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The role of carbonated steel slag on mechanical performance of ultra-high performance concrete containing coarse aggregates

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\textbf{Abstract}

Carbonated fine steel slag (CSS) can be used as supplementary cementitious materials (SCM) to enhance the sustainability of ultra-high performance concrete (UHPC). However, the role of CSS on the mechanical performance of UHPC containing coarse aggregates (UHPC-CA) has not been well understood. Here, the influence of cement substitution by CSS on the hydration products, microstructure, mesoscale fracture characteristics and macroscopic strength of UHPC-CA is investigated. Results reveal that the C-S-H content in UHPC increases with the increase of CSS substitution up to 15%. Replacement of cement by CSS results in a more porous interfacial transition zone (ITZ), consequently, a lower mechanical contribution from CA. Both the compressive and the flexural strength decrease with the increase of CSS substitution, and the negative effect is rather limited till 30% CSS substitution. Moreover, due to a more porous ITZ at a higher cement substitution, the ratio of flexural to compressive strength decreases with the increase of CSS substitution.

1. Introduction

Ultra-high performance concrete (UHPC) is a kind of newly developed building material, which possesses excellent mechanical strength, normally higher than 150 MPa, and superior energy absorption capability [1,2]. Generally, a large volume of cement (900–1300 kg/m\textsuperscript{3}) is used in UHPC to obtain the satisfied performance, which however results in a higher cost and autogenous shrinkage compared to normal concrete [3,4]. To guarantee a high economic efficiency and decrease the autogenous shrinkage, coarse aggregates (CA) are introduced to UHPC [5–7]. However, introducing high volume of CA into UHPC means potentially introducing more defects, e. g. interface transition zone (ITZ), consequently, the decrease of the mechanical performance was observed [8,9]. Normally, the CA content is less than 30% by volume of the UHPC mortar [5,10,11]. That indicates that there would still be a large part of unhydrated cement particles remaining in UHPC with coarse aggregates (UHPC-CA).

Using industrial by-products as supplementary cementitious materials (SCM) to replace the cement in UHPC is another way to improve the utilization efficiency of cement and decrease the cost of UHPC [12–14]. Converter steel slag (SS) is the main by-product from steel making process [15]. Compared with other SCMs, such as silica fume, ground granulated blasted furnace slag (GGBS) and fly ash, SS only shows a relatively low reactivity [16]. Up to now, most of SS was used in road construction [17]. In addition, free lime in SS can induce soundness problem, which further limits the utilization of SS in building materials [18,19]. On the other hand, SS shows high carbonation reactivity due to its high calcium silicate content [20–22], which can not only capture and store CO\textsubscript{2}, but also stabilize the free lime [23–25]. The research of Huijgen et al., [26,27] reported that about 100–150 g CO\textsubscript{2} can be sequestered by every kilogram of steel slag powder. In addition, our previous study has proven the enhancement of SS reactivity after carbonation treatment, and the carbonated SS (CSS) was successfully applied in UHPC design [28]. This also provides a chance to utilize CO\textsubscript{2} as part of ingredient in UHPC-CA by using CSS, as well as achieving low carbon-footprint and low costs.

To make better utilization of CSS in UHPC-CA, its influence on the mechanical performance of UHPC-CA should be clarified. From the view of mesoscale, the failure of UHPC-CA can be attributed to the fractures of CA, ITZ and matrix [29–31]. Previous study has indicated that the incorporation of CSS into UHPC will affect the microstructure of matrix [28]. On the other hand, different with normal concrete, the fracture of CA was observed in UHPC-CA due to a denser microstructure of ITZ, resulting in a higher mechanical contribution from CA to the strength of...
UHPC-CA \[32\]. The fracture proportion of CA in concrete depends on the bond property of ITZ, which varies with the water to binder ratio (w/b), particle size distribution and chemical compositions, etc. \[33–36\]. It is noteworthy that the fracture of CA will influence the macroscopic mechanical performance of UHPC-CA as CA is a stronger part than ITZ and matrix \[37–39\]. Since the particle size and chemical compositions of CSS are different from cement, the incorporation of CSS in UHPC-CA is supposed to affect the microstructure of ITZ, hence its bond property, resulting in different mechanical contribution from CA in UHPC-CA.

Therefore, to better clarify the influence mechanism of CSS on the mechanical performance of UHPC-CA, the influence of CSS on the UHPC matrix and ITZ should be studied simultaneously. However, the previous research just focused on the reaction mechanism of CSS in cement based UHPC without CA \[28\], the influence of CSS on the mechanical performance of UHPC-CA has not been well understood.

This study aims to investigate the influence of CSS on the mechanical performance of UHPC-CA with a multi-scale method. Firstly, the hydration process of UHPC-CA with CSS is characterized using calorimetric test and thermo-gravimetric analysis. Then, the microstructures of matrix and ITZ are quantitatively analysed based on backscattered electron (BSE) image combining with an image process method in order to give an explanation of the macroscopic mechanical performance of UHPC-CA incorporating CSS. These results clarify the influence mechanism of CSS on the macroscopic mechanical performance of UHPC-CA and will be helpful for the utilization of CSS in the high performance building materials.

2. Materials and methods

2.1. Materials

The raw materials used in this UHPC-CA design were Portland cement CEM I 52.5 R (provided by ENCI, the Netherlands), fine sand 0–0.2 mm and sand 0–2 mm, basalt aggregate (BA) 2–5 mm, tap water, and PCE-type superplasticizer (SP) with dry matter of 35% (provided by Sika). The converter steel slag (SS) used in this study was provided by Tata steel (Ijmuiden, Netherlands). The chemical components and physical properties of cement and SS are shown in Table 1.

2.2. Preparation of CSS powders by ambient carbonation

The SS were firstly grounded into powder using a disc mill. Then, the CSS powder was prepared according to the description in our previous study \[28\]. The scanning electron microscope (SEM) images of SS and CSS particles can be found in Fig. 1. Obviously, a more rough and more porous surface can be found on CSS particles compared to SS particles, which is consistent with the previous results \[26\]. As shown in the X-Ray diffraction (XRD) results (Fig. 2(a)), the major minerals in SS are larnite, magnetite, brownmillerite and wustite, which is in line with the previous study \[40\]. More detailed information can be found in our previous study \[28\]. After ambient carbonation treatment, high-intensity calcite peaks and weak aragonite peaks can be identified in CSS. In addition, as shown in the Fourier transform infrared spectroscopy (FTIR) results (Fig. 2(b)), new peaks in 712, 873 and 1401 cm\(^{-1}\), which are related to the presence of C-O in calcium carbonate (calcite and aragonite), suggest that the SS has been carbonated. Moreover, due to the carbonation reaction of calcium silicate, a peak in 1070 cm\(^{-1}\) related to polymerized silica gel can be observed. The polymerized silica gel can be used for the pozzolanic reaction during the hydration process of cement \[41,42\].

2.3. Mix design and preparation of UHPC-CA

In this study, the reference sample was designed using the modified Andreasen & Andersen particle packing model \[43\]. The water to binder ratio (w/b) was set as 0.2 and CA content was 460 kg/m\(^3\). The particle size distribution of the used materials and the integral grading curve are shown in Fig. 3. Following the reference sample, 15%, 30% and 45% of the cement was replaced by CSS by volume based on the preliminary study to ensure acceptable mechanical properties. The recipes of the UHPC-CA mixtures are shown in Table 2. The flowability of the reference sample is 25.2 cm, whereas it increases to 28.4, 27.8 and 27.4 cm as the cement replacement increases to 15%, 30% and 45%, respectively. The samples casting was conducted as follows: firstly, the powders and sand were dry mixed, 70% of the total water was then added. Then, the remaining water together with superplasticizer, and basalt aggregates were added. Lastly, the fresh UHPC-CA mixtures were filled into the steel moulds of 50 × 50 × 50 mm\(^3\) for compressive test and 40 × 40 × 160 mm\(^3\) for three points bending test. All the samples were covered by plastic film and stored at room temperature (20 °C) for 24 h. After that, they were demoulded and cured in water at room temperature (20 °C) according to in Standard EN 12390–2 \[44\] until further tests.

2.4. Methodology

2.4.1. Calorimetric test

The calorimetry test was conducted using an isothermal calorimeter (TAM Air, Thermometric). The test was carried out at a temperature of 20 °C for 160 h.

2.4.2. Thermo-gravimetric analysis

To analyse the influence of CSS on the hydration products, the TG analysis was carried out with a Netzsch simultaneous analyser (model STA 449C). The heating rate during this measurement was 10 °C/min, from 20 °C to 1000 °C under nitrogen flow. The percentage of C-S-H in cement paste was calculated according to:

\[
\text{CSH\%} = \frac{\text{WL}_{\text{CSH}} \times m_{\text{CSH}}}{(2.1 \times m_{\text{H}_2\text{O}})} \tag{1}
\]

where \(\text{WL}_{\text{CSH}}\) is the mass loss of water during temperature of 150 ~ 400 °C. \(m_{\text{CSH}}\) is the molecular mass of C-S-H using a formular of C\(_{3}\)S\(_{2}\)H\(_{8}\) \[45,46\].

Herein, to diminish the influence of Aft and AFm, the weight loss between 150 °C and 400 °C is considered to calculate the percentage of C-S-H as the decomposition of Aft and AFm would normally occur earlier \[47\]. Nevertheless, it must be borne in mind that the results might still have slight deviations.

2.4.3. Quantitative characterization of microstructure

To quantitatively characterize the influence of cement replacement by CSS on the microstructure of UHPC-CA, the image with the CA boundary was firstly captured by a scanning electron microscope equipped with a BSEM image detector. The original BSEM image with the CA boundary is shown in Fig. 4(a). Each pixel in the BSEM image is 0.174 μm. Then, an image processing method was proposed to analyse

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|}
\hline
Substituent (%) & PC & SS \\
\hline
CaO & 64.60 & 41.55 \\
SiO\(_2\) & 20.08 & 11.47 \\
Al\(_2\)O\(_3\) & 4.98 & 2.24 \\
Fe\(_2\)O\(_3\) & 3.24 & 31.35 \\
K\(_2\)O & 0.53 & - \\
Na\(_2\)O & 0.27 & - \\
S\(_2\)O & 3.13 & - \\
MgO & 1.98 & 3.78 \\
Ti\(_2\)O\(_3\) & 0.30 & 1.56 \\
MnO & 0.10 & 4.78 \\
LOI (1000 °C) & 0.51 & 0.72 \\
BET surface area (m\(^2\)/g) & 1.004 & 1.153 \\
Specific density (g/cm\(^3\)) & 3.10 & 3.90 \\
\hline
\end{tabular}
\caption{Chemical compositions and physical properties of cement and SS.}
\end{table}
the BSEM image. The detailed procedure includes aggregates boundary delineation, strip delineation, gray threshold of porosity determination and porosity quantitative analysis. As shown in Fig. 4 (b), the gray threshold is firstly determined by combining the grayscale histogram and the tangent-slope method [48, 49]. Based on the obtained gray threshold, the BSEM image was binary, segmented and delineated into the successive binary strips with the width of 10 μm, as shown in Fig. 4 (c). 7 successive strips were obtained from each BSEM image to include both ITZ and matrix. Finally, the porosity of each strip was calculated based on the number of pixels with gray value less than the pre-set gray value threshold:
3. Results analysis

3.1. Early hydration of UHPC with CSS

The calorimetric test was carried out to study the influence of CSS on the early hydration kinetics of UHPC composites. As shown in Fig. 5(a), compared with the UHPC sample without CSS, a reduction of the main peak intensity normalized per gram of binder can be found in all the UHPC mixtures with CSS. However, as shown in Fig. 5(b), thanks to the pozzolanic reactivity of CSS, the cumulative heat of the samples with 15% and 30% cement replacement increase to be comparable with that of UHPC sample without CSS at 160 h. This confirms that the extra reaction of CSS compensates for the replacement of cement, which would lead to similar mechanical performance of UHPC [51]. As the replacement of cement by CSS increases to 45%, a longer dormant period can be observed, which might be due to the retardation effect caused by the higher SP to cement ratio [52,53]. In addition, after the main hydration peak, there is a shoulder appearing at about 50 h, which might be assigned to the formation of hemicarboaluminate and the reaction between ettringite and calcium carbonate [54].

3.2. Hydration products analysis

The TG results and C-S-H content of CSS blended UHPC binder are presented to show the influence of CSS content on the hydration products of UHPC binder. As shown in Fig. 6(a) and (b), three significant decomposition stages can be found in the curves, i.e. 105–400 °C, 400–600 °C and 600–800 °C. The first peak can be assigned to the evaporation of free water (before 105 °C) and the decomposition of ettringite (110–170 °C), carboaluminate hydrates and C-S-H (105–400 °C) [46]. The second peak is related to the decomposition of portlandite [55], while the third peak is related to the decomposition of calcium carbonates [51]. The third peak increases with the increased content of CSS due to the content of calcium carbonates in CSS. To quantify the influence of CSS on the hydration products, the content of C-S-H is evaluated. As shown in Fig. 5(c), the C-S-H content increases from 21.9% to 22.8% as the CSS content increases from 0 to 15%. As the carbonation of CS in SS produces amorphous silica gel, the improvement of the C-S-H content could be attributed to the pozzolanic reactivity between portlandite and amorphous silica gel [41,56–58]. However, the C-S-H content decreases to 21.5% and 20.2% as the CSS content increases to 30% and 45%, respectively, which could be attributed to that the dilution effect becomes more obvious, resulting in insufficient cement available for hydration reaction to generate enough C-S-H [54,59,60]. Consequently, the pore volume of UHPC filled by the formed C-S-H gel could be various, in other words, the microstructure properties of UHPC will be different.

3.3. Microstructure analysis

3.3.1. BSEM image of UHPC-CA

To investigate the influence of the CSS substitution on the microstructure of UHPC-CA, the BSEM images along the CA boundary are presented. As shown in Fig. 7(a), although some defects still exist, the area except CA in the sample without CSS is almost homogenous, which can be attributed to the low w/c ratio [2]. It is different from normal concrete, which is characterized by a clear transition zone along CA

![Fig. 3. Particle size distribution of raw materials of UHPC-CA.](image-url)

\[ p = \frac{A_{\text{porosity}}}{A_{\text{total}}} \]  

(2)

where \( p \) is the porosity of ITZ strip or matrix, \( A_{\text{porosity}} \) is the pixel number less than the gray threshold, \( A_{\text{total}} \) is the total pixel number of binary strip.

2.4.4. Mechanical test

The compressive strength and flexural strength of UHPC-CA were tested after 28 days curing. The cube sample with size of 50 mm × 50 mm × 50 mm was used for compressive test, whereas the prism sample with size of 40 mm × 40 mm × 160 mm was used for flexural test. The average strength values were obtained from three parallel samples.

2.4.5. Meso-scale fracture observation

To clarify the meso-scale failure mechanism of UHPC-CA, an image processing method was used to quantify the fractures of CA, ITZ and matrix. The detailed procedure of identification of the meso-scale fracture of UHPC-CA is as follows: image acquisition, marking CA in the fracture surface and identification of fracture type [50]. Here, a CA particle is considered fractured if a "mirrored" CA particle appears in the same position on the fracture surfaces. The quantitative fracture across CA, ITZ and matrix can be calculated as follows:

\[ P_{\text{CA}} = \frac{A_{\text{CA}}}{A_{\text{F}}} \times 100\% \]  

(3)

\[ P_{\text{ITZ}} = \frac{A_{\text{ITZ}}}{A_{\text{F}}} \times 100\% \]  

(4)

\[ P_{\text{Matrix}} = 1 - P_{\text{CA}} - P_{\text{ITZ}} \]  

(5)

where \( P_{\text{CA}} \), \( P_{\text{ITZ}} \) and \( P_{\text{Matrix}} \) are the percentage of fracture across CA, ITZ and matrix, respectively; \( A_{\text{CA}} \) is the total area of red colour; \( A_{\text{ITZ}} \) is the total area of green colour, \( A_{\text{F}} \) is the total area of the fracture surface.

### Table 2

Mixtures design of UHPC-CA.

<table>
<thead>
<tr>
<th>CEM (kg/m³)</th>
<th>CSS (kg/m³)</th>
<th>Fine sand (kg/m³)</th>
<th>Sand (kg/m³)</th>
<th>BA (kg/m³)</th>
<th>Water (kg/m³)</th>
<th>SP (kg/m³)</th>
<th>Packing density (kg/m³)</th>
<th>Flowability (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>719.8</td>
<td>0</td>
<td>310.5</td>
<td>806.5</td>
<td>460</td>
<td>122.6</td>
<td>32.9</td>
<td>2452.3</td>
<td>25.2</td>
</tr>
<tr>
<td>GS15</td>
<td>611.9</td>
<td>127.0</td>
<td>310.5</td>
<td>806.5</td>
<td>460</td>
<td>122.6</td>
<td>2471.4</td>
<td>28.4</td>
</tr>
<tr>
<td>GS30</td>
<td>503.9</td>
<td>254.2</td>
<td>310.5</td>
<td>806.5</td>
<td>460</td>
<td>122.6</td>
<td>2490.6</td>
<td>27.8</td>
</tr>
<tr>
<td>GS45</td>
<td>395.9</td>
<td>381.4</td>
<td>310.5</td>
<td>806.5</td>
<td>460</td>
<td>122.6</td>
<td>2509.8</td>
<td>27.4</td>
</tr>
</tbody>
</table>
As shown in Fig. 7(b), a small number of defects appeared along the CA boundary as the CSS substitution increases to 15%. As the CSS substitution increases to 30% and 45%, shown in Fig. 7(c) and (d), more defects can be found in the zone near or far from the CA boundary, resulting in more porous microstructure of UHPC-CA. It might be attributed to that the increase of CSS substitution results in that less available cement can be used for hydration, leading to less hydration products to densify the microstructure [54,62]. Since the micro-mechanical properties of concrete are influenced by its microstructure [63,64], these defects along the CA boundary can degrade the bond properties between CA and matrix, resulting in different fracture proportion of CA.

3.3.2. Quantitative analysis of ITZ and matrix

To quantitatively analyse the influence of CSS substitution on the microstructure of UHPC-CA, the porosities of the strips with different distances from the CA boundary are calculated. As shown in Fig. 8, regardless of the percentage of cement substitution by CSS, there is a
transition zone between CA boundary and matrix, i.e. ITZ, characterized by a higher porosity along the CA boundary. This is due to the wall effect disrupting the packing of cement grains against the CA [65–67]. Moreover, with the increase of CSS substitution, the porosities of the zones with the distance of 0 ~ 10 μm increases from 8% to 8.6%, 9.5% and 11.5%, respectively. It is suggested that replacing cement by CSS would lead to a more porous ITZ. Meanwhile, the porosity of the zone with the distance of 60 ~ 70 μm increases from 5.7% to 6.0%, 6.6% and 7.6%, respectively, suggesting that the replacement of cement by CSS would lead to a more porous matrix. Besides that, it must be noted that there is still a transition zone in the UHPC-CA sample without CSS substitution, which is inconsistent with the results of UHPC in previous studies [68]. It could be assigned to the absence of silica fume or nanosilica, which can accumulate along the CA boundary due to the smaller particle size and react with portlandite, resulting in a denser microstructure of ITZ [69,70]. Moreover, as the CSS substitution increases to 15%, although the C-S-H content increases from 21.9% to 22.8%, the porosity of matrix shows a higher value than that without CSS substitution. It could be attributed to that the incorporation of CSS disturbs the original packing distribution of particles in UHPC-CA [71].

3.4. Mechanical performance of UHPC-CA with CSS

3.4.1. Macroscopic mechanical strength

To characterize the influence of CSS substitution on the macroscopic mechanical performance of UHPC-CA, the compressive and flexural strength of UHPC-CA with different CSS substitutions are presented. As shown in Fig. 9(a), adding CSS into UHPC-CA degrades both the compressive and flexural strength of UHPC-CA. As the cement substitution by CSS increases from 0% to 45%, the compressive strength of UHPC-CA decreases from 155 MPa to 151 MPa, 146.38 MPa and 133.72 MPa, respectively, whereas the flexural strength decreases from 23.64 MPa to 22.8 MPa, 19.62 MPa and 14.91 MPa, respectively. In addition, to quantify the influence of CSS on the degradation of the mechanical strength of UHPC-CA, the relative strength is calculated by dividing the strength of sample with CSS by the strength of the reference. As shown in Fig. 9(b), compared with the reference sample, in the case of the cement substitution of 15%, 30% and 45%, the relative compressive strength is 97.4, 94.4 and 86.3%, respectively, whereas the relative flexural strength is 96.4%, 82.9% and 63.1%, respectively. The degradation of the mechanical strength of UHPC-CA could be related to the degradation of the ITZ and matrix of UHPC-CA. Moreover, it is indicated that the degradation of flexural strength is much worse than that of compressive strength, hence, leading to a lower ratio of flexural strength/mechanical strength of UHPC-CA with higher CSS substitution, as shown in Fig. 9(c). The evolution of the ratio of flexural strength/mechanical strength might be related to the different bond properties between CA and paste [72].

3.4.2. Meso-scale fracture of UHPC-CA

To explain the influence of the CSS substitution on the macroscopic mechanical performance of UHPC-CA, the meso-scale fracture of UHPC-CA was analysed. The fractures across CA, ITZ and matrix were characterized based on an image process method. As shown in Fig. 10, the

![Fig. 6. TG results and C-S-H content of UHPC binder. (a) TG results; (b) DTG results; (c) C-S-H content by mass of binder.](image-url)
fracture surface consists of fractures across CA, ITZ and matrix, which are various with the increase of the CSS substitution. In the case of the CSS substitution of 0% and 15%, the fractures across CA are observed obviously, which is different from the normal concrete, during the failure of which the fracture across CA is barely observed [30,73,74]. As the CSS substitution increases to 30% and 45%, with the increase of CSS substitution, the fracture across CA decreases gradually, whereas the fracture across matrix increases. It can be concluded that the mechanical contributions from CA, ITZ and matrix evolve with the replacement of cement by CSS.

Furthermore, the fractures across CA, ITZ and matrix are presented to quantitatively analyse the meso-scale fracture of UHPC-CA with different cement substitutions by CSS. The fractures across CA, ITZ and matrix are shown in Fig. 11. In the case of the UHPC-CA without CSS substitution, the fractures across CA, ITZ and matrix are 8.09 %, 10.68 %, and 81.23 %, respectively. As the cement substitution by CSS increases from 0% to 15%, 30% and 45%, the fracture across CA decreases from 8.09 % to 7.18%, 3.31% and 2.87%, which implies that the replacement of cement by CSS lowers the mechanical contribution from CA. As the fracture of CA is controlled by the bond properties of ITZ, the lower fracture across CA could be attributed to the more porous ITZ of UHPC-CA with a higher level of cement substitution by CSS [37]. In addition, with the increase of the cement substitution by CSS, the fracture across ITZ increases at first and then decreases, while the fracture across matrix decreases at first and then increases. The variation of the fractures of ITZ and matrix might be related to the different degradation rules of ITZ and matrix with the increase of the CSS substitution.

4. Discussion

4.1. Influence of CSS substitution on the microstructure properties of ITZ

A more porous transition zone close to the CA contains...
Fig. 9. The macroscopic mechanical strength of UHPC-CA at 28 curing ages. (a) compressive strength and flexural strength; (b) relative strength compared with reference sample; (c) flexural strength/compressive strength ratio.

Fig. 10. Meso-scale fracture of UHPC-CA with different CSS substitutions. (a) Ref.; (b) 15% CSS substitution; (c) 30% CSS substitution; (d) 45% CSS substitution.
predominately small grains is attributed to that the grain distribution is disrupted by CA due to the “wall” effect [61]. Generally, the width and porosity of ITZ are related to the particle size distribution of the cementitious system [33–36]. It is noted that the D50 of CSS is about 22 μm, whereas that of cement is about 14 μm. Thus, the incorporation of CSS results in a higher average particle size of blends, which means that, in the case of the UHPC-CA with CSS substitution, less small grains would appear in the transition zone, leading to a more porous zone close to CA boundary. Based on the “wall” effect assumption of packing of cementitious particle, a schematic concept of packing of cementitious grains along CA boundary is proposed, as shown in Fig. 12.

In the case of the sample without CSS substitution, the appearance of CA disrupts the random assembly of cementitious grains, results in a more porous zone close to CA boundary. In the case of the sample with CSS substitution, the grains distribution is similar with that of sample without CSS substitution, nevertheless, less cement grains can be found at the zone near the CA boundary. In addition, as the average grains size of CSS is larger than that of cement, some CSS grains appear in the zone further out of CA boundary. It can be deduced that replacement of cement by CSS may result in less cement grains close to the CA boundary, consequently, a more porous ITZ in UHPC-CA. It can be confirmed by the porosities of the zones with the distance of 0 ~ 40 μm from CA boundary, as shown in Fig. 13. As the CSS substitution increases from 0% to 15%, 30% and 45%, the porosity of ITZ increases from 6.8% to 7.2%, 7.8% and 9.4%, respectively.

Many previous studies have acknowledged that the fracture toughness of cementitious materials shows a decrease tendency with the increase of porosity [63,64,75]. As a higher CSS substitution results in a higher porosity of ITZ, it can be deduced that the fracture toughness ratio of ITZ/CA decreases with the increase of CSS substitution as the fracture toughness of CA is invariable, consequently, a lower fracture proportion of CA.

4.2. Influence of CSS substitution on the ratio of flexural to compressive strength

The ratio of flexural to compressive strength is an important material property of concrete. Many previous studies concerning the normal strength concrete have argued that the ratio of flexural to compressive strength usually decreases with the increase of compressive strength [76,77]. In other words, as the compressive strength increases, the flexural strength also increases but with a decreasing rate [78]. It is different from this study, where the ratio of flexural to compressive strength decreases from 0.153 to 0.151, 0.134 and 0.111, respectively.
However, the results in this study are consistent with the research concerning the curing regimes on the ratio of flexural to compressive strength of UHPC, in which an improved microstructure of ITZ of grains in UHPC is expected to improve the ratio of flexural to compressive strength [79].

This difference could be attributed to the different microstructures of UHPC-CA due to the incorporation of CSS. During the failure of concrete with low strength, especially the normal strength concrete, due to the poor bond strength of ITZ, cracks just pass through the matrix and ITZ rather than CA, consequently, the mechanical contribution from CA is almost negligible [29,80]. However, for the high strength concrete and UHPC-CA, because of the low w/c ratio, the ITZ is much denser than that of normal strength concrete, leading to more mechanical contribution from CA [37]. In the researches [34,72] about the influence of cement type on the strength of high strength concrete, it was found that the interfacial bond properties are the deciding factor for the flexural strength but play little role on the compressive strength. In this study, as the CSS substitution increases from 0% to 15%, 30% and 45%, the porosity of ITZ increases from 6.8% to 7.2%, 7.8% and 9.4%, respectively, consequently, the fracture across CA decreases from 8.09% to 7.18%, 3.31% and 2.87%, respectively. Hence, the decrease of the ratio of flexural to compressive strength can be attributed to a looser ITZ due to the incorporation of CSS.

5. Conclusions

In this study, the role of CSS on the mechanical performance of UHPC-CA is clarified. The influence of cement substitution by CSS on the hydration products, microstructure, meso-scale fracture characteristics and macroscopic strength of UHPC-CA are analysed. Based on the obtained results, the main conclusions can be drawn as follows:

- The C-S-H content in UHPC increases with the increase of CSS substitution up to 15% due to the pozzolanic reactivity of CSS. The C-S-H content increases from 21.9% to 22.8% as the CSS substitution increases from 0 to 15%. Further, because of the dilution effect, it decreases to 21.5% and 20.2% as the CSS substitution increases to 30% and 45%, respectively.
- Replacement of cement by CSS degrades the microstructure of both ITZ and matrix. With the increase of CSS substitution, the porosity of the zone with distance of 0 ~ 40 μm (i.e. ITZ) increases from 8% to 8.6%, 9.5% and 11.5%, respectively, whereas the porosity of the zone with the distance of 60 ~ 70 μm (i.e. matrix) increases from 5.7% to 6.0%, 6.6% and 7.6%, respectively.
- Replacement of cement by CSS results in a larger critical angle for the fracture across CA, consequently, a lower mechanical contribution from CA. At the cement substitution of 0%, 15%, 30% and 45%, the fracture percentage of CA is 8.09%, 7.18%, 3.31% and 2.87%, respectively.
- Both the compressive and the flexural strength decrease with the increase of CSS substitution. Nevertheless, the negative effect is rather limited till 30% replacement of cement by CSS. Moreover, due to a more porous ITZ at a higher cement substitution, the ratio of flexural to compressive strength decreases with the increase of CSS substitution.

CRediT authorship contribution statement

Shaohua Li: Methodology, Investigation, Data curation, Formal analysis, Validation, Writing - original draft. Gang Liu: Writing - review & editing. Qingsheng Yu: Conceptualization, Supervision, Funding acquisition, Project administration, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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