Using metakaolin to improve the compressive strength and the durability of fly ash based concrete

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Abstract

Partial replacement of Portland cement by pozzolanic and cimentitious by-products or mineral additions that allow for carbon dioxide emission reductions is a major issue in the current climate change context. However, the use of low pozzolanic activity by-products like fly ash can cause a decrease relatively early in compressive strength. In this paper, the effect of metakaolin and fly ash on strength and concrete durability was investigated. The durability was assessed by different means of water absorption, oxygen permeability and concrete resistivity. Results show that partial replacement of cement by 30% fly ash leads to a decrease relevantly early in compressive strength, when compared to a reference mix of 100% Portland cement. Results also show that using 15% fly ash and 15% metakaolin replacement is responsible for minor strength loss but leads to outstanding durability improvement.

Keywords: Concrete, cement, fly ash, metakaolin, strength, durability

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1. INTRODUCTION

Although Portland cement demand are decreasing in industrial nations, it is increasing dramatically in developing countries [1,2]. Cement demand projections shows that by the year 2050 it will reach 6000 million tons. Portland cement production leads to major CO₂ emissions, results from calcination of limestone (CaCO₃) and from combustion of fossil fuels, including the fuels required to generate the electricity power plant, accounting for almost 0.7 tons of CO₂ per ton. of cement [3], which represents almost 7% of the total CO₂ world emissions [4]. Other authors speak of 5% [5]. This is particularly serious in the current context of climate change caused by carbon dioxide emissions worldwide, causing a rise in sea level and being responsible for a meltdown in the world economy [6,7]. Since Portland cement is used mostly in concrete production, the most important building material on Earth (10.000 billion tons per year), partial replacement by pozzolanic by-products and mineral additions will allow relevant carbon dioxide emissions reductions. Investigations about the pozzolanic properties of fly ash, calcined clays and calcined agriculture wastes were already carried out [8-10]. Pozzolanic admixtures react with Ca(OH)₂ generating additional CSH phases, resulting in a more compact concrete with increase durability. Some supplementary cementitious material, like fly ash has very slow hydration characteristics thus providing very little contribution to early age strength [11], while others like metakaolin possess a high reactivity with calcium hydroxide having the ability to accelerate cement hydration [12]. Since current concrete structures present higher permeability levels that allows aggressive elements to enter, leading corrosion problems [13], using pozzolanic admixtures not only reduce carbon dioxide emissions but also allows structures with longer service life, thus lowering their environmental impact [14]. Nevertheless, studies on the durability performance of concrete containing pozzolanic by-products are recent [15] and still scarce. Even scarcer about the durability performance of concrete that contains blended reactive pozzolans. This paper presents experimental data about the strength and durability performance of metakaolin, fly ash based concrete.

2. EXPERIMENTAL WORK
2.1 Materials, mix design and concrete mixing

The characteristics of the aggregates used to make the concrete mixtures are shown in Table 1. An ordinary Portland cement (CEM II 42.5) was used. Four concrete mixes with a water/binder ratio of 0.55 were designed using the Faury concrete mix design method [16,17]. The concrete mixes are described in Table 1.

Table 1: Concrete mix proportions (kg/m$^3$)

<table>
<thead>
<tr>
<th>Components</th>
<th>Control</th>
<th>C_15MK</th>
<th>C_30FA</th>
<th>C_15MK-15FA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cement II 42.5 (kg)</td>
<td>346.05</td>
<td>294.15</td>
<td>242.25</td>
<td>242.25</td>
</tr>
<tr>
<td>Fine sand (kg)</td>
<td>352.35</td>
<td>352.35</td>
<td>352.35</td>
<td>352.35</td>
</tr>
<tr>
<td>Sand (kg)</td>
<td>806.25</td>
<td>806.25</td>
<td>806.25</td>
<td>806.25</td>
</tr>
<tr>
<td>Coarse aggregate 12.5 (kg)</td>
<td>466.8</td>
<td>466.8</td>
<td>466.8</td>
<td>466.8</td>
</tr>
<tr>
<td>Coarse aggregate 20 (kg)</td>
<td>669.45</td>
<td>669.45</td>
<td>669.45</td>
<td>669.45</td>
</tr>
<tr>
<td>Water (l)</td>
<td>171.75</td>
<td>171.75</td>
<td>171.75</td>
<td>171.75</td>
</tr>
<tr>
<td>MK (kg)</td>
<td>-</td>
<td>51.9</td>
<td>-</td>
<td>51.9</td>
</tr>
<tr>
<td>FA (kg)</td>
<td>-</td>
<td>-</td>
<td>103.8</td>
<td>51.9</td>
</tr>
<tr>
<td>Plasticizer (%)</td>
<td>1</td>
<td>1</td>
<td>0.2</td>
<td>1</td>
</tr>
</tbody>
</table>

A reference mixture (Control) and three more mixtures, a second with 15% replacement of cement by metakaolin (C-15MK), a third one with 30% replacement of cement by fly ash (C-30FA) and one more with 15% replacement of cement by metakaolin and with 15% replacement of cement by fly ash. A plasticizer (Pozzolith 390 NP) was used at appropriate percentages in order to retain the slump of the fresh concrete between 160 and 210 mm (class S4 of NP EN 206-1[18]).

3 EXPERIMENTAL PROCEDURES

3.1 Compressive strength

The compressive strength was performed under Standard E237 LNEC[19]. The specimens were conditioned at a temperature equal to 21 ± 2 °C cured in a moist chamber until they had reached their testing times. Tests were performed on 100x100x100 mm$^3$ specimens. Compressive strength for each mixture was obtained from an average of 3 cubic specimens determined at the time of 3, 7, 14 and 28 days of curing.

3.2 Capillarity water absorption

Capillarity water absorption was carried out using cylindrical specimens 20 cm high and with 10 cm diameter. The test consists in placing the cylindrical specimens in a container with enough water to maintain immersed one of the sides of the sample. This test his carried on according to Standard LNEC E393.

3.3 Oxygen permeability

To evaluate the specimens’ oxygen permeability the permeability cell presented in Fig. 2 was used. The permeability cell used was developed at the University of Leeds (U. K.) and it has been used broadly to determine, either oxygen or water permeability of concretes and mortars [25]. Oxygen permeability was obtained form an average of 3 specimens, (4 cm high and 5 cm diameter).

3.4 Electric resistivity

Electric resistivity was obtained from an average of 3 cubes 10 cm high. The electric resistivity of the concrete specimens were performed using the four-point Werner electrode according to others [22]. Prior
to measurements, the specimen’s surfaces were cleared of excess water with a dry cloth. The specimens were measured on three lateral sides, two readings on each side with a 180º rotation (six readings per specimen). Readings were performed for 7, 14 and 28 days of curing. Corrosion risk was assessed through recommendation to the European Concrete Committee (CEB 192) which is represented in Table 2.

<table>
<thead>
<tr>
<th>Concrete resistivity (Ω.m)</th>
<th>Corrosion risk</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt;50</td>
<td>Very high</td>
</tr>
<tr>
<td>50-100</td>
<td>High</td>
</tr>
<tr>
<td>100-200</td>
<td>Low</td>
</tr>
<tr>
<td>&gt;200</td>
<td>Very low</td>
</tr>
</tbody>
</table>

4 RESULTS AND DISCUSSION

4.1 Compressive strength

Compressive strength of concrete mixtures is shown in Fig. 1. The standard deviation was 11%. Fly ash based concrete has the worst strength performance, confirming the slow hydration characteristics found in others [11].

Strength decrease for this admixture is very severe reaching almost 40%. This is a relevant drawback for the construction industry. The 15% metakaolin based concrete possessed a higher reactivity with calcium hydroxide [12], but a direct comparison can not be made to the fly ash concrete mix because it had a different cement content. As for the metakaolin, fly ash addition it had the same cement as the fly ash based concrete but at a much higher strength meaning that the rapid reaction of metakaolin compensated the fly ash’s lower early strength. Other authors [23] use silica fume in order to compensate the low early age strength of fly ash, but in Portugal that’s not an economic option since the cost of silica fume is ten times more costly than Portland cement.

4.2 Capillary water absorption

The standard deviation of capillary water absorption was 9%. The mixture with 15% cement replacement by metakaolin performed worse than the control (Fig 2). As for the mixture with 30% fly ash, had almost
the same capillary water absorption of the control, except beyond 48 hours when absorption stopped rising.

![Capillary water absorption graph](image_url)

**Fig. 2 – Capillary water absorption**

The results for the mixture with 15% fly ash and 15% metakaolin showed a remarkable performance with a capillarity coefficient of 0.16 kg/m².h⁰.⁵, while the same coefficient for other mixtures varies between 0.23 and 0.24. It is worth noting, that a plain C30/37 strength class concrete has a capillary coefficient of 0.251 kg/m².h⁰.⁵ for 28 days curing [24]. While a plain C20/25 strength class concrete (the most used strength class in Europe [25] has capillarity coefficients between 0.85 and 2.6 kg/m².h⁰.⁵ [26], which proves that the combined effect between fly ash and metakaolin, has a very positive impact on concrete durability.

### 4.3 Oxygen permeability

Fig. 3 present oxygen permeability results (the standard deviation was 10%), which once more show the mixture with 15% fly ash and 15% metakaolin has the best performance, due to the formation of a very compacted concrete structure.

![Oxygen permeability graph](image_url)

**Fig. 3 – Oxygen permeability**
4.4 Electric resistivity

Electric resistivity measurements are shown in Fig. 4. The standard deviation was 9%. Up until 7 days curing electric resistivity is almost the same for all concrete mixes. Beyond that curing time, only the mixes with pozzolanic additions show a rising behavior.

The corrosion risk (according to CEB 192), for the control mixture is always high. The mixtures with metakaolin perform in a similar way between the 7th and 14th curing days, meaning that the higher cement content is compensated by the synergetic effect between fly ash and metakaolin. From 14 days onwards, the mixture with 15% fly ash and 15% metakaolin shows a higher rising behavior than the mixture with 15% cement replacement by metakaolin. Fly ash/metakaolin electric resistivity behavior has low risk corrosion after 3 weeks and seems to go to very low risk in a short period. Since electrical resistivity is one of the main parameters controlling the initiation and propagation of reinforcement corrosion [27,28], the use of fly ash/metakaolin based concrete seems to be a very effective option.

4.5 Conclusions

In the next 40 years Portland cement demand will have a twofold increase reaching 6000 million tons/year. The use of pozzolans in concrete can allow major carbon dioxide reductions and also increase the service life of concrete structures; furthermore, in the case of waste pozzolans it also reduces the disposal areas. Fly ash is a by-product with low pozzolanic activity being associated with early age compressive strength. This paper confirms that partial replacement of Portland cement by 30% fly ash leads to serious decrease in early age compressive strength when compared to a reference mix of 100% Portland cement. The use of 15% fly ash and 15% metakaolin based mixtures are responsible for minor strength loss but leads to an outstanding durability improvement. Fly ash/metakaolin mixtures have a low corrosion risk assessed in electric resistivity tests.

4.6 References