The Relationship between Cementitious Composition and Properties of Ultrahigh Strength Concrete

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It is well known that supplementary cementitious materials (SCMs) have obvious effects on the properties of concrete. In order to understand the relationship between cementitious materials and properties of ultrahigh strength concrete (UHSC), the cementitious compositions of UHSC were designed by the simple-centroid design method. The effects of cementitious compositions on the properties of UHSC were investigated. It was found that the incorporation of silica fume (SF) improved the flowability and strength of UHSC, but it decreased the time of acceleration period, calcium hydroxide (CH) content, and porosity of UHSC at a certain content. The incorporation of fly ash (FA) increased the flowability, time of acceleration period, and porosity of UHSC, but it decreased the strength and CH content of UHSC. The relationships between cement, silica fume, and fly ash and the properties of UHSC were calculated based on the simple-centroid design method.

1. Introduction

The compressive strength of UHSC ranges from 120 MPa to 810 MPa, which is approximately 2–16 times than that of ordinary concrete. The durability of UHSC is superior to that it prolongs the service life and reduces the maintenance of concrete structure. One of the most influential components to which UHPC owes its superiority in terms of mechanical properties and durability is SCMs.

The incorporation of SCMs influences the hydration products, pore structure, ions in pore solution, and properties of concrete due to its particle characteristics, chemical composition, mineralogical composition, and reactivity [1–3]. It was reported that the incorporation of slag decreased the CH content and Ca/Si ratio of C–S–H gel [4]. The addition of SCMs increased the mesopores percent with a particle size less than 30 nm, but the volume of macropores of concrete reduced significantly [5]. The inclusion of SCMs reduced the hydroxyl ion concentration. The hydroxyl ion concentration of Portland cement (PC) was 0.53–0.71 M [6], while the incorporation of 50% slag or 30% FA reduced half of the hydroxyl ion concentration, and incorporating 7% SF reduced the hydroxyl ion concentration to 20% [7]. An increase of Al₂O₃ and SiO₂ from SCMs had both a positive and negative effect on the zeta potential of concrete, respectively [8]. The compressive strength of concrete was proportional to the SF content when the SF content was less than 10% [9].

To improve the properties or reduce the cost of UHSC, it is a common technical method to incorporate SCMs into cementitious materials. It is reported [10] that the porosity of UHSC with 5–20% of metakaolin was similar to the UHSC without metakaolin. The incorporation of an appropriate amount of natural pozzolan had a little effect on the mechanical properties of UHSC [11]. Compared with UHSC without blast furnace slag, the three-day strength of UHSC with 30%, 50%, and 80% blast furnace slag increased by 3%, 26%, and 66%, respectively [12]. The incorporation of 53% limestone powder reduced the compressive strength of UHSC by 27%, but its compressive strength still reached 145 MPa [13]. Although the incorporation of lead-zinc tailings reduced the compressive strength, it remarkably
decreased the autogenous shrinkage of UHSC [14]. The incorporation of 50% demolition waste to replace cement reduced the compressive strength of UHSC from 125 MPa to 109 MPa, but it still met the requirement of Chinese standard [15]. The incorporation of 40% phosphorous slag reduced the compressive strength of UHSC at three days, but it presented a comparable strength at 28 days [16]. The incorporation of no more than 25% of dehydrated cementitious materials to replace cement had a little effect on the compressive strength and durability of UHSC [17]. The addition of nanosilica significantly reduced the corrosion rate of steel bars in the UHSC [18]. Compared with UHSC without nanomaterials, the incorporation of nanometakaolin [19] and nanometaclay [20] increased the compressive strength of UHSC at later ages.

In order to better design the cementitious compositions of concrete, the relationship between cementitious compositions and properties of concrete has been established. Based on the maximum wet density, the packing density of mortar could be calculated from the specific gravity of each composition and mixture proportions [21]. The heat of hydration could be calculated from the mineral composition of cementitious materials [22]. The relationship between the proportion, hydration degree, specific gravity of cementitious composition, and the shrinkage of paste was established [23]. The relationship between the chemistry and content of cementitious materials and the setting time of mortar was also established [24].

The equations of the aforementioned literatures are established in ordinary concrete, and the hydration degree of cementitious materials is relatively sufficient. However, a large amount of cement clinker does not react in UHSC due to its low W/B [25], and the aforementioned equations are not applicable to UHSC. In order to understand the relationship between cementitious materials and properties of UHSC, the cementitious composition of UHSC was designed by simple-centroid design method, and the relationship between cementitious composition and properties of UHSC was calculated.

2. Experiment and Methods

2.1. Raw Materials. Cement, silica fume, and fly ash were used as binders, and their chemical compositions are presented in Table 1. The mean particle size of cement, SF, and FA were 29.8, 0.6, and 48.0 μm, respectively. Natural quartz sand with a particle size less than 2.36 mm was used as aggregate. Polycarboxylic superplasticizer (SP) was added to UHSC.

2.2. Mixture Proportions. Based on modified Andreason and Andersen model [26], the particle size distribution of sand was optimized.

\[
P(D) = \frac{D^q - D_{\text{min}}^q}{D_{\text{max}}^q - D_{\text{min}}^q},
\]

where \( D \) is the particle size of sand, \( P(D) \) is the proportion of particles with particle size less than \( D \), and \( D_{\text{max}} \) and \( D_{\text{min}} \) are the maximum and minimum particle size of sand. The value of \( q \) is 0.22.

The mixture proportions of UHSC are listed in Table 2, and they are designed by simple-centroid design method. The W/B of UHSC was 0.16, and the sand-to-binder ratio was 1. The dosage of SP was 2 wt. % of binder. The mixtures were mixed until they were uniform. Then, they were cast and submerged in saturated Ca(OH)\(_2\) solution until test age.

2.3. Experimental Methods

2.3.1. Flowability. The mixtures were poured into a minicon in two layers. Then, the mixtures with minicone were liberated for 15 times. The minicone was lifted lightly and vibrated for 25 times. Then, the mean diameter was determined. The flowability of mortar was the average of three tested specimens.

2.3.2. Hydration Heat. The hydration heat was measured by a TAM air isothermal calorimeter. Based on the binder compositions presented in Table 2, cementitious materials, water, and superplasticizer were mixed until the mixtures were uniform. The cement pastes were filled into an ampere bottle. Then, the ampere bottle was immediately placed into the TAM air isothermal calorimeter. The experiment lasted for 72 hours.

2.3.3. Compressive Strengths. Specimens with a size of \( 40 \times 40 \times 160 \text{mm} \) were used to measure the strength. The compressive strength of mortar was the average of six tested specimens.

2.3.4. Water Absorption Porosity. The 5 mm thick discs cut from \( \phi 10 \times 150 \text{mm} \) were used to measure the porosity. Until age, three discs were dried at 105°C for 24 h, and the masses of discs were recorded as \( W_1 \). Then, the discs were saturated under vacuum for 24 h, and they were put into water to record the masses, corresponding to \( W_2 \). The saturated surface dry mass was recorded, corresponding to \( w_3 \). The porosity of mortars can be calculated as follows, and the porosity of mortar was the average of three tested specimens:

\[
\text{porosity} = \frac{(w_3 - w_1) \times 100}{(w_3 - w_2)}.
\]

2.3.5. Thermogravimetric Analysis. Thermogravimetric analysis was used to measure the CH content. The samples were heated from 20°C to 1000°C at 10°C/minute in a nitrogen environment. The Ca(OH)\(_2\) content was calculated from the weight losses from 450°C to 550°C. The CH content of mortar was the average of three tested specimens.

2.4. Factorial Design of Ternary Cementitious Materials. The relationship between binder compositions and properties of UHSC could be established by simplex-centroid design [27], which has been successfully applied in previous studies [28–31]. By measuring the properties of no less than seven different proportions of mixtures, the contour maps
could be drawn with the help of mathematical models and software, and the effects of different component on the properties of mixtures could be evaluated by simplex-centroid design. In this mathematical model, the proportions of PC, SF, and FA to cementitious materials were defined as \( x_1 \), \( x_2 \), and \( x_3 \), respectively:

\[
Y = \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_{12} x_1 x_2 + \beta_{23} x_2 x_3 + \beta_{13} x_1 x_3 + \beta_{123} x_1 x_2 x_3,
\]

where \( Y \) represents the properties of UHSC, \( \beta_i \) is the coefficient, and \( x_1 \), \( x_2 \), and \( x_3 \) are the proportions of the three cementitious materials.

### 3. Results and Discussion

#### 3.1. Flowability

Figure 1 shows the flowabilities of UHSC with different binders. The incorporation of SF increased the flowability of UHSC when its content was less than 15%, and then, it decreased the flowability of UHSC. The flowability of UHSC reached the peak value when the SF and FA content were 15% and 25%, respectively. SF could fill the pores, disperse cement particles, and release more free water, which improves the workability of concrete [32]. However, the incorporation of SF also required more free water since its specific surface area was very large [33], which decreased the workability of concrete. As a result, the optimum SF content was 15% for the flowability of UHSC.

The incorporation of FA increased the flowability of UHSC when the FA content was less than 25%, and then, the flowability of UHSC slightly decreased. The flowabilities of UHSC were improved by incorporating FA due to its morphological effect. It was also reported that the flowability of concrete was improved when FA was incorporated [34].

#### 3.2. Hydration Heat

Figure 2(a) shows the hydration evolution of UHSC. With the increase of SF content, the time of acceleration period of UHSC decreased first but increased later. The times of acceleration period of UHSC containing 0% (N1), 15% (N2), and 30% (N3) SF were 7.23 h, 4.77 h, and 6.37 h, respectively. An appropriate amount of silica fume presented heterogeneous nucleation effect, which accelerated the hydration of cement. However, when the silica fume content was excessive, the agglomeration of silica fume mainly presented dilution effect, which prolonged the hydration of cement. It was also found that the dormant period was prolonged by incorporating SF [35]. It can be seen in Figure 2(a) that the incorporation of FA (N4, N5, N6, and N7) significantly prolonged the dormant period of UHSC. When comparing with UHSC only containing SF (N2), the time of acceleration period of UHSC containing both SF and FA (N4) increased.

Figure 2(b) shows the total hydration heat of UHSC. As the SF content increased, the total hydration heat of UHSC increased first but decreased later. SF also significantly prolonged the dormancy period of UHSC. When comparing with UHSC only containing SF (N2), the time of acceleration period of UHSC containing both SF and FA (N4) increased.

#### 3.3. Porosity in UHSC

Figure 3(a) shows the 3d porosity of UHSC with different binders. The incorporation of SF decreased the 3d porosity of UHSC when the SF content was less than 20%, and then, it increased the 3d porosity of UHSC. Figure 3(b) shows that the incorporation of SF decreased the 28d porosity of UHSC. It is well known that the filling and pozzolanic effects of SF could increase the packing density of cement particles, improve the microstructure, and reduce the porosity of concrete [36, 37]. It can be seen in Figure 3(a) that the incorporation of FA increased the 3d porosity of UHSC, but its effect on the 28d porosity of UHSC was negligible. It was reported that the filling effect of FA refined the pore of concrete [38, 39]. The nucleation effect of FA increased the hydration degree of cement [40, 41]. The pozzolanic effect of FA refined the pore size and reduced the porosity of concrete [42, 43]. As a result, the incorporation of FA increased the 3d porosity due to its dilution effect, but it had a little effect on the 28d porosity of UHSC due to the combined effects of dilution, filling, nucleation, and pozzolanic effects.

#### 3.4. Compressive Strength

Figure 4(a) shows the 3d compressive strengths of UHSC with different binders. The incorporation of SF improved the 3d strengths of UHSC presented heterogeneous nucleation effect, which accelerated the hydration of cement. However, when the silica fume content was excessive, the agglomeration of silica fume mainly presented dilution effect, which prolonged the hydration of cement. It was also found that the dormant period was prolonged by incorporating SF [35]. It can be seen in Figure 2(a) that the incorporation of FA (N4, N5, N6, and N7) significantly prolonged the dormant period of UHSC. When comparing with UHSC only containing SF (N2), the time of acceleration period of UHSC containing both SF and FA (N4) increased.

Figure 2(b) shows the total hydration heat of UHSC. As the SF content increased, the total hydration heat of UHSC increased first but decreased later. The total hydration heat of UHSC was decreased when FA was incorporated into UHSC.

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**Table 1: Chemical composition of PC, SF, and FA.**

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<thead>
<tr>
<th>Chemical composition</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>CaO</th>
<th>MgO</th>
<th>SO₃</th>
<th>Na₂Oeq</th>
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<td>4.05</td>
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<td>0.56</td>
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<td>0.83</td>
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<tr>
<td>FA</td>
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<td>2.56</td>
<td>0.19</td>
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**Table 2: Mixture proportions of UHSC.**

<table>
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<tr>
<th>No.</th>
<th>PC (kg/m³)</th>
<th>SF (kg/m³)</th>
<th>FA (kg/m³)</th>
<th>Sand (kg/m³)</th>
<th>Water (kg/m³)</th>
<th>Superplasticizer (kg/m³)</th>
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<td>1100</td>
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<tr>
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<td>440</td>
<td>1100</td>
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<td>N7</td>
<td>440</td>
<td>220</td>
<td>440</td>
<td>1100</td>
<td>176</td>
<td>22</td>
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</table>

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<td>2.56</td>
<td>0.19</td>
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</tr>
</tbody>
</table>
Figure 1: Effects of different cementitious composition on the flowability of UHSC.

Figure 2: Effects of different cementitious compositions on the hydration heat of UHSC.

Figure 3: Effects of different cementitious composition on the porosity of UHSC: (a) 3 days and (b) 28 days.
when the SF content was less than 15%, and then, its effect was insignificant. The positive effect of SF on the 3d strength of UHSC could be attributed to its filling and pozzolanic effects [44, 45]. Figure 4(b) shows the 28d strengths of UHSC with different binders. The incorporation of SF increased the 28d strengths of UHSC when the SF content was less than 15%, and then, it decreased the 28d strengths of UHSC. It was probably that the agglomeration of SF reduced the flowability of UHSC, increased the porosity, and thereby decreased the strength of UHSC.

As the FA content increased, the 3d strengths of UHSC decreased. It was reported that the hydration of PC was the main chemical reaction during the early age [46], and the bond strength between FA and other solid phase was small [47]. Therefore, the 3d strength of UHSC decreased when FA was incorporated. Figure 4(b) shows that the incorporation of FA increased the 28d strengths of UHSC when the FA content was less than 20%, and then, it decreased the 28d strengths of UHSC. The PH value in pore solution of concrete increased as the hydration of cement, leading FA to be ruptured [48]. Subsequently, the pozzolanic effect of FA improved the strength of concrete [49].

### 3.6. Relationship between Cementitious Composition and Properties

In (3), the proportions of PC, SF, and FA to cementitious materials were defined as \( x_1, x_2, \) and \( x_3, \) respectively. From the test results, the relationship between cementitious composition and properties of UHSC could be established. Taking 28 day compressive strength of UHSC as an example, it was defined as \( Y_{28}, \) and the relationship between 28d strength of UHSC and cementitious composition could be calculated from (3):

\[
Y_{28} = 0.1088x_1 - 0.2139x_2 - 0.4096x_3 + 0.4933x_1x_2 + 2.6585x_2x_3 + 0.7731x_1x_3 - 2.9548x_1x_2x_3. \tag{4}
\]

Based on (4), the effects of PC, SF, and FA on the 28d strength of UHSC could be calculated as shown in (5)–(7):

\[
\frac{\delta Y_{28}}{\delta x_1} = 0.1088 + 0.4933x_2 + 0.7731x_3 - 2.9548x_2x_3, \tag{5}
\]

\[
\frac{\delta Y_{28}}{\delta x_2} = -0.2139 + 0.4933x_1 + 2.6585x_3 - 2.9548x_1x_3, \tag{6}
\]

\[
\frac{\delta Y_{28}}{\delta x_3} = -0.4096 + 2.6585x_2 + 0.7731x_1 - 2.9548x_1x_2. \tag{7}
\]

It can be seen in (5)–(7) that the effects of PC, SF, and FA on the 28d strength of UHSC depended on the cementitious compositions. Effect of PC on the 28 d compressive strength of UHSC was positive, and effects of SF and FA depended on the proportion of cementitious materials. When compared with SF, the effect of FA on the 28 d compressive strength was more negative. Effects of different compositions on the properties of concrete could be evaluated by simplex-centroid design with less testing.
However, it also reduces the accuracy of this mathematical model. To improve the accuracy of this model, it is necessary to add more experimental points or reduce the area of contour maps.

4. Conclusions

In order to establish the relationship between cement, silica fume, and fly ash and the properties of UHSC, the effects of cementitious materials on the properties of UHSC were investigated. The conclusion could be drawn as follows.

The incorporation of silica fume improved the flowability of UHSC when its content was less than 15%, and then, it reduced the flowability of UHSC. Incorporation of fly ash improved the flowability of UHSC. The flowability of UHSC reached a maximum of 296 mm when the silica fume and fly ash content were 15% and 25%, respectively.

The time of acceleration period of UHSC was shortened when the silica fume was less than 15%. However, the dormant period was prolonged by incorporating fly ash or more than 15% silica fume.

The incorporation of silica fume decreased the porosity and increased the compressive strength of UHSC when its content was less than 20%. As the fly ash content increased, the 3 d porosity of UHSC increased and its compressive strength decreased; moreover, the effect of fly ash on the 28 d porosity of UHSC was negligible. Incorporation of silica fume and fly ash decreased the calcium hydroxide content of UHSC. Compared with fly ash, the effect of silica fume on the calcium hydroxide contents of UHSC was more obvious.

The relationships between the cementitious composition and properties of UHSC were established by simplex-centroid design. Then, the effects of cement, silica fume, and fly ash on these properties of UHSC were analyzed.

4.1. Research Significance. The composition of cementitious materials of UHSC is complex, which significantly influences its properties. However, the research on the relationship between cementitious materials and properties is limited to ordinary concrete, and there are a few studies on the relationship between composition of cementitious materials and properties of UHSC. In order to understand the relationship between cementitious materials and properties of UHSC, the cementitious composition of UHSC was designed by simple-centroid design method, and the relationship between cementitious composition and properties of UHSC was calculated. According to the results of this article, it can be used to guide the design of composition of cementitious materials of UHSC.

Data Availability

Some or all of the data, models, or codes that support the findings of this study are available from the corresponding author upon reasonable request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

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