



Optimization and characterization of high-volume limestone powder in sustainable ultra-high performance concrete

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HIGHLIGHTS

- Eco-friendly UHPC is designed applying high volume limestone powder.
- Limestone powder shows a mineral plasticization effect in UHPC.
- Limestone powder promotes the secondary pozzolanic hydration.
- Proper content limestone powder contributes to denser structure and enhanced strength.
- 50 vol% limestone powder with comparable size and morphology to cement is suggested as optimal in UHPC.

ARTICLE INFO

Article history:

Received 18 November 2019

Accepted 5 January 2020

Keywords:

Ultra-high performance concrete
Sustainability
Limestone powder
Mineral plasticization
Hydration degree
Pore structure

ABSTRACT

This paper aims to optimize high-volume limestone powder in sustainable ultra-high performance concrete (UHPC), and characterize its roles on plasticization effect, hydration kinetics, microstructure and hardened properties. The spread flow, hydration products, compressive strength, porosity and pore structure, shrinkage, embedded CO₂ emission and unit cost are investigated with different substitution levels of binders by limestone powder, varying from 0 to 80 vol%. Results show that replacing high volume of binders by limestone powder is an efficient way to develop eco-friendly and low-cost UHPC. Limestone powder shows a positive mineral plasticization effect that should be considered in designing UHPC. The degree of secondary pozzolanic hydration is more intensive than C₃S/C₂S hydration, which can enhance the later-age strength development potential. An appropriate content of limestone powder can contribute to a higher strength, denser pore structure, diminished total free shrinkage and higher sustainability efficiency. The optimum content of limestone powder appears to be 50 vol% of the total powder content in UHPC.

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1. Introduction

Ultra-high performance concrete (UHPC) is an advanced and promising construction material with excellent fresh and hardened properties [1–6], characterized by a very low water amount and a high binder content [7]. However, the massive cement utilization, usually more than 900 kg/m³ [8,9], significantly increases the cost of UHPC and is not desired from an environmental point of view [10,11]. Generally, commercial UHPC is usually twenty times more expensive than the normal strength concrete, and three times

greater in terms of the cement consumption [12]. One ton Portland cement releases about 0.87–1 ton CO₂, and the whole cement industry contributes to around 8–9% of the anthropogenic CO₂ and 2–3% (4–5 GJ/ton) energy consumption [13,14]. In addition, due to the very low water-to-binder ratio, UHPC usually needs extra chemical superplasticizer, which increases the total cost of UHPC and environmental burden even further [15]. Those drawbacks of large environmental footprint and high cost currently limit the use of UHPC. Therefore, it is motivated to develop eco-friendly and low-cost UHPC for greater acceptance and wider engineering application.

Furthermore, a large proportion of binders cannot be completely hydrated under the relatively low water-to-binder ratio (usually less than 0.2) condition in a UHPC system. It is demonstrated that the maximum bound water for pure ordinary Portland

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cement is about 0.23 [16], which indicated that cement hydration is far from complete and some cement grains are functioning as fillers in UHPC [3]. For example, the hydration degree after 28 days ranged between 52% and 68% [17]. The unhydrated cement grains make it not eco-friendly nor cost-effective. Theoretically, the unhydrated cement could be replaced by grains with similar particle size distribution, without changing its packing density [18]. Some researchers showed that the microstructure could be improved in the presence of limestone powder and of a moderate rate of slag [19]. Hence, it is reasonable to substitute some part of cement by inert but eco-friendly and low-cost materials with similar sizes.

Currently, attempts have been made to reduce the cost and CO₂ emission by using less expensive and locally available eco-friendly constituents. Partial substitution of cement by supplementary cementitious materials has been proven to be efficient to reduce environmental and economic impact of concrete, such as ground granulated blast furnace slag [20], copper slag [21], fly ash [22,23], bottom ash [24] and even glass powder [25]. While, some nonreactive or weak reactive powders also showed promising contributions, such as marble [26] and granite powder [27], coral waste powder [28], palm oil clinker [29] and limestone powder [30,31]. Among those SCMs and inactive powders, limestone powder shows great potential due to its very low embedded CO₂ emission, abundant reserve on earth and low cost [32]. Furthermore, an appropriate content of limestone powder can provide some positive influence on the properties of concrete as filler, nucleation and chemical effects, as well as improving workability [30].

However, both roles and optimum content of limestone powder still need further study in UHPC systems with relatively low water-to-binder ratio and high superplasticizer dosage. For example, researches have already indicated that limestone powder has a positive effect on workability and mixing time [33,34], but some minerals addition could cause incompatibility problem in a UHPC system with low water and high superplasticizer content [35,36]. The compatibility and synergic effect between limestone powder addition and superplasticizer and/or water amount is very rarely investigated. The mechanism of the mineral plasticization effect of limestone powder is not systematically researched. Since the compactness and porosity of UHPC are very sensitive to the water amount and superplasticizer dosage, how to make full use of this positive effect and reduce water addition is of great significance. Besides, the substitution content of cement by limestone powder in normal concrete is usually less than 30% without sacrificing too much of the hardened properties [37–39]. Limestone powder was suggested to replace cement up to 15% or 100% of silica powder in UHPC [33], and it was also used to replace quartz powder in UHPC without any negative impact on strength or dimensional stability [40]. Furthermore, limits or allowable contents of limestone powder in cement have a large difference based on different standards, such as 35% in European standard (EN 197-1: 2000), 15% in Canadian standard (CSA A3001: 2010), 25% in Chinese standard (JC/T 600: 2010) and 15% in American standard (ASTM C595: 2012). It was pointed out that a reasonable range should be considered during the utilization of limestone powder [32]. However, the optimum amount of limestone powder in UHPC is still not determined yet.

This paper intends to optimize high-volume limestone powder content in sustainable UHPC and characterize its functional mechanisms. The roles of limestone powder on plasticization, hydration process and hardened properties of UHPC are analysed by investigating the fluidity, phase composition, pore structure, compressive strength and shrinkage. Then, the sustainability of designed UHPC including environmental and economic significances is evaluated by comparing their embedded CO₂ emission and unit cost. Lastly,

the optimum limestone powder content is determined and suggested for the mix design of eco-friendly and low-cost UHPC.

2. Experimental program

Materials and mix proportion

The mixtures are designed including the following materials, Portland cement CEM I 52.5 R (PC), micro-silica, limestone powder (LP), fine sand (S), water (W) and polycarboxylic ether based (PCE) superplasticizer (SP) with the solid content of 35%. To avoid any large difference of physical packing density by the size effect, in this research, the particle sizes (Blaine surface area of around 570 m²/kg) and morphology of limestone powder are similar and/or comparable to those of cement (Blaine surface area of around 520 m²/kg), as shown in Fig. 1. The densities, particle size distributions and chemical composition of those raw materials can be seen in our previous studies [15,41].

A total of 5 UHPC mixtures are designed in this study, and the detailed mix proportions can be seen in Table 1. Utilizing the key components' proportions by volume instead of by mass is more reasonable and useful in mix design [18,42]. The content of micro-silica is fixed at 13.1% by the total volume of binders (cement plus micro-silica in this study), as 10% by mass. The volume of sand-to-powder ratio is fixed at 0.846. The volume substitution of binder by limestone powder ranges from 0 to 80 vol%, with an increment frequency of 20 vol%. The water including water in superplasticizer and externally added tap water, and solid superplasticizer dosage by volume of powder (bvop) are adjusted to achieve a mini-slump spread flow of 30 ± 2 cm, which meets self-compacting property without having too much surplus fluidity [42,43]. The determining method on minimum required water content and superplasticizer dosage will be discussed and described in Section 3.1.

2.1. Testing methods

2.1.1. Mini slump flow

The mini slump flow of cement-limestone paste is tested to investigate the plasticization effect of limestone powder in a UHPC system, based on [42] without jolting. The ambient temperature is approximately 20 ± 1 °C. The water contents in cement-limestone pastes are fixed at 200 kg/m³ including the water in superplasticizer, which means the total volume of powder occupies 0.8 m³/m³ of paste. The volume substitution ratio of cement by limestone powder changes from 0 to 100 vol%, with an increment frequency of 20 vol%. Different dosages of superplasticizer are used to determine the saturation dosages at different substitution levels. The 5 designed UHPC mixtures in Table 1 are also checked by this method to ensure a comparable flow ability (30 ± 2 cm).

2.1.2. Thermal gravimetry

In order to research the effect of limestone powder on the cement hydration degree, the thermal gravimetric (TG) and differential thermal gravimetric (DTG) results of the 5 hardened UHPC at the age of 28 days are recorded by a Netzsch simultaneous analyser (model STA 449C). The heating rate during this measurement is 10 °C/min, from 20 °C to 1000 °C under the flowing nitrogen environment. The hardened UHPC is first ground. Then, the powder is collected by using a 63 µm sieve and used for the thermal gravimetric test.

2.1.3. Water-permeable porosity

The water permeable porosity of the designed UHPC is measured by using the vacuum-saturation technique [44]. The samples are cut from the 50 mm × 50 mm × 50 mm cubic specimens after

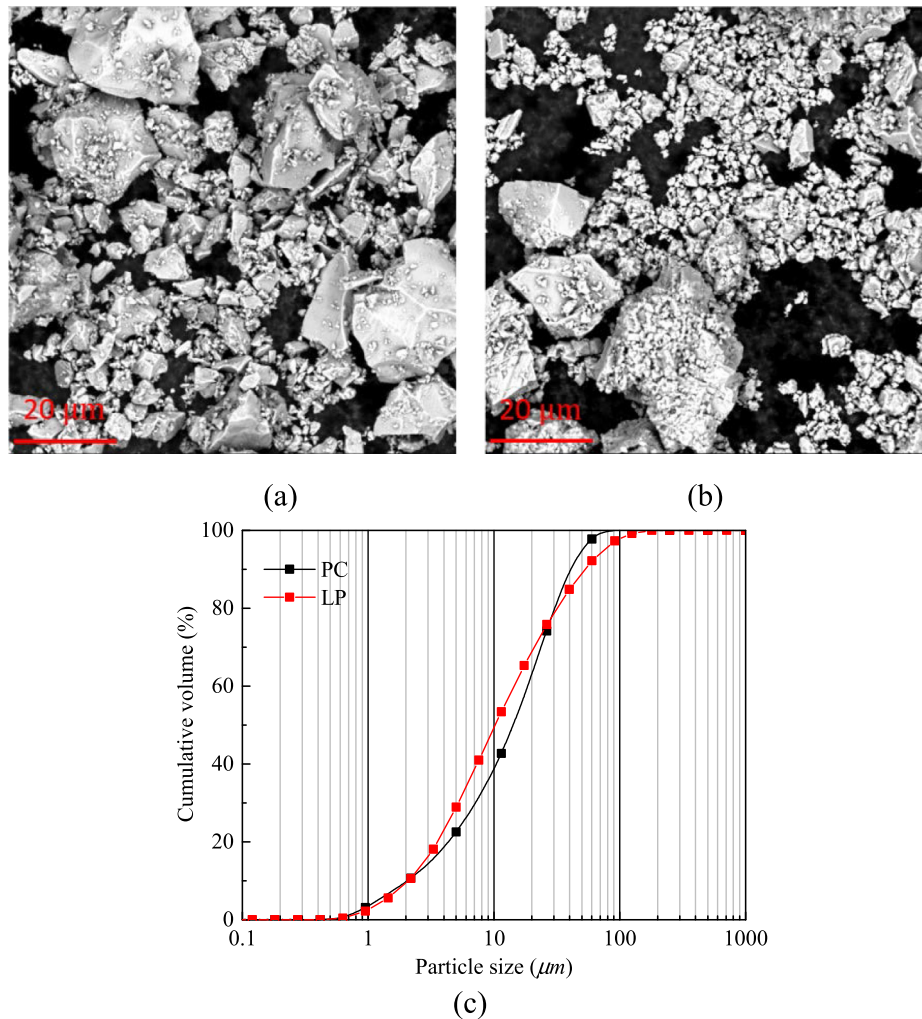


Fig. 1. Particle morphologies of (a) cement and (b) limestone powder, and their (c) particle size distributions.

Table 1

Proportion of ingredients for designed UHPC.

Mix	Powder (P)			S/P	W/P	SP/P	PC	mS	LP	S	W	SP
	PC	mS	LP									
	(by volume)											
M0	86.9%	13.1%	0.0%	0.846	0.666	0.042	1071.8	119.1	0.0	884.9	260.6	19.6
M20	69.5%	10.5%	20.0%	0.846	0.630	0.037	871.3	96.8	215.7	899.2	250.7	17.4
M40	52.1%	7.9%	40.0%	0.846	0.595	0.031	664.3	73.8	438.5	914.0	240.5	15.2
M60	34.8%	5.2%	60.0%	0.846	0.571	0.026	448.1	49.8	665.5	924.8	233.7	12.8
M80	17.4%	2.6%	80.0%	0.846	0.547	0.021	226.7	25.2	897.9	935.8	226.7	10.4

28 days with a thickness of about 20 mm. The water permeable porosity φ (%) can be calculated as,

$$\varphi = \frac{m_s - m_d}{m_s - m_w} \times 100 \quad (1)$$

where m_s , m_d and m_w are the masses of sample measured in air after water saturation by vacuum condition, in air after oven drying, in water after water saturation by vacuum condition, respectively.

2.1.4. Mercury intrusion porosimetry

The mercury intrusion porosimetry (MIP) test is conducted to determine the pore size distribution of UHPC at the age of 28 days by using a Micromeritics AutoPore IV. The central part of hardened UHPC is crushed into small pieces with diameter between 2 mm

and 4 mm, dried at 40 °C for 3 days. The intrusion pressure during the test increases from 0 to 227 MPa, with a contact angle of 130° and Hg surface tension of 485 dynes/cm.

2.1.5. Nitrogen sorption

To further analyse the gel pores in the designed UHPC, nitrogen sorption analysis is carried out with a micromeritics instrument, TriStar II 3020, at the boiling temperature of liquid nitrogen (77 K). After 28 days water curing, the hardened UHPC is crushed into small pieces with diameter less than 1 mm, following oven drying at 40 °C for 3 days [45]. The specific surface area can be measured by the Brunauer-Emmett-Teller (BET) method [46]. Meanwhile, the pore size distribution can be calculated by the

Barrett-Joyner-Hallenda (BJH) method [47] from the desorption isotherm [48].

2.1.6. Compressive strength

The compressive strength of UHPC is tested after 7 and 28 days in accordance with [49], by 50 mm × 50 mm × 50 mm cubic samples. The fresh UHPC mixtures are poured into steel mould, then covered by plastic film to keep moisture for approximately 24 h under room temperature around 20 °C. After that, all samples are demoulded and cured in water.

2.1.7. Total free shrinkage

The total free shrinkage of UHPC is recorded by using prism specimens (40 mm × 40 mm × 160 mm) in accordance with [50]. The fresh UHPC mixtures are also covered by polyethylene film to keep moisture for approximately 24 h. After demoulding, they are cured in a climate chamber with a RH of 50% at 20 ± 1 °C. The demoulding time (24 h after casting) is defined as the “zero time”. The lengths are measured periodically by using a digital length comparator (±0.001 mm) for a duration of about 56 days.

3. Results analysis

3.1. Plasticization effect of limestone powder

To explore the mineral plasticization effect of limestone powder in the UHPC system, characterized with low water-to-powder ratio and relatively high superplasticizer dosage utilization, the spread flow of cement-limestone paste is investigated under different superplasticizer dosages and limestone powder contents, as shown in Fig. 2. With the continuous addition of PCE-type superplasticizer, the mini-slump flow diameters of cement-limestone pastes firstly increase rapidly at relatively low dosages, up to the maximum values at saturation dosages (i.e. saturation point shown in Fig. 2), subsequently typical plateaus occur. This trend is attributed to the adsorption of PCE molecules that disperse the solid particles by steric and/or electrostatic forces, thus releasing free water and strengthening fluidity [51]. After achieving the saturation adsorption, extra superplasticizer only remains in free water and does not enhance fluidity anymore [15].

The saturation dosage of superplasticizer has a great application significance in UHPC, which can achieve the best workability with the lowest superplasticizer addition at a fixed water amount, or the

lowest water utilization for a desired workability. With the replacement of cement by limestone powder from 0 to 100 vol% in the cement-limestone pastes, the superplasticizer saturation dosage diminishes from approximately 2.5% to 0.6% by the volume of total powder (bvop), as shown in Fig. 3. The correlation between limestone powder content and superplasticizer saturation dosage indicates that less superplasticizer can be used in UHPC system in the presence of limestone powder, resulting in environmental and economic benefits. For example, the SP demand decreases from 2.2% to 0.2% for a desired mini slump flow of 30 cm to achieve both self-compacting and not surplus workability [42,43], as shown in Fig. 3. Although a less superplasticizer saturation dosage is needed, the maximum flow diameter (at saturation dosage of superplasticizer) improved from about 31.2 cm to 53.5 cm, as shown in Fig. 4. The correlation between limestone powder content and maximum flow diameter indicates that introducing limestone powder can improve the potential of workability in UHPC system. On the other hand, the mini slump flow between 24 cm and 26 cm already meets the requirement of self-compacting property [42,43]. Hence, the fluidity could probably be surplus when a

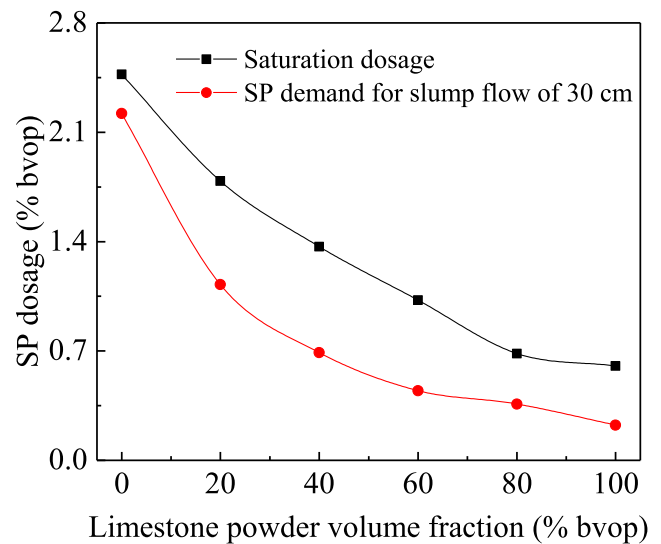


Fig. 3. SP at saturation dosage and desired slump flow.

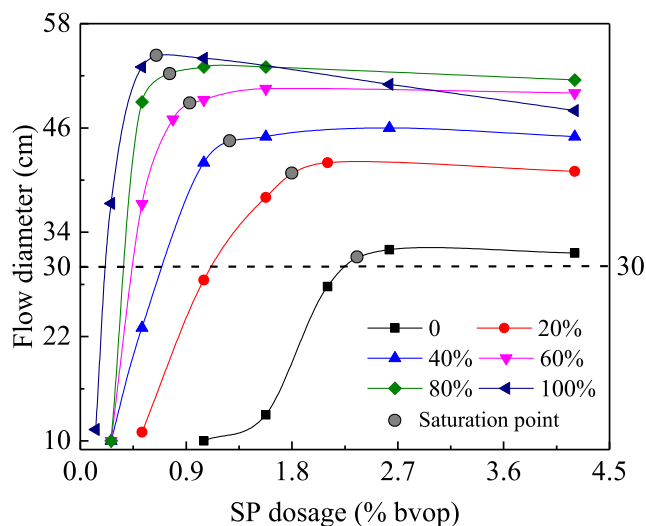


Fig. 2. Spread flow of cement-limestone pastes.

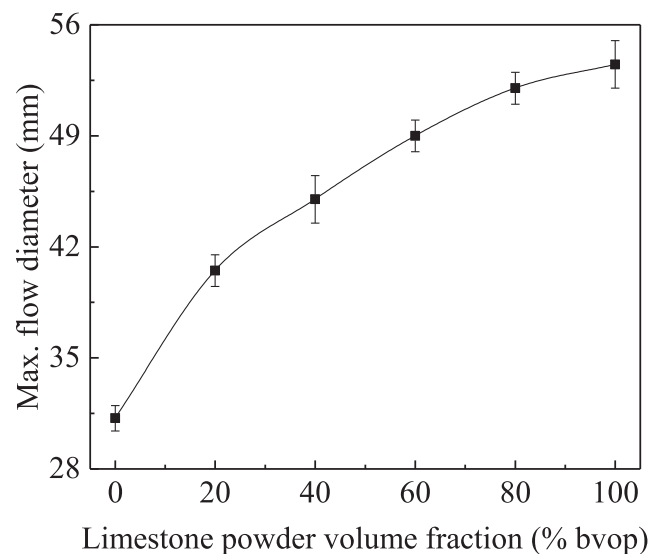


Fig. 4. Maximum flow diameter.

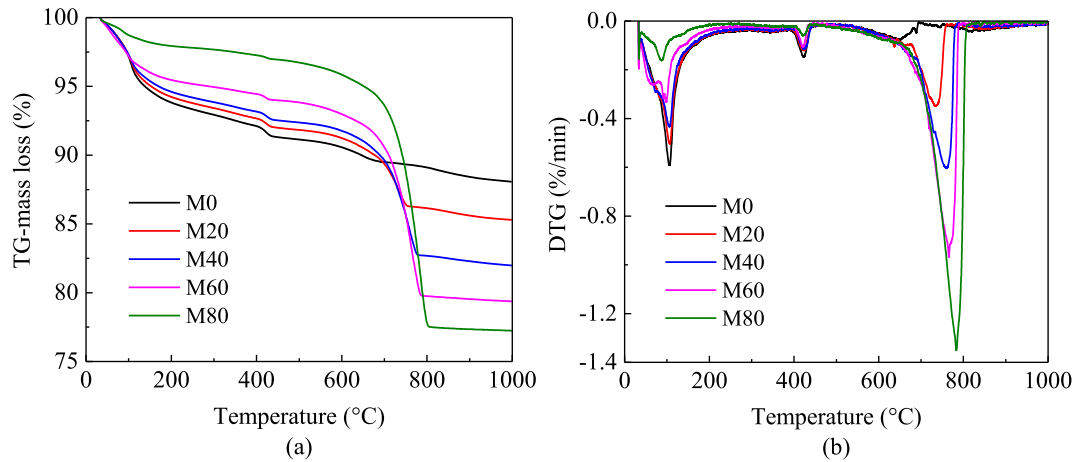


Fig. 5. TG results of UHPC.

high volume of binder is replaced by limestone powder. In other words, the water content could be further reduced, which certainly tends to improve the hardened properties of UHPC, such as the compactness, pore structure, strength, shrinkage, etc.

Based on the observation on fluidity of cement-limestone pastes, limestone powder can be regarded as a mineral plasticizer that improves the fluidity of UHPC system. The plasticization effect is mainly attributed to the following factors: (a) nucleation and chemical effects of limestone powder with comparable particle sizes to binders are quite limited or will occur after several hours of hydration [32], thus reducing the inter-particles fraction and resulting in very limited negative effect on the workability compared to reactive binders; (b) limestone powder is characterized as a neutral surface with Ca^{2+} and CO_3^{2-} ions, and OH^- groups tend to localize over the Ca^{2+} surface [37,52], which contributes to electrostatic repulsion between particles, then decreasing particle flocculation and increasing the fluidity; (c) limestone powder has weaker adsorption ability than cement and micro-silica because of a lower solubility and lower surface charge, leading to a reduced adsorption of PCE molecules and consequently reduced superplasticizer saturation dosages, as shown in Fig. 3, which is in line with the observation by [53] and [54].

Therefore, it is recommended to make full use of the positive plasticization effect of limestone powder on workability in the mix design of UHPC incorporating limestone powder, namely, using a lower water amount and superplasticizer dosage with the increase of limestone powder amount. Hence, in the mix design of UHPC with different limestone powder contents in this study, the water content and superplasticizer dosage are adjusted to achieve a comparable fluidity, in accordance with the following method: (a) predefine the mini-slump flow at 30 ± 2 cm as a precondition that is derived based on our preliminary tests, which can meet the self-compacting property without having too much surplus fluidity; (b) set initial superplasticizer dosage at relatively large value of 5% bovp. (\geq saturation dosage), then add the water content up to W_i to reach the predefined flow as the lowest water demand; (c) prepare another mixture with W_i and add the superplasticizer dosage gradually from zero to SP_i to reach the predefined flow again. In this suggested method, the lowest water amount (W_i) and corresponding most efficient superplasticizer dosage (SP_i) can be obtained for a specific UHPC with the desirable fluidity.

3.2. Thermogravimetric analysis

Fig. 5 shows the TG and DTG results of the designed UHPC with different limestone powder contents. Three dominant peaks can be

observed in Fig. 5(b), which are in accordance with the three drastic decrease of TG curves in Fig. 5(a). They are respectively related to the free water loss, dehydration of ettringite, AFm and some C-S-H (30–200 °C); portlandite (CH) decomposition (400–500 °C) mainly during 400–450 °C; calcium carbonate (CaCO_3) decarbonation (600–800 °C) [55,56]. The first and second peaks tend to be weaker and narrower with the increase of limestone powder amount, because of the dilution effect of limestone powder on the active binders. While, the third peak tends to be stronger and broader, attributed to the limestone powder addition.

To further determine the hydration products and hydration degree of binders in the presence of limestone powder, the C-S-H and CH are calculated and analysed based on the TG curves. The C-S-H and CH are mainly formed from the hydration of C_3S and C_2S , and secondary (pozzolanic) reaction between CH and SiO_2 [57]



Then, the C-S-H and CH contents can be estimated as [57]

$$\text{C-S-H}(\%) = \frac{M_{\text{CSH}}}{2.1M_{\text{H}}} \times \Delta m_{\text{CSH}}(\%) \quad (5)$$

$$\text{CH}(\%) = \frac{M_{\text{CH}}}{M_{\text{H}}} \times \Delta m_{\text{CH}}(\%) \quad (6)$$

where M_{CSH} , M_{H} and M_{CH} are the molar masses of C-S-H gel, water and calcium hydroxide, respectively. Δm_{CSH} and Δm_{CH} are the TG mass loss during 400–450 °C and 150–400 °C, respectively. The water content in C-S-H gel greatly depends on mineral condition, relative humidity and temperature [58–60], and the stoichiometric amount of water in this study is taken as 2.1 in Eq. (6), as suggested in [58], because some water of the 4 mol has already been lost below 150 °C.

The total contents of both C-S-H and CH in the designed UHPC are gradually reduced from 15.6% to 5.6% and 3.3% to 1.3%, respectively, with the increase of limestone powder amount from 0 to 80 vol%, as shown in Figs. 6 and 7. Those diminished hydration products are due to the dilution effect of reactive binders by limestone powder. However, it is remarkable that the normalized C-S-H and CH contents by mass of binders show continuous increase from 30.8% to 51.5% and from 6.5% to 12.1%, respectively. It means that the hydration degree of binders in UHPC system is considerably improved by the volume substitution of binders by limestone

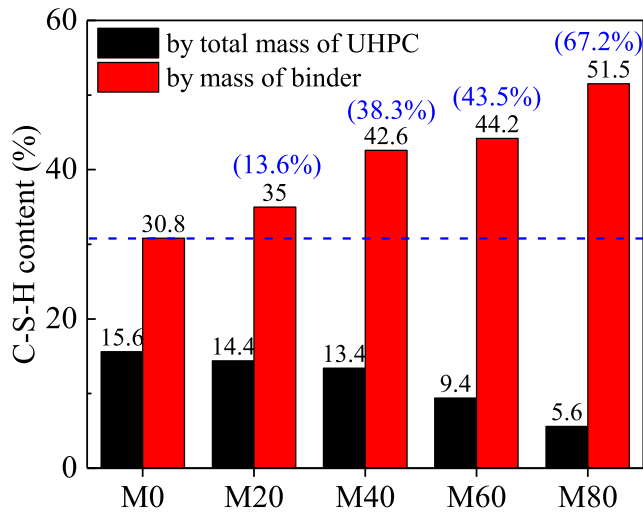


Fig. 6. C-S-H contents of UHPC.

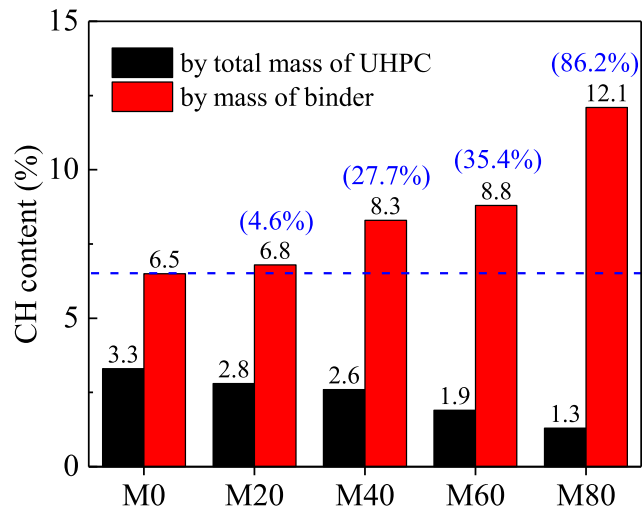


Fig. 7. CH contents of UHPC.

powder due to the increased water-to-binders, consequently enhancing binder efficiency and decreasing the environmental and economic impact. Furthermore, in the presence of limestone powder below 60 vol%, the increase ratios of normalized C-S-H contents (13.6%, 38.3% and 43.5%) in designed UHPC compared to the reference mixture (M0) are larger than those of CH (4.6%, 27.7% and 35.4%), which imply that the hydration degree of secondary (pozzolanic) reaction in Eq. (4) is larger than that of C₃S and C₂S hydration in Eq. (2)–(3), resulting in more formation of C-S-H rather than CH. The much higher hydration degree of secondary reaction is probably attributed to preferable formation of pozzolanic products under relatively higher water-to-binder ratio and nucleation effect of limestone powder. However, UHPC with too much limestone powder content, e.g. 80 vol%, shows a lower hydration degree of secondary reaction, due to the overlarge dilution of CH and mS by limestone powder, consequently making them difficult to contact to each other.

3.3. Pore structure analysis

To understand the substitution effect of binder by limestone powder on pore structure in sustainable UHPC, three experimental methods are jointly employed, including vacuum-saturation porosity, MIP and BJH pore size distributions. The vacuum-

saturation method is a relatively easy way to determine the total water-permeable “open porosity”, as shown in Fig. 8. With the increase of limestone powder content from 0 to 80 vol%, water-permeable porosity is firstly improved from 6.87% to 4.87%, after reaching to the lowest porosity of 4.52% at M40, a slight increase occurs at M60, afterwards experiences a sharp increase up to 12.15% at M80. Although the absolute intensity of hydration products is diluted by limestone powder, as confirmed in Section 3.2, an appropriate limestone powder volume substitution (20–60 vol%) shows a positive effect on the water-permeable porosity of the UHPC. It proves that the negative dilution can be compensated by reducing the water amount and enhancing the compactness by utilizing the mineral plasticization of limestone powder, as analysed in Section 3.1. Other researchers also pointed out that water reduction was an efficient way to decrease porosity of UHPC [7]. Furthermore, the higher hydration degree of UHPC with limestone powder addition can also provide some positive compensation. However, too much limestone powder addition in UHPC, more than 60 vol%, leads to significantly increased water-permeable porosity that cannot be completely compensated, which certainly weakens the macro-scope properties in hardened UHPC, such as mechanical properties and durability.

The MIP and BJH methods can further characterize the differential pore size distribution and cumulative pore volume, which cover pore sizes between 5 nm and 100 μm as shown in Fig. 9, and those between 3 nm and 100 nm as shown in Fig. 10. The critical pore diameter is defined as when the pore achieves the highest rate of mercury intrusion and begins to penetrate the interior of sample [55,61,62], illustrated by the peak in the differential pore size distribution curves. The first critical pore diameters and intensities by MIP shown in Fig. 9(a) are very similar when the limestone powder content is less than 40 vol%. As the limestone powder volume substitution ratio further increases up to 80 vol%, the first critical peak tends to be broader and more intensive, shifting from around 13.7 nm to 26.3 nm. The cumulative pore volume by MIP is first improved at M20 and then slightly weakened at M40 and M60, followed an almost triple pore volume at M80, compared to the UHPC without limestone powder. The second critical peaks of the 5 mixtures by BJH in Fig. 10(a) share the same pore diameter at around 3.9 nm, only the intensities differ, first decreasing from M0 to M40 and subsequently increasing considerably till M80. The cumulative pore volume by BJH has a similar change tendency to that by MIP when increasing the limestone powder volume substitution. While, the BJH method usually processes a larger cumu-

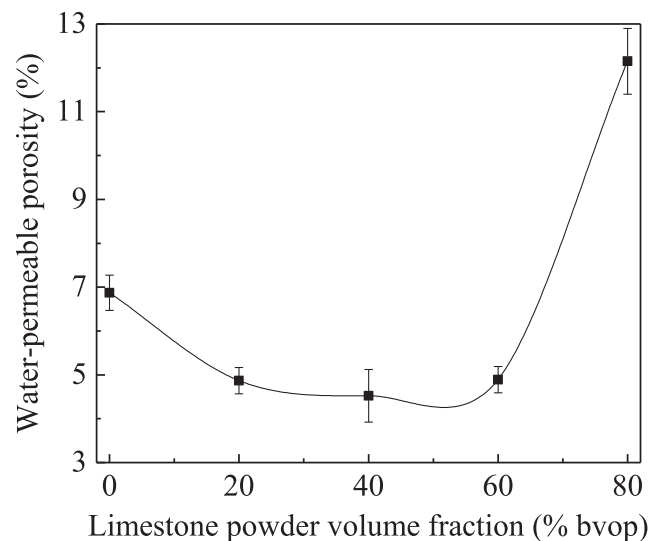


Fig. 8. Water-permeable porosity of UHPC.

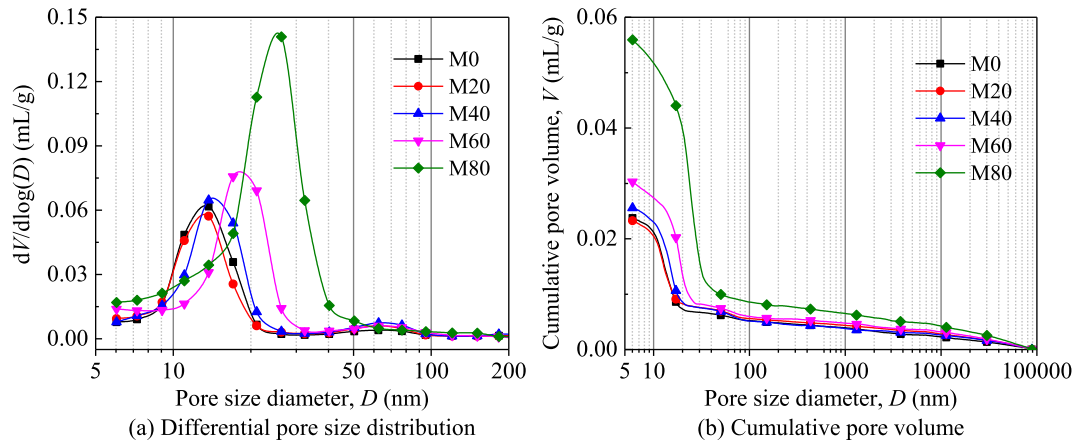


Fig. 9. Pore structure by MIP.

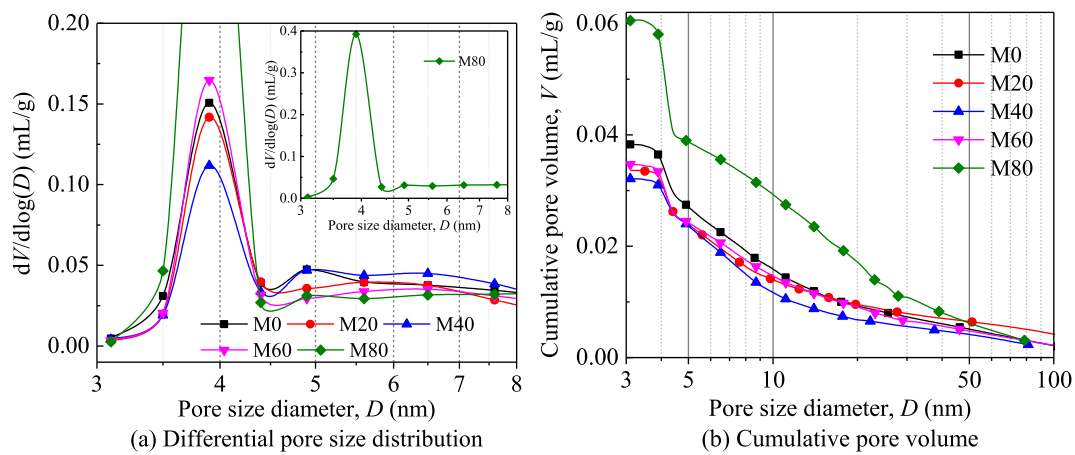


Fig. 10. Pore structure by BJH.

lative pore volume due to more efficient to detect gel pores, which occupy a large part of the total pores in UHPC.

Different pore types in cementitious materials affect different macro properties, which usually are summarized into slightly different categories by different researchers [48,63–67]. The total pores in UHPC can be classified and suggested into four categories as illustrated in Fig. 11: (a) gel pores from 2 nm to 8 nm, intrinsic to internal porosity of reaction products, e.g. C-S-H gel phase [65]; (b) small capillary pores from 8 nm to 50 nm, mainly controlled by the water amount and hydration products [48]; (c) large capillary pores from 50 nm to 10 μm , corresponding to evaporable bulk water [63]; (d) macro pores larger than 10 μm , linked to entrained air voids and initial defects [66]. With the volume replacement of binders by limestone powder within 20–60 vol%, whereas the second critical peaks vary in Fig. 10(a), the total gel pores are almost the same at 0.0171 mL/g, which is a slight improvement compared to the reference UHPC without limestone powder. The reduced total gel pores are attributed to the decreased hydration products, confirmed in Fig. 6 and Fig. 7. However, the M80 shows significantly more gel pores in Fig. 11, but less C-S-H gel phase in Fig. 6, which indicates that more low-density and porous C-S-H gel are preferably formed in the presence of large content of limestone powder. The MIP method usually acquires more small capillary pores than the BJH method, especially for the UHPC incorporating limestone powder. The small capillary pores of UHPC with limestone powder less than 60 vol% can be slightly decreased based on the BJH analysis, while they are increased by the MIP method. The pores larger than 50 nm in the five UHPC mixtures

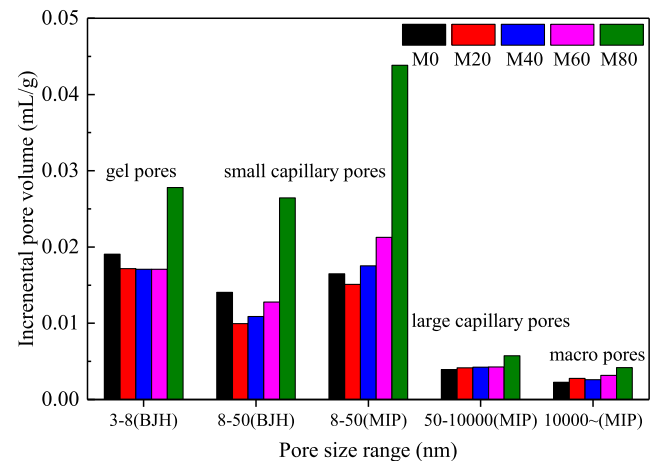


Fig. 11. Pore volume and classification.

are comparable to each other, accounting for about 10% of total pore volume.

3.4. Compressive strength and binder efficiency

Fig. 12 presents the compressive strength of UHPC with different limestone powder contents after 7 and 28 days, as well as binder efficiencies. The 7 days compressive strength shows a

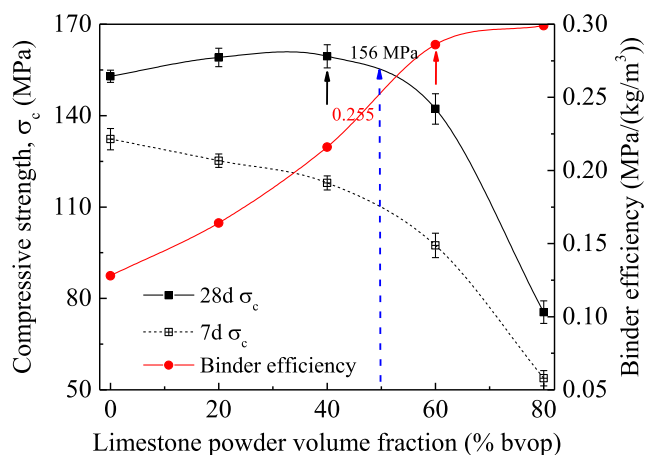


Fig. 12. Compressive strength and binder efficiency.

continuous reduction from 132.3 MPa to 53.8 MPa with the limestone powder substitution ratio changing from 0 to 80 vol%, mainly due to the dilution effect instead of the filler or nucleation effects. The 28 days compressive strength firstly shows a slight increase from 152.9 MPa at M0 to 159.5 MPa at M40, then sharply decreases to 75.5 MPa at M80. UHPC without limestone powder shows relatively high early-age strength, but an appropriate limestone powder content (less than 60 vol%) contributes to a larger strength development potential at a later age. The higher secondary (pozzolanic) reaction of UHPC incorporating limestone powder, as analysed in Section 3.2, contributes to C-S-H formation at later ages and then improves the mentioned strength development potential. Fig. 12 also indicates that ultra-high strength more than 150 MPa can be achieved by eco-friendly and low-cost UHPC incorporating high-volume of limestone powder. Normally, common sustainable UHPC needs special curing regimes or extra chemical activators [68], which certainly cause extra environmental and economic impacts.

The binder efficiency, defined as normalized compressive strength after 28 days by binder mass, is greatly improved in the presence of limestone powder, from 0.128 at M0 to 0.286 at M60, afterwards keeping at a stable level till M80. Based on the results shown in Fig. 9, the maximum compressive strength occurs at 40 vol%, while the largest binder efficiency is achieved at 60 vol%. Based on the trend lines, 50 vol% is suggested as optimum content for limestone powder in UHPC, considering both compressive strength and binder efficiency, namely around 156 MPa and 0.255 MPa/(kg/m³), respectively.

The compressive strength of cementitious material is greatly dependent on the porosity, which can be significantly improved by controlling the porosity under 30% [66]. The correlations between compressive strength and porosities by the three different methods are presented in Fig. 13. Linear trends are observed, which is in line with other researches [67]. The quality of the line fit is assessed by the coefficient of determination (R^2), and the porosity determined by MIP shows the best correlation to compressive strength with the maximum coefficient value of 0.983. In addition, the water-permeable porosity is usually lower than that measured by BJH or MIP.

3.5. Total free shrinkage

The total free shrinkage is attributed to synergetic effect of both self-desiccation induced autogenous shrinkage caused by binder hydration and water-loss induced drying shrinkage. Fig. 14 presents the total free shrinkage and water loss in UHPC within 56 days with different limestone powder contents. At relatively

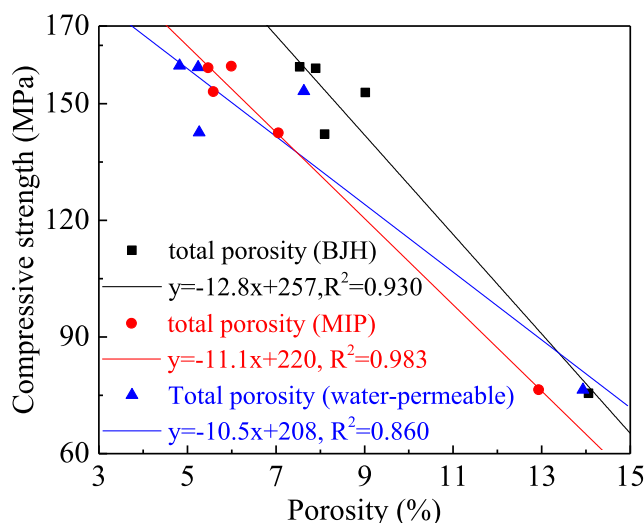


Fig. 13. Correlation between compressive strength and porosity.

early age, Fig. 14(a) shows a slower total free shrinkage development for UHPC with more limestone powder, due to a smaller absolute amount of hydration products formation and hence smaller autogenous shrinkage generation. However, at later ages, e.g. 56 days, M20 and M40 have enlarged total free shrinkages than M0 without limestone powder, while M60 and M80 tend to have diminished total free shrinkages. Because the water-to-binder ratio in UHPC with more limestone powder is higher, e.g. 0.9 in the mixture of M80, which is far more than the water needed for complete cement hydration. More free water remains in the pores and tends to evaporate in the drying environment, as shown in Fig. 14(b), consequently leading to larger water-loss induced drying shrinkage at later ages. Hence, UHPC with more limestone powder shows diminished autogenous shrinkage but enlarged drying shrinkage, and the total free shrinkage can be decreased or just slightly increased by using limestone powder.

Our previous study showed that mass replacement of cement by 20% limestone powder has a considerably negative effect on UHPC paste at a fixed water-to-powder ratio, e.g. considerably enlarged shrinkage [41]. However, the presence of limestone powder in this study shows comparable or even diminished total free shrinkage, which is due to the decreased absolute water amount with increased limestone powder content (see Table 1), thus improving the volumetric stability of UHPC [38]. It indicates that simply replacing binders by limestone powder with a fixed absolute water amount is not reasonable and negative to the total free shrinkage. While, the designed UHPC system in this study can overcome this shortage by using less water and superplasticizer amount to achieve a comparable fluidity as the precondition. It is concluded that the mineral plasticization effect of limestone powder should be considered in the mix design of UHPC based on evaluation of shrinkage, rather than simple mass substitution at a fixed water-to-binder ratio.

4. Discussion

4.1. Role of limestone powder in UHPC

Based on the results and analysis above, the role of limestone powder in UHPC can be summarized from three main aspects, namely fresh behaviour, hydration kinetics and hardened properties. The fluidity of UHPC should be considered during comparative studies, because it influences the pore structure in the hardened state [44]. Insufficient or over use of superplasticizer could lead

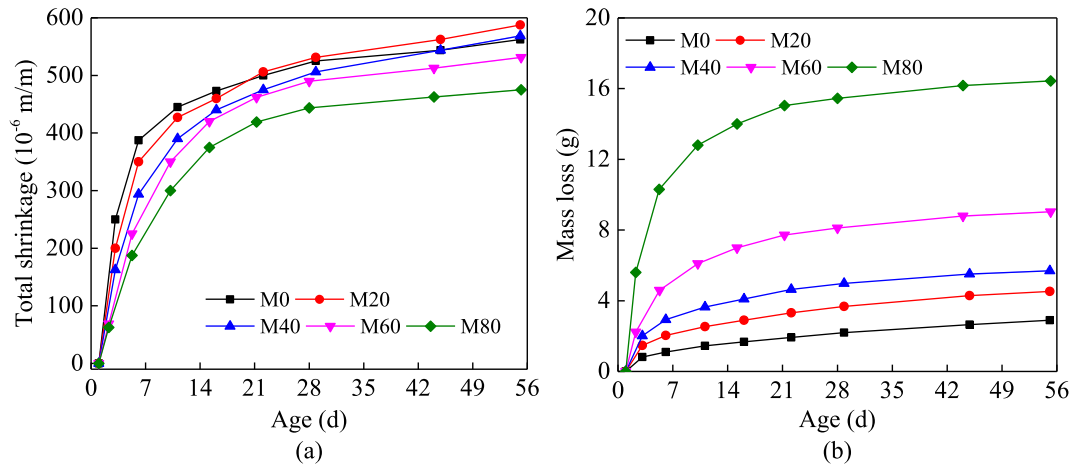


Fig. 14. Total free shrinkage and mass loss.

to enlarged macro porosity, lower compactness, segregation problems [1]. Limestone powder contributes to enhanced fluidity by reducing inter-particles friction due to limited chemical interaction, increasing inter-particle electrostatic repulsion due to OH^- groups' localization over the Ca^{2+} surface, and lowering adsorption and consumption of PCE molecules of superplasticizer due to lower surface charge. Thus, the mineral plasticization effect of limestone powder should not be neglected in the mix design of UHPC. Namely, using a lower water content and superplasticizer dosage to achieve a comparable fluidity (30 ± 2 cm) as precondition is proposed (see Section 3.1).

Even though there exists a dilution effect on hydration process of a reactive binder by limestone powder that results in less formation of hydration products, its positive functions can partly compensate or even overcome the negative dilution effect. The dilution conversely increases the water-to-binder ratio in the UHPC system where generally rather low water content is applied, which is beneficial to improve the hydration degree. In addition, the results in this study also show that hydration degree of the secondary (pozzolanic) reaction with micro-silica is more intensive than C_3S and C_2S hydration in the presence of limestone powder, which means more CH is consumed to form C-S-H gel. Furthermore, the filler and nucleation effect of limestone powder could also show certain positive significances, which tend to accelerate the hydration kinetics and generate more C-S-H gel. Meanwhile, the limestone powder can be somewhat soluble and conduce to preferably form the carboaluminate rather than monosulfate [32,37].

The hardened properties, e.g. pore structure, strength, shrinkage of UHPC with limestone powder are intrinsic to the fresh behaviour and hydration process. Generally, the dilution effect of limestone powder plays the main negative influence on the hardened properties of UHPC because of less hydration products. While, the improved pozzolanic reaction degree, formation of more and stiffer carboaluminate, filler and nucleation effects by limestone powder can provide certain extent positive effects on pore structure and compressive strength, especially in the situation of a relatively low volume replacement. Furthermore, the reduced absolute water amount can improve the compactness of UHPC, which is beneficial to the hardened properties. Generally, the hardened properties of UHPC can be enhanced with limestone powder less than 60 vol%.

4.2. Sustainability evaluation

To better understand the sustainability of the designed sustainable UHPC, environmental and economic significances are evaluated by comparing the embedded CO_2 emission and unit cost of designed UHPC.

The embedded CO_2 emission of raw materials are referred to [28] and [11], and prices are based on European market provided by ENCI without the inclusion of transportation cost, as shown in Table 2. The incorporated limestone powder in UHPC can reduce the consumption of cement and superplasticizer, which occupy the two largest unit embedded CO_2 emission, thus contributing to considerable reduction of total embedded CO_2 emission of UHPC. The total embedded CO_2 emission (m_{CO_2}) of mixture is calculated based on the CO_2 emission ($m_{\text{CO}_2}(i)$) of each ingredient ($r(i)$),

$$m_{\text{CO}_2} = \sum_{i=1}^n r(i) \cdot m_{\text{CO}_2}(i) \quad (7)$$

As shown in Fig. 15, the total embedded CO_2 emission of UHPC linearly decreases from 1011 to 234 kg/m^3 with the limestone powder increasing from 0 to 80 vol%. The eco-efficiency is defined as 28 days compressive strength normalized by CO_2 emission,

$$\beta = \sigma_c / m_{\text{CO}_2} \quad (8)$$

The eco-efficiency is in line with the binder efficiency in Fig. 12. It increases continually at relatively low limestone powder content till 60 vol%, then staying at a stable level. The total cost of UHPC is mainly dependent on the price of powders. Due to the large variations in different countries/areas and time-dependent characteristics, only prices of cement and limestone powder are compared to illustrate the economic significance of the designed UHPC. The unit price of cement is twice as that of limestone powder, which means the total cost of UHPC could be greatly reduced with incorporating high-volume of limestone powder. For example, UHPC with around 50 vol% limestone powder can decrease 47% of the embedded CO_2 emission (474 kg/m^3), and reduce the cost by about 25.5 $\text{€}/\text{m}^3$ without sacrificing the macro performance. Hence, eco-friendly and low-cost UHPC can be successfully developed by incorporating high-volume limestone powder contents.

4.3. Optimum content of limestone powder

Even though limestone powder has been extensively applied in concrete, the optimum content of limestone powder has rarely been investigated, especially in the UHPC system with relatively low water-to-binder ratio and high superplasticizer dosage. Furthermore, the content limit of limestone powder by mass is suggested varying from 15% to 35%, based on different standards [32,69].

Table 2
Embedded CO₂ emission and price of raw materials.

Raw materials	PC	mS	LP	S	W	SP
CO ₂ emission (kg/ton)	930	28	17	4	0	378
Price (€/kg)	0.090	–	0.045	–	0	–

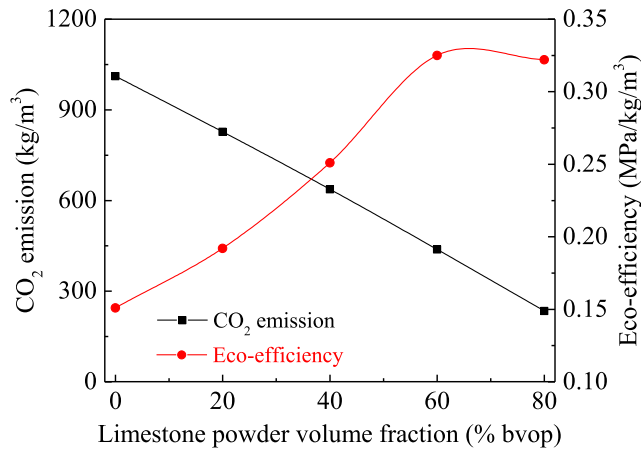


Fig. 15. Environmental significance.

In this study, a higher content of limestone powder in UHPC shows improved fluidity (or less water demand to a comparable fluidity), an increased hydration degree of the binder and a diminished self-desiccation induced autogenous shrinkage caused by binder hydration, but reduced absolute hydration products and enlarged water loss. To be specific, 20 vol% replacement of binder by limestone powder in UHPC can slightly improve the pore structure, compressive strength, binder efficiency, but slightly enlarge the total free shrinkage. 40 vol% of limestone powder can further strengthen compressive strength and binder efficiency with comparable pore structure and total free shrinkage. 60 vol% of limestone powder tends to weaken both pore structure and strength, but decrease total free shrinkage. 80 vol% of limestone powder contributes to a further decrease of total free shrinkage without any further improvement of binder efficiency, but the UHPC gets a rather weak pore structure and cannot meet the demand of high strength (75.5 MPa).

To sum up, considering the main roles of limestone powder on fresh behaviour, hydration, hardened properties, as well as sustainability, 50 vol% is suggested as the optimum content of limestone powder in UHPC, achieving compressive strength of 153 MPa with the significantly low cement content of 560 kg/m³.

5. Conclusions

This study optimizes high-volume limestone powder in sustainable UHPC and characterizes its functional mechanisms. The roles and optimum content of limestone powder in eco-friendly and low-cost UHPC are assessed by investigating the fluidity, hydration products, pore structure, strength, shrinkage and sustainability. The key conclusions of in this paper can be summarized:

- Limestone powder shows a mineral plasticization effect in UHPC by reducing inter-particles fraction due to limited chemical reaction, increasing inter-particle electrostatic repulsion due to OH⁻ groups' localization over the Ca²⁺ surface, and lowering adsorption and consumption of PCE molecules of super-plasticizer due to lower surface charge. The positive

plasticization effect should be considered to enhance the performance of UHPC by optimizing the water amount and super-plasticizer dosage.

- Although less hydration products are formed in absolute terms due to dilution effect by limestone powder, positive effects simultaneously work to compensate or even overcome its negative influence, including enlarged hydration degree, increased formation of stiffer carboaluminates, and promoted C-S-H gel by the filler and nucleation effect. The degree of secondary pozzolanic hydration with micro-silica is more intensive than C₃S/C₂S hydration, which enhances the later-age strength development potential.
- An appropriate limestone powder content contributes to a denser pore structures, enhanced strengths and comparable total free shrinkages. While, excessive addition over 60 vol% considerably weakens both pore structure and strength. The limit contents of limestone powder (25%–35% by mass) in various standards seem to be conservative in UHPC system, 50 vol% is suggested as the optimum content for the limestone powder with comparable size and morphology to cement, by considering both performance and sustainability.
- UHPC incorporating the suggested optimum limestone powder content (50 vol%) can reduce 47% of the embedded CO₂ emission (474 kg/m³) and the cost by about 25.5 €/m³, with 28 days compressive strength of 153 MPa and a low cement content of 560 kg/m³.

Acknowledgements

This study was supported by China Scholarship Council and Eindhoven University of Technology. The authors also express their gratitude to ENCI and Sika for raw material support.

Declaration of interests

None

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