Effect of fly ash particles packing on performance of OPC-activated GGBS slag

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Abstract

An important way to produce concrete with a lowered CO₂ embodiment is to use high levels of supplemental cementitious materials (SCMs), such as slag and fly ash, in place of Portland cement. This paper is focused on the influence of fly ash on Portland cement (OPC)-activated GGBS cement, a very low OPC formulation. The study examined the effect of particle packing as well as the effect of fly ash on strength development. First the influence of fly ash on strength development on mortars with optimized particle size distribution and packing was conducted. Then, keeping the levels of the cementitious materials the same, mortars with non-ideal particle packing were studied. The mortar packing was optimized following the modified Andreassen model, demonstrated to have a significant impact on the mechanical properties, both at early and late compressive strengths of OPC-activated slag, compared with the non-packing compositions. Substitution of fly ash for fine aggregates significantly affected the mechanical properties depending on the class and particle shapes of the fly ash.

1. Background and Objectives

1.1. Why use GGBFS

Approaches to reducing the carbon impact of OPC include the production of lower-energy cements ¹,², such as calcium sulfoaluminate cements ³,⁴, alkali-activated binders ⁵, pozzolan-based materials, and supersulfated cements, just to give a few examples. Some of these solutions still require high energy processes (firing raw materials at high temperatures for CSA cements), or highly alkaline chemicals (for geopolymers).

Ground granulated blast furnace slag (GGBFS) is a product of steel making, where molten slag is quenched in water to form a glassy material that has both pozzolanic and latent hydraulic properties ⁶. As GGBFS is an industrial byproduct, it has inherently low carbon footprint and can play an important role in the reduction of carbon from OPC based concrete. The primary use for GGBFS is as a pozzolanic supplementary cementitious material (SCM) in OPC based concrete ⁷, where it is used to replace OPC at levels of 30% to 70%, but typically ~50% in the United States. A particular study found that the optimal amount of slag that can be introduced in OPC/slag blends is 40% by weight, as above this value the early compressive strength is negatively affected. ⁸

1.2. Optimization of slag cement compositions

At very high levels of GGBFS substitution for OPC, the blends are benefited by “activation”. Activation methods include thermal, mechanical and chemical approaches. Thermal methods require the curing of slag cement concrete and mortar at elevated temperatures. ⁹,¹⁰ Grinding slag to a higher fineness as a mechanical method demonstrates to increase especially the early compressive strength of OPC/slag compositions. ¹⁰–¹³ Chemical activation is more complex than the previous two methods, as it involves various parameters, such as the alkalinity and the chemical reactions between the components,
depending on the added admixtures. Admixtures can be alkalis, Portland cement, water glass, and many others additives. For example, blends of OPC/slag with additions of alunite, mirabilite (hydrous sodium sulfate mineral, Na₂SO₄.10H₂O) and calcined gypsum were tested for flexural and compressive strength tests, and the optimized parameters were the additions of both mirabilite and calcined gypsum as it improved both early and late strengths. In another study, additions of sodium hydroxide (NaOH), potassium hydroxide (KOH) and water glass (Na₂SiO₃.9.35H₂O, or also called liquid sodium silicate) to a mixture of 50/50 OPC/slag were studied and proved to accelerate the strength development.

Studies have also been performed on activating the slag with addition of alkaline activators such as NaOH, KOH and liquid sodium silicate (or waterglass) directly, i.e. without the use of OPC. It was found that NaOH was more effective than KOH at room temperature, as it affected the slag dissolution. In another example, Teoreanu et al. studied the mechanical properties of binders free of Portland cement, made of slag with and without fly ash (from 0 to 50% by weight), and additions of sodium and calcium compounds as activators. Zhao et al. also presented a cement composed exclusively of slag and fly ash, and as activators a mixture of desulphurized gypsum, slaked lime, Burkeite and lignosulfonate.

1.3. Objectives of this work

None of the previous studies, which we are aware of, have looked over the influence of fly ash as admixtures to OPC/slag cement, as fly ash was always added in very large proportions compared to the amount of slag, and thus the chemical effects were never really studied in detail. As a consequence, this work engaged in studying the influence of different fly ash as ultra-fine and fine aggregates to OPC/slag cement. For this work, ultra-fine aggregates were defined as aggregates of size below 63µm, while fine aggregates were defined as aggregates of size range between 63µm and 1mm. By doing so, addition of fly ash on OPC/slag cement may be identified as a chemical activation of slag cements. Besides the addition of fly ash, mortar packing was constantly tracked. Influence of fly ash as ultra-fine aggregates was studied while keeping mortar packing constant. However, influence of fly ash as fine aggregates involved changes in mortar packing, which was also studied. In summary, the study of both fly ash as a chemical activator and mortar packing as a mechanical activator of slag cements are studied in this paper.

2. Experiments

2.1. Description of the three different fly ash

The chemical compositions and scanning electron microscope (SEM) images of the three fly ash used during this work are shown in Table 1 and Figure 1, respectively. These fly ash strongly differ in chemical and physical compositions. According to ASTM C-618 (regarding the chemical compositions only), WE PP and Orcem B are class F and C fly ash, respectively. Orcem A does not meet the ASTM C-618 criteria, due to its high content of sulfur trioxide. Physically, particles of Orcem A present sharped edges, while Orcem B present both sharped edges and spherical particles. WE PP fly ash contains only small spherical particles. Their particle size distributions are also different, Orcem A fly ash is finer than WE PP, which are both very fine compared to Orcem B.

<table>
<thead>
<tr>
<th></th>
<th>CaO</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>SO₃</th>
<th>MgO</th>
<th>Na₂O</th>
<th>K₂O</th>
<th>P₂O₅</th>
<th>TiO₂</th>
<th>d(50) in µm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Orcem A</td>
<td>38.52</td>
<td>23.27</td>
<td>3.44</td>
<td>5.62</td>
<td>13.21</td>
<td>9.56</td>
<td>4.40</td>
<td>0.40</td>
<td>0.04</td>
<td>0.24</td>
<td>9.23</td>
</tr>
<tr>
<td>Orcem B</td>
<td>8.13</td>
<td>67.03</td>
<td>11.85</td>
<td>8.1</td>
<td>1.00</td>
<td>2.63</td>
<td>0.15</td>
<td>1.56</td>
<td>0.07</td>
<td>0.92</td>
<td>35.11</td>
</tr>
<tr>
<td>WE PP</td>
<td>23.57</td>
<td>33.63</td>
<td>22.34</td>
<td>4.81</td>
<td>3.86</td>
<td>4.46</td>
<td>1.64</td>
<td>0.59</td>
<td>1.39</td>
<td>1.15</td>
<td>14.22</td>
</tr>
</tbody>
</table>

Table 1: Chemical compositions and particle size distribution of fly ash
2.2. Description of mortar packing

Optimum packing presents various advantages, as it reduces cement content in concrete and it benefits compressive strength, as well as other parameters such as water/cement ratio, flowability, porosity and microstructure. Different particle optimization methods have been developed over the years and are well explained in the Mangulkar et al. review. For this work, the mortar packing was optimized through the use of a software called EMMA (Elkem Materials Mixture Analyzer), which is defined as a “program for evaluation of particle-packing”. Two methods can be used within this software for the determination of the mortar packing:

- Andreassen Model which assumes that the smallest particles would be infinitesimally small:
  \[ \text{CFPD} = (d/D)^n \times 100 \]

- Modified Andreassen Model, derived by Dinger and Funk, which considers the minimum particle size in the distribution into the previous equation:
  \[ \text{CFPD} = \left( \frac{d-d_0}{D-d_0} \right)^q \times 100 \]

During this work, only the Modified Andreassen Model was used.

3. Results and discussion

3.1. Influence of mortar packing

Influence of mortar packing was studied on a mortar compositions made of 20% OPC and 80% slag by weight. The particle size distribution of M1 was identified as the optimized mortar packing for this work, as it closely matched the Modified Andreassen Model with the following parameters: \( q = 0.25, \ d_{\text{min}} = 0.40 \ \mu m, \ d_{\text{max}} = 1500 \ \mu m \). (Figure 2) The aggregates contained in M1 were from different size ranges of river sand as fine and ultra-fine aggregates, as well as some quartz flours, limestone and ultrafine limestone as ultrafine aggregates. The optimized sample M1 was then “degraded”, by means of its mortar packing as seen on Figure 2, as M1-1, M1-2 and M2 were not matching the Modified Andreassen Model as well as M1 did. The aggregates present in M2 were entirely graded sand as used in ASTM C109, representing a standard mortar cube composition.

Packing significantly influenced the compressive strength of OPC/slag mortar cubes, as shown in Figure 3. In standard conditions, while using graded sand in M2, mortar cubes did not set after 2 days, and compressive strength at 7 and 28 days were 11.7 and 54.1MPa, respectively. However, improving the mortar packing with M1-2, M1-1 and M1 greatly enhanced the strength development, as all of the mortar cubes were set after 2 days. The results were impressive at 7 days between M1-2 and M2, where the compressive strength was five times higher for M1-2 than without any optimized packing in M2.
Optimization of packing affected the flow of mortar mixes by producing a more liquid system, and did not alter the pH of the mortar cubes.

**Figure 2:** Particle size distribution of the Modified Andreassen Model ($q=0.25$, $d_{\text{min}}=0.40\mu\text{m}$, $d_{\text{max}}=1500\mu\text{m}$) compared with optimized mortar packing M1, and degraded mortar packing M1-1, M1-2 and M2.

**Figure 3:** Compressive strengths of optimized and degraded mortar packing compositions of 2-in mortar cubes M1, M1-1, M1-2 and M2, with a constant water/cement ratio of 0.31 (cement includes slag and OPC), and a cement/sand ratio of 1:2.75. Cubes were cured in a room at 25°C and a relative humidity of 100%.

### 3.2. Influence of different fly ashes as partial replacement for ultra-fine aggregates

The influence of fly ash in OPC/slag (Figure 4) and anhydrite/slag (Figure 5) blends as ultra-fine aggregates was performed by replacing some of the ultra-fine aggregates with the same amount of fly ash. The particle size distributions (PSDs) were not affected by these changes, and were all similar to the particle size distribution of M1, as shown in Figure 2.

In OPC/slag blends, the substitution of ultra-fine aggregates with fly ash did not significantly affect the strength development, as presented in Figure 4. Orcem A in M4-OA was the only fly ash to exhibit higher compressive strengths than M1, at 2 and 7 days. Orcem B and WE PP fly ash, in M4-OB and M4-WE, never exceeded M1 compressive strength results, but were not far below neither. The pH of these mortar cubes was not affected by the different fly ash.

In anhydrite/slag blends, all OPC in M1 and M4 was replaced with anhydrite. Without any substitution of ultra-fine aggregates with fly ash, the anhydrite/slag mortar cubes (M3) never set, even with an optimized mortar packing. However, the fly ash did have a significant impact when replacing some of the ultra-fine aggregates, as presented in Figure 5. Only Orcem A fly ash was able to "activate" the anhydrite/slag blend (M11-OA) and even exhibited higher compressive strengths after 2 and 7 days than the OPC/slag mixture M1. It also greatly increased the mortar cubes pH with Orcem A, compared to the other compositions M11-OB and M11-WE. Replacement of ultra-fine aggregates with Orcem B fly ash in M11-OB did not affect the strength development as in M3. The mortar cubes made with WE PP fly ash, M11-WE, were removed from the molds after 7 days, but the cubes did not exhibit any strength later on.

An explanation for the influence of Orcem A with anhydrite/slag compositions could be due to the specific chemical composition of this fly ash, as calcium oxide and sulfates are highly present in Orcem A, and could be responsible for the production of ettringite, and thus the high compressive strength resulting from it after 2 days.

All compositions had a relatively good workability, except M4-OA, M3 and M11-OB. The pH of all OPC/slag blends were similar with each other (11.7-11.9) at all days. However, the pH of anhydrite/slag...
blends of M3, M11-OB and M11-WE were low, at around 10, but addition of Orcem A in M11-OA increased the pH to a value close to 11.2.

Figure 4: Influence of fly ash as ultra-fine aggregates in OPC/slag (20/80% by weight) blends on the strength development, w/c=0.31, cement/sand=1:2.75

Figure 5: Influence of fly ash as ultra-fine aggregates in anhydrite/slag (20/80% by weight) blends on the strength development, w/c=0.31, cement/sand=1:2.75

3.3. Influence of fly ash as fine aggregates

In this part, fly ash were replacing part of the fine aggregates in OPC/slag blends (CL# even numbers), and in slag only (CL# odd numbers), and the compositions are described in Table 2. Particle size distributions of mortar compositions made from only slag and OPC/slag blends are presented in Figures 6 and 7, respectively. CL#1 and CL#2 PSDs were very similar to the Modified Andreassen Model, which defined them as optimized mortar packing. However, the replacement of 0.5 parts in CL#3 and CL#4, and 1.0 part in CL#5 and CL#6 of fine aggregates with fly ash “drew” their PSDs further away from the optimized mortar packing, and significantly affected the PSD between 2 and 200µm, leaving the ultra-fine particles under 2µm “almost untouched”, due to the constant addition of ultrafine limestone (UF-FL).

CL compositions made with Orcem A (CL#3/4/5/6-OA) were very difficult, even impossible, to produce at the water/cement ratio of 0.31, as they were too dry and stiff. As a consequence, all of the mixtures containing Orcem A were produced with a higher water/cement ratio of 0.5.

Slag on its own with an optimized mortar packing, CL#1, never set, as presented in Figure 8. Replacement of fine aggregates with fly ash assisted the strength development, as all compositions made with only slag were able to set after only 2 days, with the exception of CL#3-OB. The more fly ash was replacing the aggregates, the better were the compressive strengths, except for CL#3-OA and CL#5-OA at 2-day, which may be explained by the different water/cement ratio used. Orcem A demonstrated to be a better aggregate replacement than Orcem B and WE PP.

Regarding the OPC/slag blends, all mortar cubes were set after 2 days, as shown in Figure 9. The influence of Orcem B in OPC/slag blends (CL#4/6-OB) did not significantly affect the compressive strength after 2 and 7 days, but did increase it after 28 days and even surpassed CL#2 (without fly ash) compressive strength. WE PP fly ash in CL#4-WE and CL#6-WE produced similar compressive strengths to CL#2 after 2 days. In the long term, WE PP fly ash assisted positively the strength development at a replacement rate of 0.5 part (CL#4-WE) with fine aggregates, but negatively at a replacement rate of 1.0 part (CL#6-WE). Addition of Orcem A significantly affected early compressive strength in both CL#4-OA and CL#6-OA, and exhibited lower compressive strengths than CL#2 after 7 and 28 days.

Figures 8 and 9 presented the influence of three fly ash in slag and OPC/slag mortar cubes, but these data can be “rearranged” to study the effect of OPC in fly ash/slag blends instead. With this new
configuration, the PSDs of the compositions were the same when comparing with the same fly ash and the same replacement rate of fine aggregates, for example CL#3-OA and CL#5-OA. With this new approach, OPC can be seen as an excellent admixture to fly ash/slag blends.

Table 2: Compositions of CL samples

<table>
<thead>
<tr>
<th>Composition</th>
<th>Coarse aggregates</th>
<th>UF-FL</th>
<th>OPC</th>
<th>Mix Slags</th>
<th>OA</th>
<th>OB</th>
<th>WE</th>
<th>w/c</th>
<th>Flow</th>
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<tbody>
<tr>
<td>CL#1</td>
<td>1.0 0.5 0.5 0.5 0.2</td>
<td>-</td>
<td>1.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.395</td>
<td>121</td>
</tr>
<tr>
<td>CL#3-OB</td>
<td>1.0 0.5 0.5 - 0.2</td>
<td>-</td>
<td>1.0</td>
<td>0.5 -</td>
<td>0.31</td>
<td>100</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CL#3-OA</td>
<td>1.0 0.5 0.5 - 0.2</td>
<td>-</td>
<td>1.0</td>
<td>0.5 -</td>
<td>0.5</td>
<td>Liq.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CL#3-WE</td>
<td>1.0 0.5 0.5 - 0.2</td>
<td>-</td>
<td>1.0</td>
<td>0.5 -</td>
<td>0.5</td>
<td>Liq.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CL#5-OB</td>
<td>1.0 0.5 - - 0.2</td>
<td>-</td>
<td>1.0</td>
<td>1.0 -</td>
<td>0.31</td>
<td>90</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CL#5-OA</td>
<td>1.0 0.5 - - 0.2</td>
<td>-</td>
<td>1.0</td>
<td>1.0 -</td>
<td>0.5</td>
<td>Dry</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>CL#5-WE</td>
<td>1.0 0.5 - - 0.2</td>
<td>-</td>
<td>1.0</td>
<td>1.0 -</td>
<td>0.31</td>
<td>90</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>CL#2</td>
<td>1.0 0.5 0.5 0.5 0.2</td>
<td>0.2</td>
<td>0.8</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.31</td>
<td>108</td>
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<tr>
<td>CL#4-OB</td>
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<td>0.2</td>
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<td>0.5</td>
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<td>-</td>
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<td>117</td>
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<tr>
<td>CL#4-OA</td>
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<td>0.2</td>
<td>0.8</td>
<td>0.5 -</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.31</td>
<td>90</td>
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<tr>
<td>CL#4-WE</td>
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<td>0.2</td>
<td>0.8</td>
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<td>0.5</td>
<td>-</td>
<td>-</td>
<td>0.31</td>
<td>90</td>
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<tr>
<td>CL#6-OB</td>
<td>1.0 0.5 - - 0.2</td>
<td>0.2</td>
<td>0.8</td>
<td>1.0 -</td>
<td>0.31</td>
<td>90</td>
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<tr>
<td>CL#6-OA</td>
<td>1.0 0.5 - - 0.2</td>
<td>0.2</td>
<td>0.8</td>
<td>1.0 -</td>
<td>0.5</td>
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<tr>
<td>CL#6-WE</td>
<td>1.0 0.5 - - 0.2</td>
<td>0.2</td>
<td>0.8</td>
<td>-</td>
<td>1.0</td>
<td>-</td>
<td>-</td>
<td>0.31</td>
<td>90</td>
</tr>
</tbody>
</table>

Compositions made with Orcem A were produced with a water/cement ratio of 0.5, as the compositions were completely dry with a w/c ratio of 0.31.
4. Conclusions

The influence of mortar packing and of several fly ash as ultra-fine and fine aggregates in slag, OPC/slag and anhydrite/slag blends were studied. The strength development, as well as the workability, the pH and the water/cement ratio were greatly affected by the use of different fly ash, mainly due to their different chemical compositions and particle size distributions.

Mortar packing did participate in the strength development, as the better was the mortar packing, the higher were the compressive strengths. When used as replacement for ultra-fine aggregates in OPC/slag blends, Orcem A fly ash exhibited the highest compressive strengths, while Orcem B and WE PP fly ash were almost similar to the reference blend M1 without fly ash. However, the selection of the fly ash in anhydrite/slag blends was critical, as only Orcem A was able to "activate" the blends in M11-OA, due to supposedly its high calcium oxide and sulfate contents. When used as fine aggregates in slag and OPC/slag blends, fly ash did not affect the mortar cubes similarly, depending on their chemical and...
physical properties, but they all contributed to the setting of mortar cubes made from only slag, which was not possible when replacing the ultra-fine aggregates (except Orcem A). Another interpretation of the CL experiments would be to identify OPC as an admixture to fly ash slag blends, as it participates significantly to the strength development. Further studies will focus on the hydration processes and complete the hypotheses made in this work.

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References


