EFFECT OF MINERAL ADMIXTURES ON THE PROPERTIES OF A SUSTAINABLE ULTRA-HIGH PERFORMANCE CONCRETE (UHPC)

R. Yu (1), P. Spiesz (1, 2) and H.J.H. Brouwers (1)

(1) Department of the Built Environment, TU Eindhoven, the Netherlands
(2) ENCI HeidelbergCement Benelux, the Netherlands

Abstract
To reduce the environmental impact of Ultra-High Performance Concrete (UHPC), a method to produce a sustainable UHPC is presented in this study. The design of the concrete mixtures is based on the aim to achieve a densely compacted cementitious matrix, employing the modified Andreasen & Andersen particle packing model. Fly ash (FA), ground granulated blast-furnace slag (GGBS) and limestone powders (LP) are used to replace cement, and their effects on the properties of the developed UHPC are analysed. The experimental results show that the influence of FA, GGBS or LP on the early hydration kinetics of cement in UHPC is very similar during the initial five days, while the hydration rate of the blends with GGBS is mostly accelerated afterwards. Due to the very low water amount and relatively high superplasticizer (SP) dosage in the UHPC, the pozzolanic reaction of FA is significantly retarded and the mechanical properties of the mixture with FA are relatively poor.

1. INTRODUCTION
With the development of the construction industry, except the compressive strength, concrete is also required to have high flexural strength, flowability and durability, which resulted in the development of Ultra-High Performance Concrete (UHPC) and Ultra-High Performance Fibre Reinforced Concrete (UHPFRC) [1-3]. Nevertheless, as the sustainable development is currently a pressing global issue and various industries have strived to achieve energy savings, the high material cost, high energy consumption and CO2 emission for UHPC are the typical disadvantages that restrict its wider application [4-6]. Therefore, it is important to increase the UHPC sustainability.

To reduce the economic and environmental disadvantages of UHPC, the approaches are limited in most cases to the application of industrial by-products or waste materials without sacrificing the UHPC mechanical performance [2, 3, 7-10]. Nevertheless, for the mix design of UHPC, the amounts of mineral admixtures in the literature (e.g. fly ash (FA), ground granulated blast-furnace (GGBS), limestone powder (LP) and silica fume (SF)) are normally given directly, without any detailed explanations or theoretical support. Moreover, due to the complex cementitious system of UHPC (extremely low water amount and relatively high SP
content), the influence of different mineral admixtures on the hydration kinetics and properties of UHPC still needs further clarification [1-3, 6-10]. As commonly known, GGBS has hydraulic properties although the rate of the reaction with water is low [11]. The reaction can be activated by several methods, but the hydration product is always C-S-H. On the contrary, the pozzolanic reaction of FA is relatively slow, and the addition of FA can retard the hydration of cement [12-14]. The retardation phenomenon is related to the presence and condition of the FA particles surface. Additionally, the activity of LP in the cementitious system is still under a debate. Many researches treat LP as filler and experimentally demonstrated that the principal properties of cement are not negatively affected if small quantities of LP (5-6%) are added during the cement grinding [15-18]. On the other hand, some investigations [19-21] showed that, during the hydration process of cement with LP, tricalcium aluminate (C\textsubscript{3}A) can react with calcium carbonate to form both high- and low carbonate forms of calcium carboaluminate (CCA) in much the same manner as C\textsubscript{3}A reacts with calcium sulphate to form high- and low-sulphate forms of calcium sulpoaluminate (CSA). Although a significant part of investigations regarding the effect of mineral admixtures on the physical and chemical characteristics of mortar or concrete can be easily found, they are mainly focused on normal strength concrete (NSC), in which the water to binder ratio is relatively high and a limited SP is utilized. As commonly known, the cementitious system of UHPC is very different from that of NSC, which causes that it is difficult to evaluate the influence of mineral admixtures on the cement hydration and properties development of UHPC, based on the knowledge obtained from NSC. Therefore, to efficiently develop UHPC, it is important to understand the effect of different mineral admixtures on the properties and hydration process of UHPC.

Consequently, the objective of this study is to firstly develop UHPC and then evaluate the influence of different mineral admixtures on the properties of the developed UHPC.

2. MATERIALS AND METHODOLOGY

2.1 Materials

The cement used in this study is Ordinary Portland Cement (OPC) CEM I 52.5 R, provided by ENCI HeidelbergCement Benelux (the Netherlands). A polycarboxylic ether based superplasticizer is used to adjust the workability of UHPC. The FA, GGBS and LP are used to replace cement. Two types of sand are used, one is a normal sand with the fraction 0-2 mm and the other one is a microsand with the fraction 0-1 mm (Graniet-Import Benelux, the Netherlands). One type of nano-silica slurry is selected as highly active pozzolanic material.

2.2 Methodology

For the design of mortars and concretes, several mix design tools are in use, particularly the modified Andreasen & Andersen particle packing model [22-24]. Based on the previous experiences and investigations of the authors [25], by applying this model, it is possible to produce a dense and homogeneous skeleton of UHPC or UHPFRC with a relatively low binder amount (about 650 kg/m\textsuperscript{3}). Consequently, it can be shortly concluded that such an optimized design of the concrete with appropriate amount of mineral admixtures can be a promising approach to efficiently produce Ultra-High Performance Concrete (UHPC).

The UHPC mixtures developed in this study based on the modified Andreasen & Andersen particle packing model are listed in Table 1. In total, three different types of UHPC and one
reference are designed, and three different water to binder ratios are chosen. Compared to the reference sample, about 30% of Portland cement (by mass) is replaced by FA, GGBS or LP in the UHPC mixtures. It can be noticed from Figure 1 that the resulting integral grading curves of all the designed concretes are comparable to each other.

Table 2: Mix recipes of the designed concrete

<table>
<thead>
<tr>
<th>NO.</th>
<th>OPC (kg/m³)</th>
<th>FA (kg/m³)</th>
<th>GGBS (kg/m³)</th>
<th>LP# (kg/m³)</th>
<th>S (kg/m³)</th>
<th>MS (kg/m³)</th>
<th>nS (kg/m³)</th>
<th>W (kg/m³)</th>
<th>SP (kg/m³)</th>
<th>W/B</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>582.1</td>
<td>259.9</td>
<td>0</td>
<td>0</td>
<td>1039.5</td>
<td>216.6</td>
<td>24.3</td>
<td>173.2</td>
<td>43.3</td>
<td>0.2</td>
</tr>
<tr>
<td>2</td>
<td>591.9</td>
<td>264.3</td>
<td>0</td>
<td>0</td>
<td>1057.0</td>
<td>220.2</td>
<td>24.7</td>
<td>159.3</td>
<td>44.0</td>
<td>0.18</td>
</tr>
<tr>
<td>3</td>
<td>600.0</td>
<td>267.9</td>
<td>0</td>
<td>0</td>
<td>1071.4</td>
<td>223.2</td>
<td>25.0</td>
<td>147.8</td>
<td>44.6</td>
<td>0.165</td>
</tr>
<tr>
<td>4</td>
<td>596.1</td>
<td>0</td>
<td>266.1</td>
<td>0</td>
<td>1064.5</td>
<td>221.8</td>
<td>24.8</td>
<td>177.4</td>
<td>44.4</td>
<td>0.2</td>
</tr>
<tr>
<td>5</td>
<td>606.4</td>
<td>0</td>
<td>270.7</td>
<td>0</td>
<td>1082.9</td>
<td>225.6</td>
<td>25.3</td>
<td>163.2</td>
<td>45.1</td>
<td>0.18</td>
</tr>
<tr>
<td>6</td>
<td>614.9</td>
<td>0</td>
<td>274.5</td>
<td>0</td>
<td>1098.0</td>
<td>228.8</td>
<td>25.6</td>
<td>151.5</td>
<td>45.8</td>
<td>0.165</td>
</tr>
<tr>
<td>7</td>
<td>592.6</td>
<td>0</td>
<td>0</td>
<td>264.6</td>
<td>1058.3</td>
<td>220.5</td>
<td>24.7</td>
<td>176.4</td>
<td>44.1</td>
<td>0.2#</td>
</tr>
<tr>
<td>8</td>
<td>602.8</td>
<td>0</td>
<td>269.1</td>
<td>1076.5</td>
<td>224.3</td>
<td>25.1</td>
<td>162.2</td>
<td>44.9</td>
<td>0.18#</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>611.2</td>
<td>0</td>
<td>272.9</td>
<td>1091.4</td>
<td>227.4</td>
<td>25.5</td>
<td>150.6</td>
<td>45.5</td>
<td>0.165#</td>
<td></td>
</tr>
<tr>
<td>Ref.1</td>
<td>868.8</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1072.5</td>
<td>223.4</td>
<td>25.0</td>
<td>178.8</td>
<td>44.7</td>
<td>0.2</td>
</tr>
<tr>
<td>Ref.2</td>
<td>883.9</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1091.2</td>
<td>227.3</td>
<td>25.5</td>
<td>164.4</td>
<td>45.5</td>
<td>0.18</td>
</tr>
<tr>
<td>Ref.3</td>
<td>896.3</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1106.6</td>
<td>230.5</td>
<td>25.8</td>
<td>152.7</td>
<td>46.1</td>
<td>0.165</td>
</tr>
</tbody>
</table>

(OPC: Cement, FA: Fly ash, GGBS: Ground granulated blast-furnace slag, LP: Limestone powder, S: sand, MS: Microsand, nS: Nano-silica, W: Water, SP: Superplasticizer, Ref.: reference samples, W/B: water to binder ratio, #: LP is treated as a binder in the calculation)
Figure 1: The target and optimized grading curves of the developed UHPCs
After appropriate mixing, the fresh concrete is cast in moulds with the dimensions of 40 mm × 40 mm × 160 mm. The prisms are demolded approximately 24 h after casting and then cured in water at about 21 °C. After curing for 28 and 91 days, the flexural and compressive strengths of the specimens are tested according to the EN 196-1 [26]. At least three specimens are tested at each age to compute the average strength.

Following the recipes shown in Table 1, the pastes (without sands) are produced for the calorimetry analysis. The water to binder ratio of the prepared mixtures is fixed at 0.18 (based on the results of mechanical tests that will be shown later). All the pastes are mixed for two minutes and then injected into a sealed glass ampoule, which is then placed into the isothermal calorimeter (TAM Air, Thermometric). The instrument is set to a temperature of 20 °C. After 7 days, the measurement is stopped and the obtained data is analysed. All results are ensured by double measurements (two-fold samples).

3. RESULTS AND DISCUSSIONS

3.1 Mechanical properties

The flexural and compressive strengths of the developed UHPC at 28 and 91 days are shown in Figure 2. A very slight variation of the strengths can be observed when the water/binder ratio increases from 0.165 to 0.18. Nevertheless, with a further increase of the water/binder ratio (from 0.18 to 0.20), the mechanical properties of the UHPC decrease. This phenomenon should be attributed to the fact that a large amount of powder and limited water are utilized to produce the UHPC. When the water to binder ratio is relatively small, the added water is more significantly absorbed by the powders (cement, FA, GGBS or LP in this study), and thus cannot react with cement, which causes that the amount of cement hydration products is limited and the strength development of UHPC is restricted. Hence, in this study, the strengths difference between the mixtures with the lowest and medium water amount is not significant. There is an optimal value of water/binder ratio at which the strengths of the UHPC can be highest. Furthermore, it can be found here the mixture with GGBS has superior mechanical properties at both 28 and 91 day, while that the strengths of the mixtures with FA or LP are similar to each other. This phenomenon implies that the pozzolanic reaction of FA is significantly restricted in the UHPC cementitious system investigated in this study.

![Diagram of mechanical properties](image-url)
3.2 Hydration kinetics of the developed UHPC

Based on the calorimetry test results, the influence of the different mineral admixtures on the cement hydration of UHPC is investigated and presented in Figure 3. It is apparent that the influence of FA, GGBS or LP on the early hydration kinetics of the developed UHPC is very similar, which can be demonstrated by that the relatively small difference between the observed dormant period (calculated as the time between the lower point of the heat flow curve and the first inflection point in the main peak), relative setting time (calculated as the time between the first and the second inflection point in the heat flow curve), as well as the time to reach the maximum hydration peak. The observed phenomena should be attributed to the relatively large amount of superplasticizer and low water content, which significantly
retard the cement hydration and restrict the generation of Ca(OH)$_2$. Due to the insufficient amount of portlandite in the mixtures, the pozzolanic reaction cannot well progress, which causes that the difference of the pozzolanic activity between FA and GGBS is not easy to be observed in the calorimetry tests. Consequently, according to the results obtained in this study, it can be found that the hydration kinetics of UHPC is different from that of normal concrete. Due to the effects related to the superplasticizer and water dosages, the cement hydration and pozzolanic reaction of mineral admixtures are significantly retarded.

4. CONCLUSIONS

In this study, based on the modified Andreasen & Andersen particle packing model, UHPC with different mineral admixtures (FA, GGBA, and LP) is produced. The experimental results show that the mechanical properties of UHPC with GGBS are higher than that with FA or LP at both 28 and 91 days. Furthermore, very slight variation of the strengths can be observed when the water/binder ratio increases from 0.165 to 0.18. Nevertheless, with a further increase of the water/binder ratio (from 0.18 to 0.20), the mechanical properties of the produced UHPC decrease. Additionally, the hydration heat development curves of the UHPC mixtures with FA, GGBS and LP are similar to each other during the initial five days. Afterwards, the hydration rate of the mixture with GGBS is obviously accelerated. Due to the specific cementitious system of UHPC (very small water/binder ratio and relatively high SP amount), it is observed that the pozzolanic reaction of FA is significantly retarded, which causes that a very limited amount of FA can react with Ca(OH)$_2$ after curing for 91 days.

ACKNOWLEDGEMENTS

The authors wish to express their gratitude to Ir. G.C.H. Doudart de la Grée for assisting the experimental work and for valuable discussion. Moreover, the appreciation also goes to the following sponsors of the Building Materials research group at TU Eindhoven: Graniet-Import Benelux, Kijlstra Betonmortel, Struyk Verwo, Attero, ENCI HeidelbergCement Benelux, Provincie Overijssel, Rijkswaterstaat Zee en Delta - District Noord, Van Ganswinkel Minerals, BTE, V.d. Bosch Beton, Selor, Twee “R” Recycling, GMB, Schenk Concrete Consultancy, Geochem Research, Icopal, BN International, Eltomation, Knauf Gips, Hess ACC Systems, Kronos, Joma, CRH Europe Sustainable Concrete Centre, Cement&BetonCentrum, Heros and Inashco (in chronological order of joining)

REFERENCES


