INFLUENCE OF RECYCLING FLUID CATALYTIC CRACKING ON PROPERTIES OF FRESH CEMENT PASTES

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ABSTRACT

Industry wastes used as a supplementary or mineral addition in cementitious materials have always become “by-products” and not wastes. These by-products when incorporated into cements diminish the environment impact, reduce the cement consumption and improve several properties on fresh and hardened mortars and concretes. Fluid catalytic cracking waste (FCCW) produced at petroleum industries is a by-product that can be used as a mineral addition in cements. Researches had been attained and results showed that it has pozzolanic characteristics. The study of this by-product is recent and its influence on the cementitious materials could be more understanding. The aim of this work was to verify FCCW influence on properties of fresh paste, such as setting time, temperature evolution during setting and the consistency of mortars. Pastes and mortars studied were produced with natural and grounded FCCW (30% cement replacement by mass). Results showed that FCCW, when used as supplementary material in cement, affect the workability, reduces setting time, increasing the kinetics reaction and mortars consistency.

Keywords: FCC, Pozzolans, Setting Time, Temperature Evolution, Heat of Hydration, Workability

INTRODUCTION

Inorganic materials that take part in the hydration reactions of Portland cement have been used as supplementary cementing materials. These inorganic materials are called mineral additions and could be classified as pozzolanic or latent hydraulic materials. Pozzolanic materials have high SiO2 and Al2O3 content, they have reactivity, and their mixture with water and CaO produce a new compound called calcium silicate hydrate (C-S-H). In this way, they act as hydraulic cements, improving several fresh and hardened properties on cement materials [1].

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Natural and artificial mineral addition, such as fly ashes, silica fume, blast furnace slag, steel slag, volcanic ashes, diatomaceous earth, rice husk ash, have been used as pozzolanic materials [1] [2] [3].

Most of mineral additions used as supplementary cementing materials are wastes from industry and offer environmental, economic and technological advantages such as (i) reduce the natural resource mining; (ii) prevention of disposal problems; (iii) reduce the energetic coast of Portland cement production and (iv) improve the properties of cementitious materials [1] [2] [3] [4].

Conversion processes at a refinery are used to increase the quantity and the quality of the end product (gasoline). Various conversion processes are used and the most common is to crack the high molecular-weight into smaller. catalytic cracking is the most important and the Fluid Catalytic Cracking (FCC) is by far the most widely used.

The waste generated from this process is a problem for the petroleum industry. This waste is sent to the cement industry to be used in clinker production because of the silica oxide in its chemical composition. Its waste is classified as inert material from the environmental point of view, and the quantity is significant. Furimsky reported that about 400,000 tons were produced annually [5].

Fluid catalytic cracking waste (FCCW) is an inorganic material that could be used as a mineral addition on cementitious materials. This material has pozzolanic characteristics [4] as similar as silica fume and fly ash [5]. Studies about chemical, physical and mechanical properties on mortars containing FCCW as supplementary cementing materials have been done by several authors [4] [5] [6] [7] [8] [9].

The aim of this work was to contribute to these studies observing the influence of FCCW on fresh mortars properties. The properties evaluated are the mortars workability by consistency measured by initial flow, setting times and the temperature evolution during setting of pastes.

**FLUID CATALYTIC CRACKING WASTE (FCCW)**

Fluid Catalytic Cracking waste (FCCW) is a residue from naphtha cracking process in the petroleum refineries industry. FCCW consists, basically, of silicates and aluminates compounds with opened atomic structure (zeolite type) and high specific surface, which could be responsible for the high pozzolanic material activity [4] [7] [8].

FCCW presents a spherical morphology when observed by Scanning Electron Microscopy (SEM). These spherical particles, with 0,1 to 30 μm of diameter, has a porous appearance with internal caves and connected channels. Specific gravity value for FCCW is about 2450 kg/m3 [4] [7] [8]. Porous structure of the FCCW is responsible for speeding up the kinetic cement hydration reactions when used as a mineral addition on cementitious materials. They act as nucleation points for precipitation of hydrate products, providing pozzolanic characteristics to this material [7].
When finely grounded, FCCW presents particles with irregular shape, less than 2 μm in diameter and porous structure, that increase their reactivity and its specific gravity ranged from 2450 kg/m3 to 2510 kg/m3 [4] [9].

Pacewska; Wilinâska e Kubissa [5] studied the influence of FCCW on hydration of cement paste. The use of FCCW accelerated considerably the hydration process with a strongly exothermic process, making cement paste sets much more rapidly.

The pozzolanic activity of FCCW was studied by Payá, Monzó and Borrachero [6] on mortars produced with grounded FCCW. They concluded that in the first ages the material did not show pozzolanic activity. The initial action of grounded FCCW was restricted to act as filler, an inert addition. The increase of compressive strength occurred after 7 days of age, and with the obtained results it could be considered as a pozzolanic mineral addition.

Payá, Monzó and Borrachero [4] had shown the workability reduction on mortars produced with FCCW and grounded FCCW. The studied mortars showed a significant relation with the reference mortar; however, there were not differences in results with FCCW and with grounded FCCW. It suggested that the effect of FCCW used on mortars workability is recurrent, much more, for the internal structure of the FCCW than the material fineness.

EXPERIMENTAL PROGRAM

Experimental work consisted of testing pastes and mortars produced with FCCW, described as follows.

1.1 Materials

Materials used in this experimental work were: high initial strength Portland cement (named CPV ARI RS) which characteristics were according to Brazilian standard NBR 5733 [10], natural FCCW (FCCWn), grounded FCCW (FCCWg) and water.

The FCCW source was from Paulínia-SP petroleum refinery. The color of material was slightly grey. A laboratory ball mill was used to obtain FCCWg.

Natural and grounded FCCW were used as a cement replacement by mass (30%) and mixtures used 0.53 water/cement or water/cement+FCCW ratio (water/binder ratio).

Specific gravity and fineness on 75 μm sieve opening were determined in accordance with Brazilian standards NBR 6508 [14] and NBR 11579 [15], respectively.

Morphologies from natural FCCW (FCCWn) and grounded FCCW (FCCWg) were obtained by scanning electron microscopy (SEM-LV JSM 5900) at National Laboratory of Synchrotron Light (LNLS), equipped by X-ray diffraction energy dispersive microanalysis (SEM-EDS).
1.2 Mix design

Pastes were produced with cement, FCCW (natural and grounded) and water. All pastes had the same mixing proportions and they were 1: 0.53 (1 part of cement: 0.53 part of water/binder ratio), in mass (Table 1). The mixture procedure followed Brazilian Standard NBR NM 43 [11].

<table>
<thead>
<tr>
<th>Prepared Pastes – 1:0,53 (in mass)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mixtures</td>
</tr>
<tr>
<td>----------</td>
</tr>
<tr>
<td>P1</td>
</tr>
<tr>
<td>P2</td>
</tr>
<tr>
<td>P3</td>
</tr>
</tbody>
</table>

Mortars were cast with cement, FCCW (natural and grounded) and natural sand. All mortars had the same mixing proportions and they were 1: 3: 0.53 (1 part of cement: 3 parts of natural sand: 0.53 parts of water/binder ratio), in mass (Table 2).

Fresh mortar was prepared using a 5 liters countercurrent pan-type mixer. At first, cement and FCCW powder (previously mixed) were mixed with the mixing water. After that, further mixing was done with the addition of natural sand. The mixing operation was completed in 5 minutes. The mixture procedure followed Brazilian Standard NBR 7215 [12].

<table>
<thead>
<tr>
<th>Prepared Mortars – 1:3:0,53 (in mass)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mixtures</td>
</tr>
<tr>
<td>----------</td>
</tr>
<tr>
<td>M1</td>
</tr>
<tr>
<td>M2</td>
</tr>
<tr>
<td>M3</td>
</tr>
</tbody>
</table>

1.3 Test methods

In order to evaluate the characteristics of each mixture, it was prepared pastes and mortars to perform tests in fresh state (Figure 1).
In fresh pastes it was evaluated setting times by Vicat needle, according to Brazilian Standard NBR NM65 [13]. Temperature evolution during setting was also determined using a semi-adiabatic recipient. Three thermocouples were used to measure pastes temperatures. They were connected to a datalogger Testo 177 which registered the temperatures.

In fresh mortars the workability was measured by the initial flow in accordance with Brazilian Standard NBR 7215 [12]. Each property was measured in three samples of every paste and mortar, and the arithmetic mean of the results calculated.

RESULTS AND DISCUSSION
The results of the tests conducted with the pastes and mortars produced with natural and grounded FCCW are presented in this section.

1.4 FCCW characteristics
Morphologies from FCCWn and FCCWg were obtained with a scanning electron microscopy (SEM-LV JSM 5900), and an elementary composition with a X-ray diffraction dispersive energy microanalysis (SEM-EDS). Figures 2 and 3 show the particles of FCCWn and of FCCWg, respectively.
Natural FCCW (FCCWn) particles were spherical and their diameter ranging from 40 μm to 150 μm (Figure 2a). These particles showed a roughness on their surface (Figure 2b). After grinding FCCWg particles changed their shape. These grounded particles showing angular and spherical ones. Their diameter ranged from 25 μm to 75 μm (Figure 3a). Some particles had a very porous structure showing many internal channels (Figure 3b).

In order to evaluate its composition, both natural and grounded FCCW were analyzed by EDS. The results are observed on Figure 4 and Table 3.

The chemical nature showed the major presence of silicates and aluminates compounds in FCCWn and FCCWg. This can explain the pozzolanic performance of this waste.
Table 3. EDS chemical elementary composition from diagrams showed on Figure 4

<table>
<thead>
<tr>
<th>Material</th>
<th>O</th>
<th>Al</th>
<th>Si</th>
<th>Fe</th>
<th>Au</th>
</tr>
</thead>
<tbody>
<tr>
<td>FCCWn</td>
<td>41</td>
<td>23</td>
<td>25</td>
<td>0</td>
<td>8</td>
</tr>
<tr>
<td>FCCWg</td>
<td>52.07</td>
<td>13.86</td>
<td>14.25</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Specific gravity and fineness are presented on Table 4.

Table 4. Physical properties measured from FCCWn and FCCWg

<table>
<thead>
<tr>
<th>Material</th>
<th>Physical properties</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>specific gravity (kg/m³)</td>
</tr>
<tr>
<td>FCCWn</td>
<td>2713</td>
</tr>
<tr>
<td>FCCWg</td>
<td>2697</td>
</tr>
</tbody>
</table>

FCCWn and FCCWg have (i) the same chemical nature, Si an Al and (ii) the same particle appearance as the materials used by Payá, Monzó and Borrachero (4). Therefore they have significant difference on size and specific gravity. Values were greater than values (2450 kg/m³ until 2510 kg/m³) reported on their research.

1.5 Mortars consistency

The summary of the results obtained in terms of mortar initial flow are presented in Table 5. Figure 5 show mortar spreading on flow table.
Table 5. Initial flow results of mortars

<table>
<thead>
<tr>
<th>Mixtures</th>
<th>M1</th>
<th>M2</th>
<th>M3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial flow value (mm)</td>
<td>209</td>
<td>142</td>
<td>146</td>
</tr>
</tbody>
</table>

Initial flow mortars produced by FCCW (M2 and M3) were lower than mortar produced only CPV ARI RS (M1). There were a significant reduction on workability properties. The particle roughness from natural and grounded FCCW can be responsible for this reduction [4]. There were no significant difference on initial flow resulting from mortars produced with both FCCWn and FCCWg.

1.6 Setting times

Setting times measured by Vicat needle are presented on Table 6.

<table>
<thead>
<tr>
<th>Setting</th>
<th>Pastes</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>P1</td>
</tr>
<tr>
<td>Initial setting (h:min)</td>
<td>4:00</td>
</tr>
<tr>
<td>Final setting (h:min)</td>
<td>7:00</td>
</tr>
</tbody>
</table>

Natural and grounded FCCW accelerated initial and final setting times of pastes. The same result was obtained by Pacewska; Wilinâska e Kubissa [5]. There were no significant difference on initial setting from pastes produced by FCCWn and FCCWg; and a slightly difference between final setting from FCCWn and FCCWg. The grounded of FCCW accelerated final setting.
1.7 Pastes temperature evolution

Data from temperature evolution of pastes with and without FCCW are shown on Figures 6 to 8. Temperatures were measured by a datalogger which registered the values with time.

The vertical lines on figures represent the setting times measured by Vicat needle.

From these Figures it is observed that FCCWn and FCCWg accelerated the hydration reaction with a high exothermic process. Cement pastes with FCCW addition (P2 and P3) quickly had its initial setting times (around one hour). The hydration process continued rapidly, and final setting is reached after 4:30 hours (P2) and 3:30 hours (P3).

Relatively to reference results (reference paste, with no addition) (Figure 6), which had its initial setting at 4:10 hours, both pastes P1 (Figure 7) and paste P2 (Figure 8), at this time, reached their final setting.

Figure 6. Temperature evolution from pastes P1 – 100% CPV ARI RS.
Figure 7. Temperature evolution from pastes P2 – 70% CPV ARI RS+30%FCCWn.

Figure 8. Temperature evolution from pastes P3 – 70% CPV ARI RS+30%FCCWg.

The same behavior of pastes with FCCW have been observed by Pacewska; Wilinâska e Kubissa [5]. It can be explained by a typical behavior from the kinetic reactions when mineral additions with pozzolanic characteristics are used with cement products [7].
CONCLUSIONS

The results obtained on this experimental study from pastes and mortars properties with 30% cement replacement (by mass) to FCCWn and FCCWg, enable us to conclude:

FCCWn and FCCWg accelerated reactions of pastes with a high heat of hydration;

Cement pastes produced with FCCWn and FCCWg quickly have initial and final setting times;

Paste produced by FCCWg reduced final setting time when compared to paste produced with FCCWn;

Mortars initial flow with FCCWn and FCCWg were lower than reference mortars. There were no significant difference between mortars produced with both FCCWn and FCCWg;

These properties studied affect the pastes and mortar workability. Low values from consistency, quickly won for setting times and the accelerated hydration kinetic reactions, that could be observed on pastes and mortars produced with FCCW, reduce the material workability.

ACKNOWLEDGMENTS

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REFERENCES


