Physico-chemical Properties of the Hardened Blended Cement Pastes Made of OPC-MK Blends CKD

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Abstract

In blended cement, it was known that, metakaolin (MK) has a pozzolanic activity. It is reported that MK is more active when it fired. On the other side, cement kiln dust (CKD) with high alkali and sulfate content can be considered an excellent activator for pozzolanic materials. This study deals with the investigation of the hydration characteristics of pozzolanic cement pastes by blending various proportions of CKD with OPC (75%)-MK(25%) blend. The hydration characteristics of hardened cement pastes were investigated with respect to compressive strength, combined water content, free lime content, bulk density, and total porosity under different curing ages up to 180 days. The microstructure of hydrates was investigated using SEM technique.

1. Introduction

In recent years, there has been an increasing interest in the utilisation of metakaolin (MK) as a supplementary cementitious material [1, 2, 3]. The use of pozzolans at an effective replacement level was found to be more efficient than lowering the w/c ratio in enhancing the durability of concrete [4]. MK is an ultra-fine pozzolana, produced by calcining kaolin at temperatures between 700 and 900 °C, it consists of silica and alumina. The use of MK is reported
to increase the concrete strength, especially during the early ages of hydration [5, 6]. After 14 days of curing, the contribution that MK provides to concrete strength is reduced [2]. The increase in compressive strength of MK concrete is thought to be due to the filling effect where MK particles fill the space between cement particles and it accelerates cement hydration and pozzolanic reaction of MK. This effect is similar to that of silica fume. Although, the pore volume slightly increases in pastes containing MK and the pore structure of the paste is found to be refined [7,8]. The improvement in pore structure of the paste is increased, when the amount of MK increases as a partial substitution of PC [7]. The incorporation of 30 of the MK increases the sulphate resistance of the mortar [24].

The portlandite content in MK paste is reduced due to the reaction between PC hydrated product and MK [8, 9]. Therefore, the increased sulphate resistance in mortars containing MK was attributed to the reduction in portlandite system [10], which in turn would reduce the gypsum and ettringite formation. The other possible reason for the improved sulphate resistance is the refinement in pore structure, which would hinder the ingress of sulphate ions. The effects of metakaolin and rice husk ash on the hydration behavior and mechanical properties of blended cement were investigated [11]. The incorporation of MK in concrete increases the penetration resistance of chloride ions [4]. The pastes containing MK showed higher capacity to bind chloride ions compared with PC pastes [12]. Taher et al. [13] indicated that partial substitution of ordinary portland cement with 5 to 25 % burnt Kalabsha kaolinite clay will produce pozzolanic cement with higher hydraulic properties than ordinary portland cement and the optimum substitution value is 5 %. The effects of high temperatures on the mechanical properties and microstructure of nanometakaolin cement mortars were investigated [14]. The hydrothermal curing accelerates the hydration characteristics of cement materials due to enhance the progress of hydration of clinker phases and pozzolanic reactions have been studied [15]. Cement kiln dust (CKD) is a by-product of cement manufacture. It is a fine powdery material similar in appearance to portland cement. It is composed of micron-sized particles collected from electrostatic precipitators during the production of cement clinker. Fresh CKD can be classified as belonging to one of the four categories, depending upon the kiln process used and the degree of separation in the dust collection system.

The chemical composition of CKD depends both on the raw materials used to produce the clinker, and on the type and source of carbon-based fuel to heat the material in the rotary kiln. Free lime can be found in CKD and its concentration is typically highest in the coarser particles collected closest to the kiln. Finer particles tend to exhibit higher concentrations of sulfates and alkalis. If the coarser particles are not separated out and returned to kiln, then the dust will contain higher free lime, as it contains some coarser particles. CKD from wet process kilns also tends to be lower in calcium content than the dust from dry-process kilns. The X-ray diffraction analysis of the kiln dust indicates that it consists mainly of limestone as a main component, small quantity of quartz together with CaSO₄, NaCl, K₂SO₄, spurite [2(C₂S).CaCO₃] and sulphospurite [2(C₂S).CaSO₄] [16].

The physicochemical responses induced in kaolinite clay treated with 25 of a high free lime content CKD were investigated [16]. Atterberg limits, unconfined compressive strength and stiffness of the compacted, CKD-treated kaolinite were measured as function of curing period. These
properties were compared with those of the untreated clay and of the clay treated with quicklime, so as to determine the comparative extent of enhancement induced by the CKD treatment. The CKD-treated clay developed significantly higher strength than quicklime-treated clay containing the same amount of lime. The remarkable enhancement in clay properties observed suggests significant potential for use of some CKDs as soil stabilizers. Pozzolanic activity of dealuminated kaolin (DK) and burnt kaolinite clay (BK) was studied using cement kiln dust (CKD) or hydrated lime (CH) as activators [17].

In this study, the on the hydration characteristics of of pozzolanic cement pastes produced by blending various proportions of CKD with OPC (75%)-MK (25%) has been reported. The hydration characteristics of hardened cement pastes were investigated with respect to compressive strength, combined water content, free lime content, bulk density and total porosity for different curing ages up to 180 days. The microstructure of the formed hydrates was investigated using scanning electron microscopy (SEM) technique.

2. Materials and Experimental Techniques

Materials used in the present work, OPC and CKD from Assuit Cement Co., Egypt, Kaolinite clay was collected from Kalabsha, Aswan, Egypt. Kaolinite clay was calcined in an electrical muffle furnace with at 800 °C for 2 h, to give metakaolin (MK). MK recharged from the muffle furnace, cooled to room temperature in desiccator and ground to pass 90 µm sieves. The mixes and their compositions are shown in Table 1. Each dry was homogenized for one hour in porcelain ball mill provided with four balls to obtain complete homogeneity then kept in airtight containers until the time of cement paste preparation. Each dry was mixed for three minutes with the suitable water/solid ratio required to attain the standard consistency. The resulting paste was then pressed by hand molding pressure into stainless steel cylindrical moulds of 3.14 cm2 cross-section and 2 cm height. The moulds were vibrated for one minute to remove any air bubbles and voids. Immediately after molding, the cylindrical specimens were cured in humidity cabinet at about 100% relative humidity at room temperature for 24 h in order to attain the final setting of the specimens. The specimens then were demolded and cured under tap water for hydration periods such as, 1, 3, 7, 28, 90 and 180 days.

<table>
<thead>
<tr>
<th>Sample Code</th>
<th>OPC</th>
<th>MK</th>
<th>CKD</th>
</tr>
</thead>
<tbody>
<tr>
<td>B0</td>
<td>75</td>
<td>25</td>
<td>0</td>
</tr>
<tr>
<td>B1</td>
<td>75</td>
<td>25</td>
<td>5</td>
</tr>
<tr>
<td>B2</td>
<td>75</td>
<td>25</td>
<td>10</td>
</tr>
<tr>
<td>B3</td>
<td>75</td>
<td>25</td>
<td>15</td>
</tr>
<tr>
<td>B4</td>
<td>75</td>
<td>25</td>
<td>20</td>
</tr>
<tr>
<td>B5</td>
<td>75</td>
<td>25</td>
<td>25</td>
</tr>
</tbody>
</table>

Bulk density was determined using Archimedes principle [18]. The compressive strength was measured using a manual compressive strength machine for a set of three cubes according to ASTM designation [19]. Free water content was determined using domestic microwave oven (Olympic electric model KOR-131G, 2450 MHz, 1000 W) [20]. The combined water content was determined using hydration stopped specimen after being ignited in porcelain crucibles at 1000 °C for 1 h in a muffle furnace. The total porosity of the hardened cement paste was calculated from the values of bulk density, free and total water contents as described elsewhere [21]. Free lime CaO were determined at
curing times after stopping the hydration of the hardened pastes [22, 23].

3. Results and Discussion

Table 2 illustrates the chemical composition of the OPC, CKD and MK for 3 h determined by XRF analysis. According to Bouge’s calculations, OPC is composed of (51.4 wt. %) C₃S, (20.15 wt.) % C₂S, (15 wt. %) C₃A and (14.24 wt. %) C₄AF. The mineralogical composition of Kalabsha kaolinite clay was found to be: (97 %) kaolinite, and (3 %) quartz [24].

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Portland cement</th>
<th>Kaolinite clay</th>
<th>CKD</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>20.48</td>
<td>44.18</td>
<td>13.69</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>4.76</td>
<td>36.75</td>
<td>3.21</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>4.69</td>
<td>1.36</td>
<td>2.41</td>
</tr>
<tr>
<td>CaO</td>
<td>62.15</td>
<td>0.26</td>
<td>46.09</td>
</tr>
<tr>
<td>SO₃</td>
<td>2.63</td>
<td>-----</td>
<td>4.05</td>
</tr>
<tr>
<td>MgO</td>
<td>1.47</td>
<td>0.16</td>
<td>1.44</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.46</td>
<td>0.18</td>
<td>4.89</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.27</td>
<td>0.25</td>
<td>4.94</td>
</tr>
<tr>
<td>Cl</td>
<td>0.06</td>
<td>-----</td>
<td>6.92</td>
</tr>
<tr>
<td>Mn₂O₃</td>
<td>0.55</td>
<td>-----</td>
<td>-----</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.58</td>
<td>2.94</td>
<td>-----</td>
</tr>
<tr>
<td>L.O.I</td>
<td>1.85</td>
<td>13.55</td>
<td>12.06</td>
</tr>
<tr>
<td>Total</td>
<td>99.96</td>
<td>99.63</td>
<td>99.70</td>
</tr>
</tbody>
</table>

3.1 Compressive Strength

The effect of pozzolana on the strength of pozzolanic cement pastes depends on number of factors such as the content, type and surface area and the individual characteristics of the OPC. It is well known that substitution of Portland cement with pozzolan materials reduces the initial rate of strength development at early ages. This may be explained by the slow rate of the pozzolanic reaction. At early ages, pozzolana acts as filler which dilutes. Hence the strength of pozzolanic cement paste is than that of OPC at early ages. Later ages the situation is reversed and pozzolanic cement paste attains the same or even a higher compressive strength than the corresponding OPC paste because as the hydration proceeds more hydration products and more cementing materials are formed such as CSH as well as CAS leading to increase compressive strength of hardened cement pastes.

The results of compressive strength of the blended cement pastes made from OPC-MK blends including different ratios of CKD curing time up to 180 days is given in Fig 1. The compressive strength of the all hardened blend in absence and presence of CKD increases with curing time. As the hydration proceeds, more hydration products and more cementing materials are formed leading to increase compressive strength of cement pastes. This is mainly due to that the hydration products possess a large specific volume than the unhydrated cement. Therefore, the accumulation and compaction of these hydrated products give higher strength.

Figure 1: Compressive strength (Kg cm⁻²) of hardened specimens as function of curing time
The compressive strength values of the hardened pastes made from PC-MK blends including CKD, increase continuously with increasing age of hydration, it is clear that the best mixes are those with 10 and 15 % CKD (mixes B2&B3); these mixes show reasonable values of compressive strength compared to the mix without CKD (B0). Therefore, such mixes can be considered optimum for the utilization of CKD in the production of blended cement.

The pastes with 5 and 10 % CKD show relatively higher compressive strength compared to B0, at early ages up to 7 days of hydration. This can be attributed to the activation effect of the high alkali, sulfate content of CKD. The compressive strength decreases with increasing CKD content as a result of dilution of portland cement. In addition, the large amounts of alkalies present in CKD caused a sort of crystallization of hydration products, which resulted in opening of pore system of the hardened sample leading to the reduction of the compressive strength.

3.2 Bulk Density

The results of bulk density of the hardened blended cement pastes made from OPC-MK in absence and presence of ratios of CKD at different hydration ages are illustrated graphically in Fig. 2. The density is an important factor in the determination of porosity, assessment of durability and strength and estimation of lattice constants for the CSH phase in hydrated portland cement. The hydration products fill some of pores because the volume of hydration products is more twice than that of the anhydrous cement; this decreases the porosity and increases the bulk density of hardened cement paste.

The bulk density of all hardened cement pastes increases with curing time as a result of the hydration of clinker phases and formation of further hydration products that fill some of pores in the cement paste as well as due to the pozzolanic reaction of MK with librated CH. The bulk density of mixes B0, B1, B2, B3, B4 and B5 increases with curing time. This is mainly due to progress of the cement pastes. As the hydration proceeds, the hydration products fill a part of the pore volumes, therefore, the bulk density increases and total porosity decreases. In addition, the bulk density values of pozzolanic cement pastes made from OPC-MK blends including CKD mixes B1, B2 and B3 give the highest values and mix B5 give the lowest values which is in a good agreement with the compressive strength values.

![Bulk density of hardened samples as function of curing time](image)

Figure 2: Bulk density of hardened samples as function of curing time

3.3 Total Porosity

The results of total porosity of the hardened blended cement pastes made from OPC-MK in absence and presence of ratios of CKD at different hydration ages are illustrated graphically in Fig. 3. The porosity is an intrinsic property of cement paste which influences the strength and permeability of cement pastes. The porosity of the paste depends on many factors and typically increases with the W/C and decreases with the curing period. Also porosity depends on the type of cement. The results show that for all pastes, Total porosity decreased as the curing age
increased. The pastes containing CKD, The total porosity deceased with small amounts of CKD (5-10) %, This indicates that the MK and CKD used in this study are effective in the refinement of the pore structure of the blended cement system due to the accumulation of hydration products in the open pores of cement pastes. The cement pastes containing 25 % CKD (B5) showed higher porosity than all mixes beside the control paste (B0), indicating the lower pozzolanic activity MK in presence excess amounts of CKD due to the large amounts of alkalies present in CKD caused a sort of crystallization of hydration products, which resulted in opening of pore system of the hardened samples leading to the increase of total porosity.

**Figure 3:** Total porosity of hardened samples as function of curing time

3.4 Free lime content (CaO, %)

The results of Free lime content (CaO,%) of the hardened blended cement pastes made from OPC-MK in absence and presence of CKD at different hydration ages are illustrated graphically in Fig. 4. All mixes show that, the Free lime content (CaO,%) of all mixes decreases as the curing age increases this due to the pozzolanic reaction of metakaolin (MK) with free lime. the quantity of free lime increases with increasing CKD content in the blended cement pastes. This may be attributed to the leaching of Ca$^{2+}$ ions from CKD, in addition to the lime liberated due to the hydration of OPC.

**Figure 4:** Free lime content of hardened samples as function of curing time

3.5 Combined Water Content ($H_2O$, %)

The degree of hydration of Portland cements may be estimated by the determination of the combined water content of the hardened cement pastes. The definite chemical composition of different hydrates as well as the changes caused by pozzolana in their chemical composition is not accurately known. Accordingly the determination of combined water is far being useful in determining the degree of hydration of blended cement. The combined water content of hardened cement paste depends on the amount and type of hydration products. It is well known that the combined water content increases with curing time due to formation of hydration products which have high combined water contents such as CSH, C$_4$AH$_{13}$ and C$_2$ASH$_8$.

On the other side, combined water may decreases with curing time of cement pastes due to the transformation of the hydration products of lime to that of low lime contents. Combined water content of the blended cement pastes made from OPC-MK in absence and presence of CKD with curing time up to 180 days are shown in Fig. 5. It
is clear that the combined water content increases with curing time for all cement pastes due to the progress of the hydration with curing time. The results of combined water content of all blended cement pastes containing CKD are lower than that of control paste (B0). This is due to the decrease of clinker content with increasing of CKD.

Figure 5: Combined water content of hardened specimens as function of curing time

Obviously, the change of combined water contents of such mixes show three stages namely; (i) “pre-dormant” period where a rapid interaction between water and the grains of blended cement constituent (1-3 days), (ii) “the dormant” period where the hydration reaction was slow down due to the formation of an almost impermeable layer of amorphous hydrates around the cement grains which hinders the diffusion through this amorphous layer to the remaining unhydrated cement grains (3-7 days) and (iii) “the acceleration” stage where the hydration reaction is accelerated as a result of stabilization (via crystallization) of the initially formed hydrates and the diffusion of water becomes unhindered leading to the formation of larger amounts of hydration products (up to 7 days). The duration of these hydration stages depend on the constitution of each cement blend.

3.6 Morphology and Microstructure

Some samples were investigated using scanning electron microscopy (SEM) as representatives for the hardened OPC-MK pastes. These samples were made from mix B0 (75% OPC: 25% MK) without CKD at different curing age of hydration; their SEM micrographs are shown in Fig. 6 (a-f). The scanning electron micrographs shown in Fig. 6(a) and (b) displayed the formation of various hydration products after 3 days of hydration; there are: microcrystalline calcium silicate hydrates (CSH), fibrous crystals of ettringite (C₃A·3CS·32H₂O) and some hexagonal crystals of monosulfate hydrate (C₃A·CS·12H₂O). These hydrates appeared as clear binders between the remaining unhydrated parts of cement grains. After 28 days, the SEM micrographs indicated the formation of more crystalline calcium silicate hydrates (Fig. 6(c) and (d)); these hydrates appeared as bundles of short and long fibers inter-connected within the pore system of the hardened blended cement paste. On prolonged hydration, however, the microstructure appeared as close-textured hydration products with amore denser structure (Fig. 6(e) and (f)).

4. Conclusions

It can be concluded that the pozzolanic cement paste made from 75 wt % OPC, 25 wt % metakaolin and 5-10 wt % of CKD is characterized by high ultimate compressive strength and bulk density as well as low total porosity, this results in close to the control cement paste results due to the combined pozzolanic activities of MK and CKD. Accordingly, it is recommended to use this pozzolanic cement mix for general construction purposes. In addition, the utilization of CKD in construction purposes solves the problem of its disposal thus keeping the environment free from pollution.
Figure 6: SEM images of hardened pastes of the hardened pozzolanic cement pastes of mix. B0 after 3 days (a) and (b), 28 days (c) and (d) and 180 days (e) and (f) of hydration

Reference


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