>
<td>2.82</td>
<td>21.93</td>
<td>4.98</td>
<td>2.21</td>
<td>62.06</td>
<td>1.69</td>
<td>0.26</td>
<td>1.16</td>
<td>2.15</td>
<td>1.00</td>
<td>1.62</td>
</tr>
<tr>
<td>F3</td>
<td>2.64</td>
<td>21.81</td>
<td>4.71</td>
<td>2.88</td>
<td>61.63</td>
<td>1.53</td>
<td>0.51</td>
<td>0.32</td>
<td>2.42</td>
<td>0.96</td>
<td>1.78</td>
</tr>
<tr>
<td>F4</td>
<td>2.93</td>
<td>22.06</td>
<td>4.75</td>
<td>2.52</td>
<td>61.85</td>
<td>2.17</td>
<td>1.32</td>
<td>0.21</td>
<td>2.31</td>
<td>0.91</td>
<td>1.82</td>
</tr>
<tr>
<td>F5</td>
<td>3.08</td>
<td>21.76</td>
<td>4.69</td>
<td>2.83</td>
<td>61.18</td>
<td>1.28</td>
<td>0.26</td>
<td>0.13</td>
<td>2.21</td>
<td>0.87</td>
<td>1.96</td>
</tr>
</tbody>
</table>

Figure 4. Free lime content and insoluble residue of the prepared cement clinkers.

The major four phases (C₃S, β-C₂S, C₃A and C₄AF) of the various formed Portland cement clinkers containing different proportions of PFa (F0-F5) as calculated from Bogue Equations [24, 28] are listed in Table 4, and then are plotted in Figure 5. It is obvious that the percentage of C₃S is decreased with the increase of PFa content as shown in Table 4 and Figure 5. In contrast, the percentage of β-C₂S increased as the PFa content increased, except that of F4 which was little lower. However, all values of either C₃S and/or C₂S are very close or near to each other. This means that all mix composites are suitable to be exactly match to ASTM specifications [26]. The other two phases (C₃A and C₄AF) are similar to those of the blank clinker sample (F0). It could be concluded that the PFa could be used as a raw meal in the starting raw mix of cement clinker in the ratio 25-35 wt. % without any adverse effects.

Figure 5. The major phases of the prepared Fa cement clinker.
between 25 and 35 wt. % can be said that they are the nearly same. This is primarily (F0). As a result, the optimum PFa content would be in contents decreased and also the firing or clinkering temperature decreased. The optimum PFa content must not exceed than 35 wt.%. This is essentially attributed to that any further increase resulted in adverse effects on all characteristics of the produced clinker.

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Compliance with Ethical Standards
The authors declare that they have no competing interests.

References

Table 4. The major cement phases of the resulting cement clinkers.

<table>
<thead>
<tr>
<th>Phase Mixes</th>
<th>C3S</th>
<th>C2S</th>
<th>C3A</th>
<th>C4AF</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>F0</td>
<td>46.9549</td>
<td>26.3297</td>
<td>9.0167</td>
<td>12.5248</td>
<td>94.8261</td>
</tr>
<tr>
<td>F1</td>
<td>45.4771</td>
<td>27.7310</td>
<td>7.4786</td>
<td>11.4304</td>
<td>92.1171</td>
</tr>
<tr>
<td>F2</td>
<td>43.1628</td>
<td>30.3943</td>
<td>9.4621</td>
<td>6.7184</td>
<td>89.7376</td>
</tr>
<tr>
<td>F3</td>
<td>42.9245</td>
<td>30.2296</td>
<td>7.6173</td>
<td>8.7552</td>
<td>89.5266</td>
</tr>
<tr>
<td>F4</td>
<td>41.9664</td>
<td>31.6698</td>
<td>6.3287</td>
<td>7.6608</td>
<td>87.6257</td>
</tr>
<tr>
<td>F5</td>
<td>41.7644</td>
<td>30.9068</td>
<td>7.6458</td>
<td>8.6032</td>
<td>88.9202</td>
</tr>
</tbody>
</table>

Figure 6. Compressive strength of the prepared Fa cement clinkers.

3.4. Compressive Strength of the Formed Clinkers

The compressive strength of the various prepared Portland cement clinkers containing PFa (F0-F5) is plotted as a function of hydration periods from 1 day up to 90 days in Figure 6. The results indicated that the values of compressive strength for all hardened cement pastes at any age of hydration are much near or close to each other so that it can be said that they are the nearly same. This is primarily attributed to the similar composition of PFa to normal cement [16, 34, 35] as shown in Tables 1, 2 and also Figure 4, where even the major cement phases responsible for the cementation properties are near to each other [16, 21, 24, 36, 37]. Also, the blaine surface area or fineness of the various cement clinkers (F0-F5) increased with the addition of PFa [24, 30, 37]. Moreover, although the cement clinkers containing PFa are manufactured at lower firing temperatures, they exhibited compressive strength near to that of the blank (F0). As a result, the optimum PFa content would be in between 25 and 35 wt. % does not only save expensive natural resources, but also it can save energy as well. The formed major phases in presence of PFa are more or less the same as those of the blank as experimentally achieved and approved by the compressive strength. As the PFa content increased, the free lime contents decreased and also the firing or clinkering temperature decreased. The optimum PFa content must not exceed than 35 wt.%. This is essentially attributed to that any further increase resulted in adverse effects on all characteristics of the produced clinker.

4. Conclusion

The mineralogy and chemical properties of pulverized fly ash (PFA) was studied so as to determine its possibility to use it as a raw material in cement industry. It can be concluded that the oxide composition of the used PFa sample supplied by a local plant in Egypt can justify or apply as a raw material in the raw meal of Portland cement clinker manufacturing, and the result resulting clinker can gain some important characteristics in its durability. This

Figure 6. Compressive strength of the prepared Fa cement clinkers.


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