applied sciences

MDPI

Article

Compressive Strength Development of High-Volume Fly Ash Ultra-High-Performance Concrete under Heat Curing Condition with Time

Pham Sy Dong [1], Nguyen Van Tuan [2,*], Le Trung Thanh [3], Nguyen Cong Thang [2], Viet Hung Cu [4] and Ju-Hyun Mun [5]

1 Faculty of Building and Industrial Construction, National University of Civil Engineering, 55 Giai Phong road, Hanoi 100000, Vietnam; dongps@nuce.edu.vn
2 Faculty of Building Materials, National University of Civil Engineering, 55 Giai Phong road, Hanoi 100000, Vietnam; thangnc@nuce.edu.vn
3 Vietnam Institute for Building Materials, Hanoi, Vietnam, 235 Nguyen Trai road, Hanoi 100000, Vietnam; thanhlt@vibm.vn
4 Faculty of Bridge and Roads, National University of Civil Engineering, 55 Giai Phong road, Hanoi 100000, Vietnam; hungcv@nuce.edu.vn
5 Department of Architectural Engineering, Kyonggi University, Suwon 16227, Korea; mjh@kgu.ac.kr
* Correspondence: tuannv@nuce.edu.vn; Tel.: +84-909-886-386

Received: 24 September 2020; Accepted: 10 October 2020; Published: 13 October 2020

Abstract: This research investigated the effect of fly ash content on the compressive strength development of ultra-high-performance concrete (UHPC) at different curing conditions, i.e., the standard curing condition and the heat curing. A total of 20 mixtures were prepared to cast specimens to measure the compressive strength at different ages from 3 days to 180 days. Additionally, 300 specimens were prepared to estimate the appropriate heat curing period at the early ages in terms of enhancing the 28-day compressive strength of UHPC with high content of fly ash (FA). From the regression analysis using test data, empirical equations were formulated to assess the compressive strength development of UHPC considering the FA content and maturity function. Test results revealed that the preference of the addition of FA for enhancing the compressive strength of UHPC requires the early heat curing procedure which can be recommended as at least 2 days under 90 °C. Moreover, the compressive strength of UHPC with FA under heat curing mostly reached its 28-day strength within 3 days. The proposed models based on the *fib* 2010 model can be a useful tool to reliably assess the compressive strength development of UHPC with high-volume fly ash (HVFA) (up to 70% fly ash content) under a heat curing condition that possesses a different performance from that of normal- and high-strength concrete. When 50% of the cement content was replaced by FA, the embodied CO_2 emission for UHPC mixture reduced up to approximately 50%, which is comparable to the CO_2 emission calculated from the conventional normal-strength concrete.

Keywords: ultra-high-performance concrete (UHPC); high-volume fly ash (HVFA); compressive strength; curing conditions; prediction model

1. Introduction

Ultra-high-performance concrete (UHPC) has commonly been considered as a new class of concrete that has gained a strong interest in research and application since the late 1990s [1–3] with outstanding characteristics including high fluidity, compressive strength (over 120 MPa [4]), high modulus of elasticity, low permeability, and excellent durability compared to conventional concrete and high strength concrete [5–7]. Because of these outstanding properties, application of UHPC can create many possibilities such as lighter structures, larger-span structures, hybrid structures, new design, and new products with a potential for a better economy and resource consumption in comparison with conventional concrete, steel, and other building materials [2,5,8]. In Vietnam, research on UHPC has been also implemented since 2011 and several results have been published elsewhere [9–11].

Manufacturing UHPC usually needs high material costs, high cement content (around 1000 kg/m^3), and high-temperature curing. These are all limiting factors for the broader application and sustainability of UHPC. Replacement of a certain amount of cement content in UHPC composition is a scientific and practical topic that UHPC research groups have been undertaking [12–14] to reduce costs as well as to minimize the negative impacts on the environment caused from the cement production. In particular, the potential for the partial replacement of cement by coal-fired fly ash (FA) discharged from coal-fired power plants has being increased recently in Vietnam. More than 20 power plants with a capacity of 13,100 MW in Vietnam generate an amount of approximately 15.7 million tons of coal ash annually and mainly has been dumped in landfills. The number of power plants is increasing every year and it is forecasted that thermal energy will account for more than 50% of the total electricity generation in 2030. These power plants will consume approximately 171 million tons of coal and discharge a huge amount of coal ash, significantly exceeding the current consumption of coal ash of about 3–4 million tons per year [15]. Therefore, development of UHPC using FA has the "double benefit" of enhancing the applicability of UHPC as it reduces the amount of cement used and also reduces the amount of FA dumped in landfills near the coal-burnt thermal power plants in Vietnam.

High-volume fly ash (HVFA) concrete, which was firstly introduced by Malhotra at Canada Center for Mineral and Energy Technology (CANMET), Ottawa in the 1980s, and defined as FA replacement above 50% cement content, addresses the aforementioned issue. FA levels of around 15%–20% by mass of total cementitious material in structural concrete have become generally accepted worldwide in normal practice, even in some recent attempts to apply in producing UHPC [16,17]. In the past, concrete containing high volumes of low-calcium FA was mostly used in mass concrete works such as roller-compacted concrete dams and highway base courses, where high strength and high workability are not required. As stated by Mehta [18], half and more substitution of FA is possible to produce sustainable and high-performance concrete with lower water demand, good workability, minimized cracking due to thermal and drying shrinkage, and improved durability. However, cost-effective and less-energy intensive curing methods of UHPC using HVFA have not been sufficiently studied.

The compressive strength of UHPC is enhanced significantly by using a very high cement content and silica fume (SF) combined with very high superplasticizer dosage to allow excessively lower water-to-binder ratios. This is also supported by heat curing for the concrete after setting. The development of compressive strength of UHPC is mostly dependent on the hydration of cement and pozzolanic reactions of mineral admixtures at lower temperatures and higher temperatures. Due to a slower rate of hydration, it has become inevitable to induce thermal regime to enhance the reactions. Hence a proper thermal regime is required to derive a proper microstructure of C-S-H hydrates by heat curing [8]. The properties of UHPC are significantly affected by the history of curing temperatures [14,19,20]. In addition, the addition of HVFA results in more difficulty in controlling the compressive strength of UHPC cured under different temperatures. Up to now, understanding the compressive strength development of UHPC with HVFA is still limited as there is a lack of research on this topic.

The objective of this research is to predict the compressive strength development of UHPC with various contents of FA under different histories of curing temperatures. A total of 20 UHPC mixtures were prepared with the variations of water-to-binder ratios (W/B) and FA contents added as a replacement material of cement. Specimens to measure the compressive strength of concrete were cured at different curing conditions: (1) standard environment with consistent temperature of 27 ± 2 °C and relative humidity (RH) exceeding 95%; and (2) heat curing with hot water (90 ± 3 °C) curing for initial 48 h followed by standard environments. The appropriate heat curing periods at early ages for enhancing 28-day compressive strength of UHPC with high-volume contents of fly ash were assessed using 300 specimens prepared additionally at different heat curing ages. Ultimately, empirical equations were formulated from a non-linear regression analysis using the test data to predict the compressive strength development of HVFA UHPC under heat curing condition with time. The embodied CO_2 emissions of HVFA UHPC were also evaluated.

2. Materials and Methods

2.1. Materials

Portland cement PC50 Nghi Son (according to Vietnamese standard TCVN 2682 [21]), condensed silica fume (SF), and FA conforming to class F specified in ASTM C 618 [22] were used for the binder of the UHPC mixture. The chemical compositions and properties of cementitious materials are given in Tables 1 and 2, respectively. For the aggregate, silica sand with a mean particle size of approximately 300 µm was used for all the mixtures (Figure 1). To obtain reliable workability (flow value between 200 mm and 250 mm) of concrete, a polycarboxylate based-superplasticizer with 30% solid content by mass was used within a recommended range of dosage.

Table 1. Chemical composition of materials.

Material	Chemical Composition (%)									
	SiO_2	Fe_2O_3	Al_2O_3	CaO	MgO	Na_2O	K_2O	SO_3	TiO_2	LOI
Cement	20.3	5.05	3.51	62.81	3.02	-	-	2.00	-	1.83
SF	92.3	1.91	0.86	0.32	0.85	0.38	1.22	0.30	-	1.68
FA	46.82	12.3	25.29	1.20	1.16	1.09	2.50	0.60	0.08	4.04

Table 2. Properties of cementitious materials.

Properties		Unit	Cement	SF	FA
Fineness (Blaine)		cm^2/g	4130	-	-
Mean particle size		µm	10.76	0.15	5.43
Specific gravity		g/cm^3	3.15	2.20	2.44
Pozzolanic reactivity index		%	-	111	103
Compressive strength	After 3 days	MPa	36.1	-	-
	After 28 days	MPa	55.0	-	-

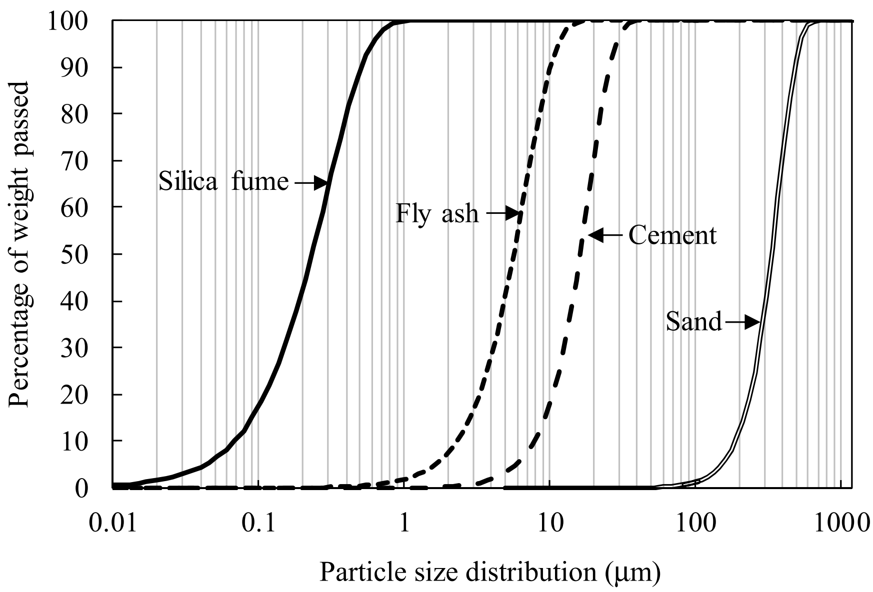


Figure 1. Particle size distribution of raw materials used in this study.

2.2. Mixture Proportioning

The de Larrard and Sedran methodology [23] was employed to optimize particle packing densities of sand and cementitious materials. In the calculation of packing density for UHPC mixtures, the sand to the cementitious material ratio of 1.0 by mass was chosen. The addition of 10% SF was reported to improve both fresh and hardened properties of UHPC. According to previous researches [7,10], the reliable range of SF is recommended to be 10% to 20% of cementitious material by mass with regard to the compressive strength development. Moreover, with the high cost and limited resources of SF in Vietnam, this leads to the fact that the use of 10% SF is considered as the optimal option in this research.

The FA content was selected with various cement replacement levels from 0% to 70% by mass of binder. Having combined with 10% SF, consequently, the total amount of SF and FA was investigated in the range of 10% to 80% of binder to optimize the UHPC composition.

Based on the results of the optimized packing density of granular mixtures, 20 UHPC mixtures were designed with a sand-to-binder ratio (*S/B*) of 1.0 by mass. The water-to-binder (*W/B*) ratios by mass of the mixtures were selected from 0.12 to 0.18. It should be noted that the SF content was fixed at 10% by mass of binder. The flow measurements were controlled in the range of 200–250 mm by adjusting the superplasticizer (SP) dosage, as listed in Table 3.

Table 3. Summary of designed ultra-high-performance concrete (UHPC) mixtures.

Mix. No	*W/B* (by Mass)	*S/B* (by Mass)	FA (% by Mass of Binder)	SF (% by Mass of Binder)	SP (% by Mass of Binder)	C, kg/m^3	FA, kg/m^3	SF, kg/m^3	S, kg/m^3	Water, kg/m^3	SP, kg/m^3
1	0.18	1	0	10	0.39	1013	0	113	1125	205	14.6
2	0.18	1	20	10	0.31	772	221	110	1103	201	14.3
3	0.18	1	30	10	0.29	655	327	109	1091	199	14.2
4	0.18	1	50	10	0.16	428	535	107	1070	195	13.9
5	0.18	1	70	10	0.13	210	734	105	1049	191	13.6
6	0.16	1	0	10	0.58	1036	0	115	1151	182	22.3
7	0.16	1	20	10	0.52	789	225	113	1127	180	19.5
8	0.16	1	30	10	0.49	669	335	112	1116	179	18.2
9	0.16	1	50	10	0.27	437	547	109	1093	181	9.8
10	0.16	1	70	10	0.19	214	750	107	1072	179	6.8
11	0.14	1	0	10	0.81	1061	0	118	1179	156	31.8
12	0.14	1	20	10	0.69	807	231	115	1153	156	26.5
13	0.14	1	30	10	0.60	685	342	114	1141	157	22.8
14	0.14	1	50	10	0.48	447	559	112	1118	157	17.9
15	0.14	1	70	10	0.28	219	767	110	1095	159	10.2
16	0.12	1	0	10	1.60	1086	0	121	1207	114	64.4
17	0.12	1	20	10	1.10	826	236	118	1181	125	43.3
18	0.12	1	30	10	0.93	701	350	117	1168	128	36.2
19	0.12	1	50	10	0.78	457	572	114	1143	130	29.7
20	0.12	1	70	10	0.57	224	784	112	1120	132	21.3

2.3. Methods

All UHPC mixtures were prepared using a 60-L capacity mixer. To produce UHPC concrete with high-workability, the following mixing procedure was considered (Figure 2): (1) cementitious materials and sand were dry-mixed for 5 min; (2) 70% of the designed unit water was added and then mixed for another 4 min; and (3) the other 30% of the unit water including superplasticizer was added and mixed for 9 min.

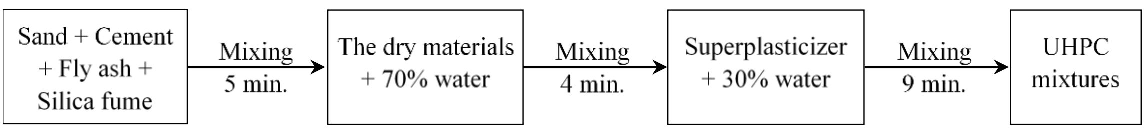


Figure 2. Mixing procedure of UHPC mixtures.

Mixtures were cast into 100 mm cubic molds to examine the compressive strength gained at different ages. All specimens were cured at a standard curing room with the temperature of 27 ± 2 °C and relative humidity (RH) of exceeding 95%, and then demolded after casting of 24 h. After demolding, the specimens were cured under two different curing conditions:

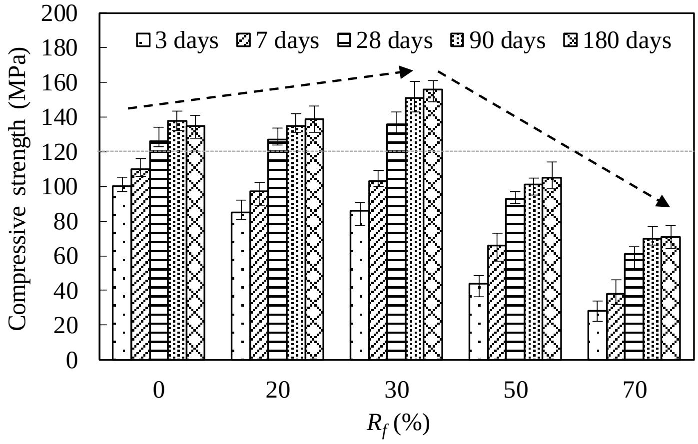
(1) Standard curing condition (27 ± 2 °C, RH ≥ 95%) until testing.
(2) Heat curing condition: in hot water (90 ± 3 °C) for 48 h followed by the standard curing condition until testing.

The compressive strength of specimens cured at the above conditions was tested at ages of 3, 7, 28, 90, and 180 days complying with ASTM C109 [24]. To examine the effect of heat curing age on 28-day compressive strength of UHPC specimens, more specimens were cured in the hot water condition at different ages varied from 1 to 7 days. A total of 100 sets of specimens or 300 specimens cured in different heat curing ages were tested at 28 days.

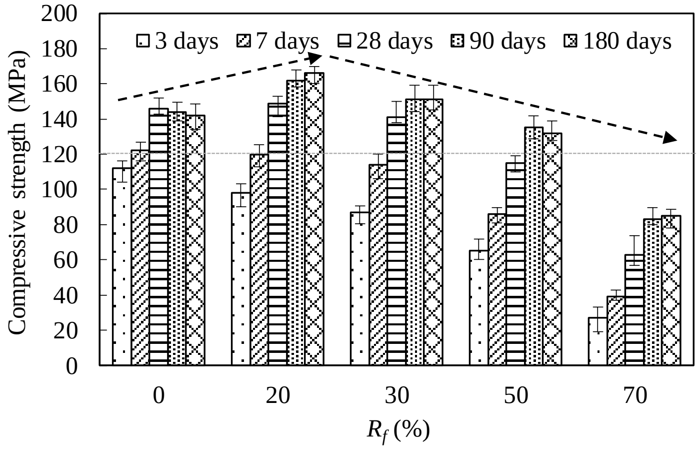
3. Results and Discussions

3.1. Development of Compressive Strength of HVFA UHPC

The results in Figures 3 and 4 show that the development of the compressive strength with time of UHPC with different *W/B* ratios and different FA contents from 0% to 70% by mass of binder, in which the SF content was fixed at 10% by mass of binder under the standard curing condition and the heat curing, respectively.

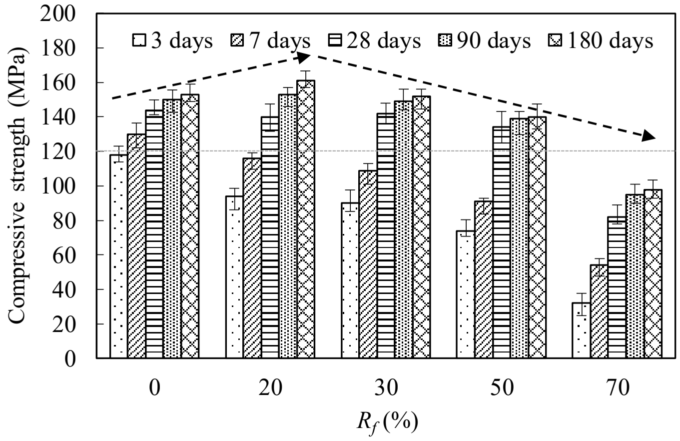


(a) *W/B* = 0.18

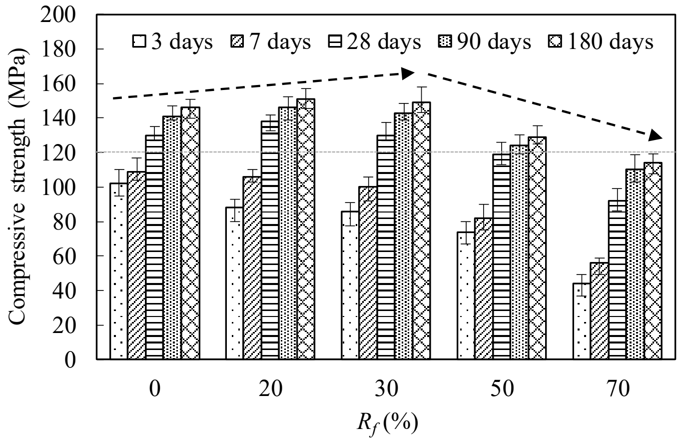


(b) *W/B* = 0.16

Figure 3. *Cont.*

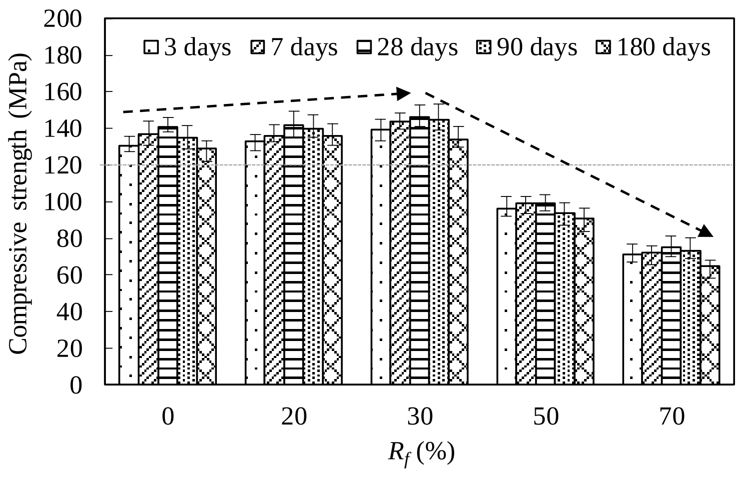


(c) $W/B = 0.14$



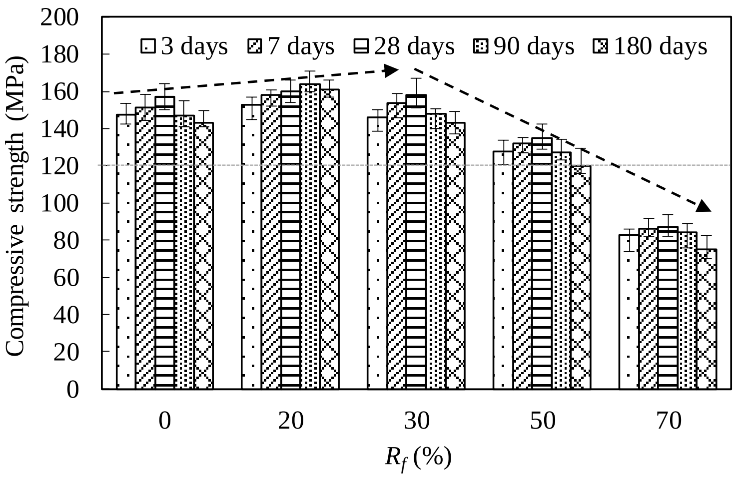
(d) $W/B = 0.12$

Figure 3. Effect of fly ash content on compressive strength of UHPC with time at different W/B ratios from 0.12 to 0.18 under standard curing condition.

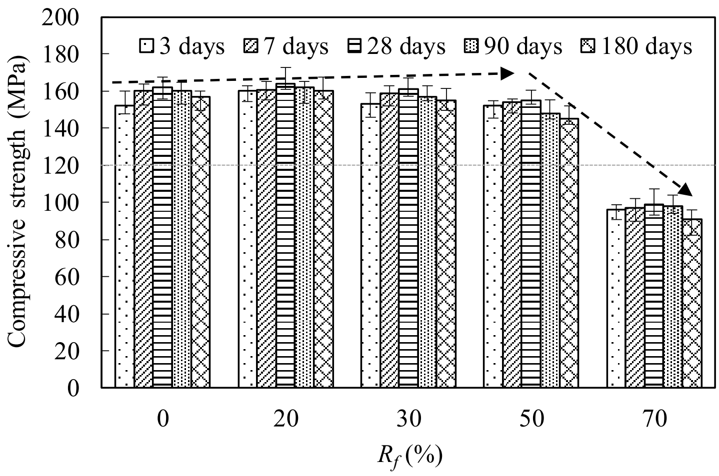


(a) $W/B = 0.18$

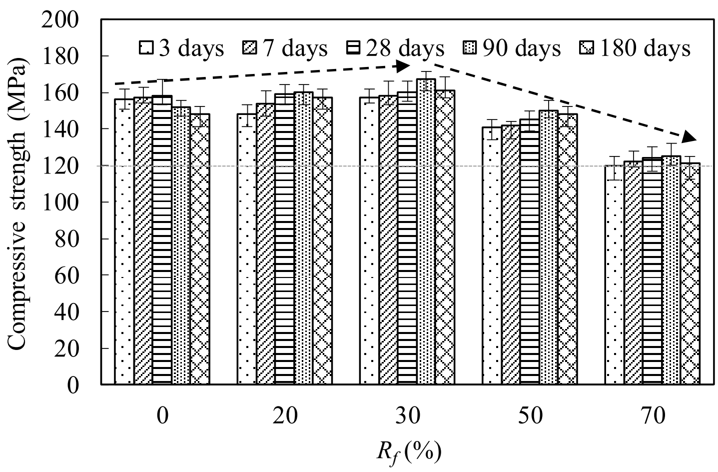
Figure 4. *Cont.*



(b) $W/B = 0.16$



(c) $W/B = 0.14$



(d) $W/B = 0.12$

Figure 4. Effect of fly ash content on compressive strength of UHPC with time at different W/B ratios from 0.12 to 0.18 under heat curing condition.

Under the standard curing condition, the compressive strength of UHPC developed slowly during the first 7 days (particularly the UHPC using 70% FA) and then increased highly at the age of 28 days. Meanwhile, if the heat curing condition was applied, the compressive strength could be developed quickly even at early ages, and the ultimate compressive strength could be achieved just after 2 days heat curing.

It can be observed that under standard curing, the addition of FA decreased the compressive strength of UHPC at early ages, i.e., 3 days and 7 days, especially when the FA content increased to 50% and 70%. The compressive strength of UHPC was significantly reduced, from 25% to 75% depending on the *W/B* ratio and the FA content, compared to that of the control specimen. It should be noted that when cement was replaced with 20%–30% FA, compressive strength of UHPC reached the maximum value at a later age. Besides, with the same FA content, when the *W/B* ratio decreased from 0.18 to 0.12, the compressive strength of UHPC increased 9%–57% depending on the FA content, in which the higher FA content gave a higher positive effect. The interesting point is that the incorporation of 70% FA increased the compressive strength of the UHPC specimens sharply from 50% to 57%, in comparison with that of specimens using 20%–50% FA (in which the compressive strength was improved only about 9%–23%).

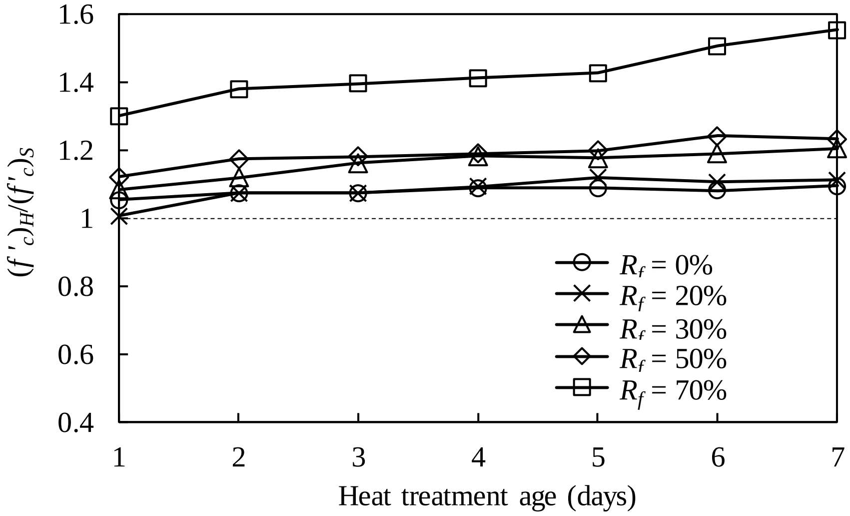
It can be observed that the similar tendency occurred with the development of the compressive strength of UHPC when adding FA under the heat curing condition. However, the compressive strength of UHPC increased rapidly at early ages, i.e., 3 days and 7 days, reaching 92% to 99% compared to that of UHPC at 28 days, respectively. It should be noted that at later ages, i.e., 90 and 180 days, the compressive strength of UHPC specimens is similar. As discussed above, the water to binder of UHPC is very low, normally less than 0.24. Therefore, minimal water is available for cement hydration and the resulting pozzolanic reaction can occur after 90 days. This means that the 90-day and 180-day strengths are very close to each other. This is different from normal strength concrete as the amount of water is still available, thus the hydration is still kept going and the strength keeps gaining up to a year.

Moreover, when the percentage of cement replacement by FA increased to 30%, the compressive strength of UHPC was increased, but it reduced with an increase of the replacement content up to 50% and 70% and this reduction depended significantly on the *W/B* ratio. For example, when the *W/B* ratio decreased from 0.18 to 0.12, the compressive strength of concrete increased with all FA contents. However, the compressive strength of UHPC was not increased significantly, i.e., about 10% with adding 20% and 30% FA, but increased very rapidly, i.e., from 45 to 65%, with the cement replacement content from 50% to 70% FA when the *W/B* ratio reduced from 0.18 to 0.12.

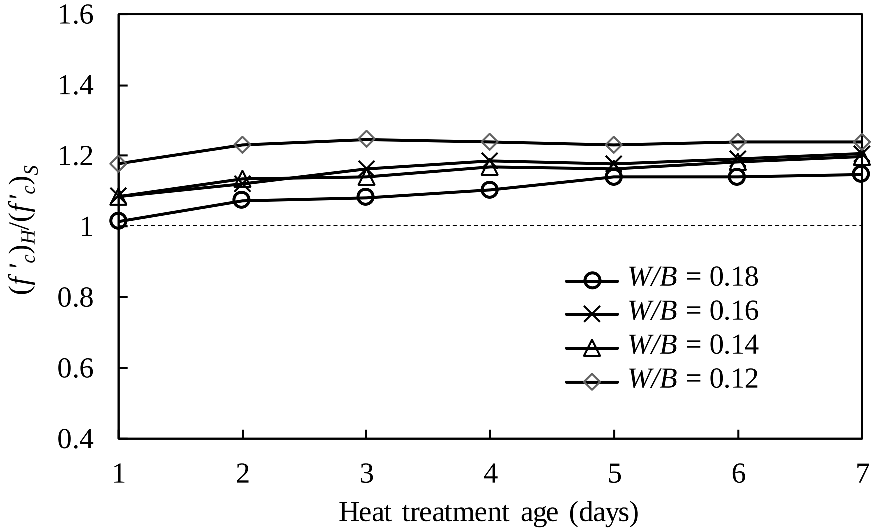
It is clear from these experimental results that, for the UHPC using high-volume FA, the very low *W/B* ratio in combination with the 48-h heat curing gave the highest efficiency in improving the compressive strength of UHPC.

3.2. The 28-Day Compressive Strength

Figure 5 shows the typical normalized 28-day compressive strength of UHPC cured under different durations of heat curing. The vertical axis of the figure indicates a ratio of 28-day compressive strength ($(f'_c)_H$) of UHPC under heat curing condition relative to that one under standard curing condition ($(f'_c)_S$) of the counterpart specimen without fly ash. The ratio of $(f'_c)_H/(f'_c)_S$ slightly increased as the heat curing age increased up to 2 days, beyond which it was insignificantly affected by the heat curing age, although higher compressive strength (f'_c) was obtained at a heat curing age of 7 days for UHPC specimens with the fly ash content $R_f \geq 50\%$ (Figure 5a). At the same heat curing age, higher values of $(f'_c)_H/(f'_c)_S$ were observed for UHPC mixtures with more contents of fly ash. For specimens prepared to investigate the heat curing ages, $(f'_c)_H/(f'_c)_S$ ranged between 1.14 and 1.47 for UHPC with R_f = 70% and 1.0 and 1.29 for UHPC with R_f = 20%. This implies that the preference of the addition of fly ash for enhancing the compressive strength of UHPC requires the early heat curing procedure which can be recommended as at least 2 days under 90 °C from the present tests. The compressive strength enhancement of UHPC with fly ash due to heat curing was also affected by *W/B* (Figure 5b). At the same heat curing ages, higher values of $(f'_c)_H/(f'_c)_S$ were obtained for UHPC specimens with lower *W/B*. For example, $(f'_c)_H/(f'_c)_S$ ranged between 1.09 and 1.50 for UHPC with *W/B* = 0.12, and 1.03 and 1.34 for UHPC with *W/B* = 0.18.



(a) Effect of fly ash content (*W*/*B* = 0.16)



(b) Effect of water-to-binder ratio (R_f = 30%)

Figure 5. Typical normalized 28-day compressive strength of UHPC with fly ash.

As curing time of heat curing increased, $(f'_c)_H/(f'_c)_S$ increased, including sharply with 70% FA content (in Figure 5).

3.3. Discussion

The increasing compressive results when applying heat curing can be explained in that the heat curing enhances the microstructure and results in increasing strengths and fracture energy in a shorter time than the standard curing procedure [5,25,26]. This is because heat curing accelerates the hydration reactions of cement and the pozzolanic reaction of mineral admixtures, i.e., SF, FA, and calcium hydroxide generated from the hydration of cement. This was also confirmed by the research results of Richard and Cheyrezy [5] regarding the pozzolanic reaction ratio of UHPFRC heat treated at 70 °C, 90 °C, 200 °C, 250 °C and 400 °C, compared with UHPC cured at 20 °C. This research also revealed that the pozzolanic ratio of UHPC heat treated at 90 °C was 90% for soft cast samples and 93% for pressed cast specimens, whilst this was only 72% for soft cast specimens and 82% for pressed cast specimens which were cured at 20 °C. Therefore, heat curing condition is known as one of the important principles to make UHPC.

Moreover, it can be seen from the experimental results that the UHPC specimens using a combination of 10% SF and different FA contents attained the different highest 28-day compressive strength with the different *W/B* ratios and curing conditions, which are given in Table 4.

Table 4. The highest 28-day compressive strength of UHPC with different *W/B*.

Mix	The Highest 28-Day Compressive Strength (MPa)	Curing Condition	*W/B* (by Mass)	SF (% by Mass of Binder)	FA (% by Mass of Binder)
1	146.0	Standard curing	0.16	10	0
	162.0	Heat curing	0.14		
2	149.0	Standard curing	0.16	10	20
	164.0	Heat curing	0.14		
3	142.0	Standard curing	0.14	10	30
	161.0	Heat curing	0.14		
4	134.0	Standard curing	0.14	10	50
	155.0	Heat curing	0.14		
5	92.0	Standard curing	0.12	10	70
	124.0	Heat curing	0.12		

For a very interesting point, a hyperbolic relationship was observed between the highest compressive strength f_c' of UHPC and FA content, as presented in Figure 6. The ratios of the highest f_c' of UHPC with early heat curing relative to that of the counterpart UHPC cured under the standard environment corresponded to approximately 1.22, irrespectively of the variation of FA content. This implies that the increasing ratios in f_c' of UHPC due to early heat curing were indepentent of R_f. Furthermore, when compared with the highest f_c' of the UHPC with R_f = 0 under the standard environment, UHPC with early heat curing exhibited a higher value when R_f was 50% and slightly lower value when R_f was 50% for UHPC with early heat curing, while considering a comparable value to the compressive strength of UHPC with no FA and cured under the standard environment. Based on the results from Figure 6, it can be also proposed that the optimum UHPC composition to attain the compressive strength of 120 MPa includes the total mineral admixture content of about 62.5% (10%SF + 52.5%FA) and over 80% (10%SF + 70%FA) under standard curing and heat curing conditions, respectively. It means that UHPC can be produced with only about 220 and 450 kg cement per m^3 under these corresponding curing conditions. Recently, the desired compressive strength of UHPC is up to 150 MPa or higher, and this leads to the total mineral admixture content of about 62.5% (10%SF + 52.5%FA) or about 450 kg cement per m^3 which can be used to produce UHPC under the heat curing condition (Figure 6). This plays an important role in the research and development of sustainable construction.

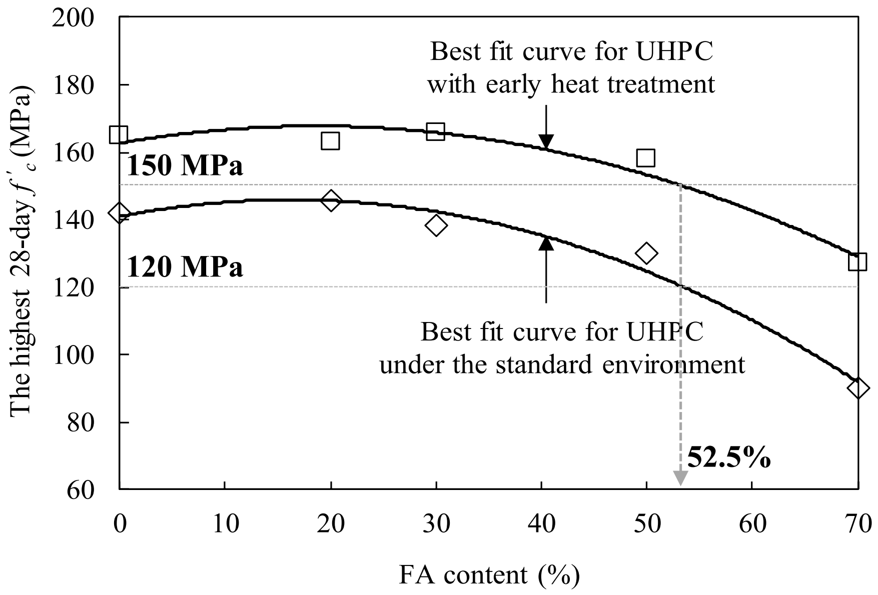


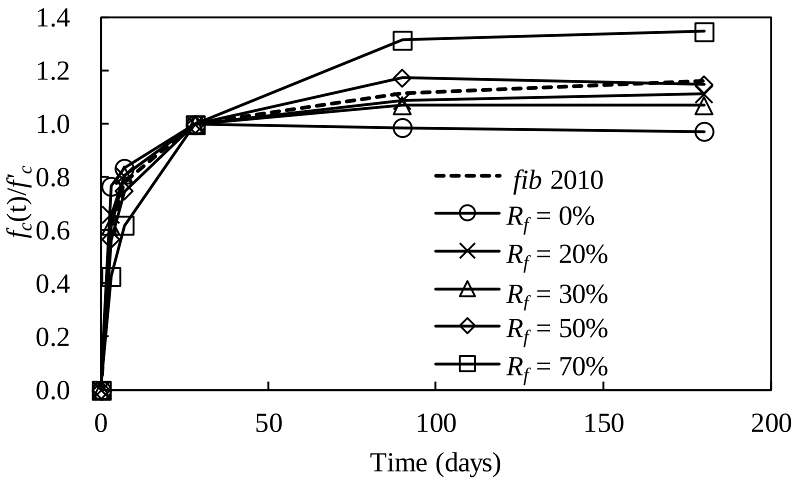
Figure 6. The relation between the highest 28-day f'_c of UHPC and fly ash (FA) content.

4. Predictions for Compressive Strength Development of HVFA UHPC

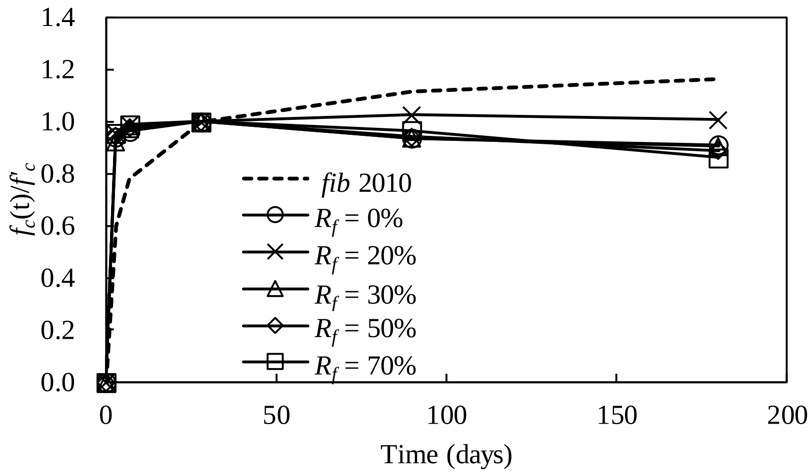
4.1. Typical Compressive Strength Development

Figure 7 shows typical compressive strength development ($f'_c(t)$) normalized by 28-day compressive strength for UHPC mixture with *W/B* of 0.16. In the same figure, predictions by empirical equations specified in *fib* 2010 model [27] are also presented for comparisons. The compressive strength gains of UHPC cured under standard condition were significantly affected by R_f. With the increase in R_f, the strength gain rate ($f'_c(t)/f'_c$) at early ages tended to decrease whereas lower values for the rate were obtained at the long-term ages, showing a clear crossover behaviour. The rate at 3 days ranged between 0.79 and 0.82 for UHPC with R_f = 0% and 0.39 and 0.48 for UHPC with R_f = 70%. The corresponding values at 180 days ranged between 0.97 and 1.12 for the former mixtures and 1.16 and 1.35 for the latter mixtures. This pozzolanic effect is similar to the trends commonly observed in normal-strength concrete.

On the other hand, $f'_c(t)/f'_c$ obtained from the UHPC with the heat curing for 2 days exhibited a different phenomenon from the common trend. The strength gain rate of UHPC cured under heat curing condition was insignificantly affected by R_f. The rates at 3 days ranged between 0.92 and 0.99 for all the specimens. The corresponding values at 180 days ranged between 0.86 and 1.02. The compressive strength of UHPC with fly ash under heat curing mostly reached its 28-day strength at just 3 days. The initial heating curing plays an important role in the rate of hydration degree at early age of UHPC with fly ash whereas its effect becomes minimal at long-term age because the hydration reaction gradually reaches a stable state with age. It should be noted that heat curing was somewhat unfavorable for compressive strength development of UHPC with fly ash, indicating a slight lower 180-day compressive strength than 28-day strength. This can be caused by the rapid reaction and porous microstructure of the system. Verbeck and Helmuth, cited by [28], revealed that a rapid hydration of cement from high curing temperatures will result in a high early strength because of more hydration products being formed. However, the rapid hydration does not allow the generated hydration products sufficient time available to diffuse properly away from the cement particles due to the low solubility and diffusivity of the hydration products. This leads to a high concentration of hydration products in a zone immediately surrounding the cement grain, and forms a relatively dense shell around the hydrating cement grains. As a consequence, this retards any subsequent hydration which makes a more porous structure and a reduction of long-term strengths. Mindness and Young [29] also suggested that the heat curing could induce a non-uniform precipitation of the hydration products within the hardened cement paste. Furthermore, Keil, cited by [30], reported that high temperatures would result in a coarser crystal structure compared to long, defect-free crystals formed at low temperatures. Besides, Bentur et al., cited by [30], found an increase of the macro porosity and a decrease of the meso and micro porosity without any change in total porosity for a temperature increase from 25 °C to 65 °C. This situation does not occur in normal temperature curing where there is adequate time for the hydration products to diffuse and precipitate uniformly throughout the interstitial space among the cement grains that keeps gaining strength with time.



(**a**) Standard curing condition



(**b**) Heat curing condition

Figure 7. Typical normalized compressive strength development (W/B = 0.16).

When cement is partially substituted by FA, the real volume of FA is higher than that of cement because the specific gravity of FA is smaller than that of cement. Besides, the particle size of FA is smaller than that of cement, which makes FA to fill in the pores and results in a denser microstructure compared to that of the reference specimen without FA. This probably causes a lesser negative effect in later ages, i.e., after 28 days, particularly at higher cement replacement levels.

The empirical equations of *fib* 2010 model [27] do not consider the effect of pozzolanic reaction of fly ash on the compressive strength gain of concrete at early and long-term ages. Thus, under- or overestimated results for predictions by the *fib* 2010 model [27] depended on R_f, in estimating the compressive strength development of UHPC mixtures with fly ash cured under standard condition.

In addition, for predicting the compressive strength development of UHPC mixtures cured under heat curing condition, underestimation and overestimation were observed for early ages and long-term ages, respectively, irrespective of R_f. Overall, a new straightforward model is required to reliably predict the compressive strength development of UHPC with different fly ash contents.

4.2. Empirical Equations for Compressive Strength Development

As presented in Figure 7, the compressive strength development of UHPC with age can be characterized as a parabola, which agrees with the observation that the increasing rate of compressive strength development decreases with the increase of age. Therefore, the compressive strength development of UHPC can be identified by using a parabolic time function, which is a common approach for normal-strength concrete. To formulate straightforward empirical equations for compressive strength development of UHPC, the present study follows the exponential function specified in the *fib* 2010 model [27]:

$$f_c(t)/f'_c = EXP\left[S_l\left(1-\left(\frac{28}{t}\right)^{0.5}\right)\right] \quad (1)$$

where S_l is the parameter to identify the slope of the parabolic curve at different ages (t; in days). The compressive strength of UHPC with fly ash at age of 28 days is significantly affected by R_f, *W/B*, and early heat curing, as presented in Figure 7. Considering these influencing parameters, non-linear regression analysis (NLRA) was conducted using the current 200 datasets. In establishing the fundamental models for f'_c, each influencing parameter investigated was combined and adjusted repeatedly by the trial-and-error approach until a relatively higher correlation coefficient (R_2) was obtained. The influence of early heat curing on f'_c was reflected by introducing a maturity concept. From the NLRA approach, f'_c for UHPC with fly ash can be estimated as follows (Figure 8):

$$f'_c = 6.4\left[\xi(M/M_0)^{1.3}/(W/B)\right]^{0.4} f_{c0} \quad (2)$$

where ξ is the coefficeient depending on the fly ash content R_f as follows

$$\xi = \left(1 + R_f\right)^{0.1} \text{ for } R_f \le 0.3 \quad (3)$$

$$\xi = \left(1 - R_f\right) \text{ for } R_f > 0.3 \quad (4)$$

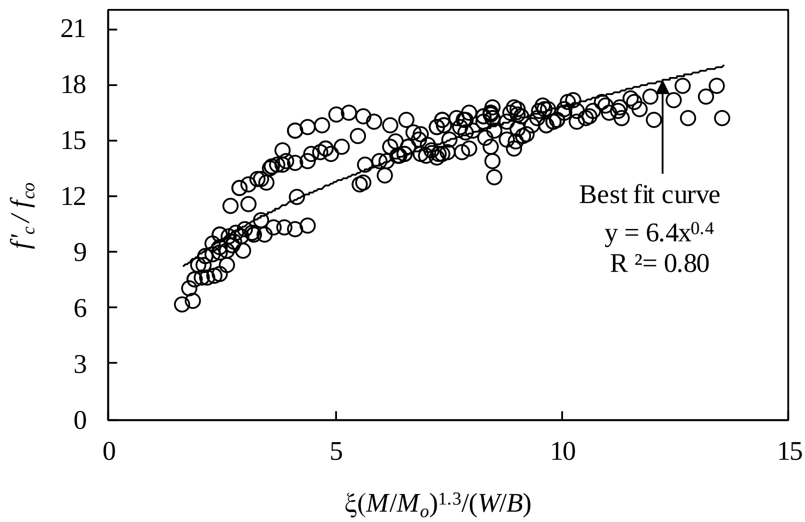


Figure 8. Regression analysis for the 28-day compressive strength of UHPC.

M is the maturity function ($=\sum\{\Delta t \times (T+10)\}$) of the time interval ($\Delta$t)-temperature ($T$: in °C) combination, M_o is the reference value (= 1036 °C-days) for maturity of concrete cured under standard condition of 27 °C, and f_{c0} is the reference value for compressive strength of concrete. In Equation (2), the coefficient ξ is to explain the effect of fly ash on f_c', indicating that f_c' increases with the increase of R_f up to 30%, beyond which f_c' decreases gradually, as shown in Figure 8. Note that it is quite hard to achieve a high value of R_2 while establishing the model for f_c' because of a relatively great scatter of the current test data with regard to the variations of R_f and heat curing ages.

The value of parameter S_l in Equation (1) for each specimen was determined through regression analysis using the present test data until the best fitting curve was obtained. UHPC specimens cured under heat curing exhibited very consistent shape for the normalized compressive strength development, irrespectively of *W/B* and R_f, as shown in Figure 7b. The values of S_l determined for UHPC specimens under heat curing ranged between 0.01 and 0.03. Therefore, the present study fixed the S_l value to be 0.02 for UHPC cured under heat curing condition. Meanwhile, the value of S_l determined for UHPC specimens cured under standard condition was affected by R_f and *W/B*, varying from 1.67 to 9.28. With the increase in R_f and *W/B*, a higher S_l value was obtained. From NLRA considering these influencing parameters, the parameter S_l in Equation (1) can be expressed in the following form (Figure 9):

$$S_l = 0.083\left[\left(1 + R_f\right)^3/(W/B)^{0.3}\right]^{0.65} \text{ for the standard curing condition} \quad (5)$$

$$S_l = 0.02 \text{ for the heat curing condition (at 90 °C)} \quad (6)$$

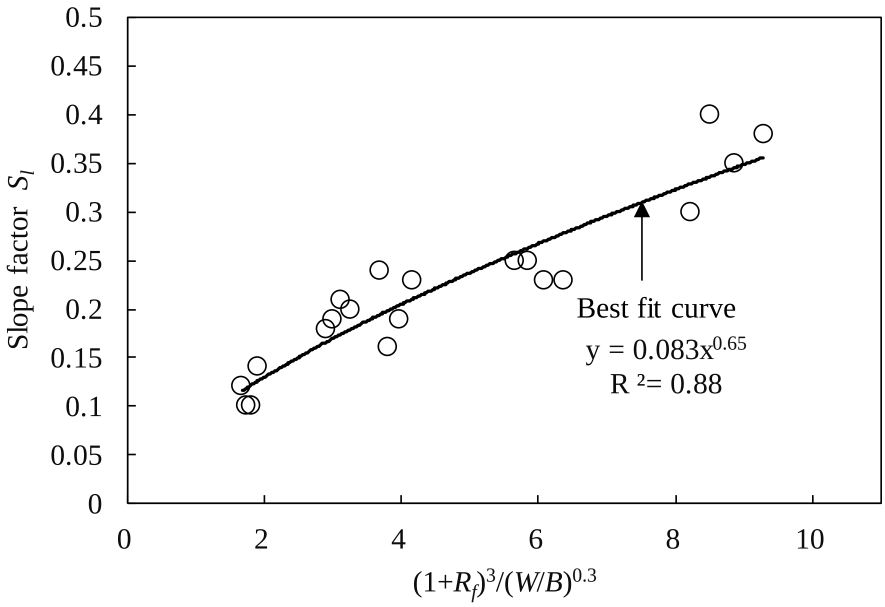


Figure 9. Modeling of S_l in Equation (1) to predict compressive strength development.

4.3. Calibration of the Proposed Models

Comparisons of measured compressive strength at different ages and the predictions using the proposed models are made by introducing the statistical values. The mean (γ_m) and standard deviation (γ_s) of the ratios (γ) between the experiments and predictions are summarized in Table 5. As the unreliability of the equations specified in *fib* 2010 model [27] is ascertained in Figure 7, the present comparisons focus on examining the validity of the proposed models. For the UHPC specimens cured under standard condition, the values of γ_m and γ_s range between 0.95 and 0.99 and 0.10 and 0.15, respectively. The corresponding values for the UHPC specimens cured under heat curing are from 1.01 to 1.09 and 0.11 and 0.12, respectively. Note that the proposed equation for 28-day compressive strength of UHPC gives a relatively good accuracy, although a slight overestimation tendency was observed for UHPC specimens cured under heat curing. In addition, the predictions are in good agreement with test results measured at early ages of 3 and 7 days and long-term age of 180 days. While very few studies are available to predict the compressive strength of UHPC, the proposed models have a good potential to assess reliably the compressive strength development of UHPC with different fly ash contents and cured under different conditions.

Table 5. Summary of the statistical values determined from the comparisons of experiments and predictions.

	Ratio of Experimental Compressive Strength and Predictions at Different Ages											
	Standard Curing Condition						Heat Curing Condition					
	3d	7d	28d	90d	180d	Total	3d	7d	28d	90d	180d	Total
γ_m	0.95	0.93	0.99	0.99	0.97	0.97	1.08	1.09	1.09	1.06	1.01	1.07
γ_s	0.15	0.13	0.12	0.10	0.10	0.12	0.12	0.12	0.11	0.11	0.12	0.12

5. Embodied CO_2 Emissions of HVFA UHPC

As mentioned above, UHPC normally requires very high content of binder incorporation cement and mineral admixtures, from 800 to 1000 kg/m^3, which induces an adverse impact in terms of economic, technical, and environmental aspects [31] because producing cement is responsible for about 6%–7% of total global CO_2 emissions. This will open the doors for studying efforts on reducing CO_2 in producing normal concrete in general, and UHPC in particular, i.e., four alternative solutions [32] such as (1) using a lower carbon content fuel; (2) using a chemical agent to absorb CO_2; (3) altering the clinker manufacturing process; and (4) incorporating high volumes of mineral admixtures. Of these four solutions, the fourth one can help to conserve the natural resource and also to recycle the industrial by-products, such as ground granulated blast-furnace slag (GGBS), FA, and/or SF, and that has been considered the most practical and economical solution. This can also be favorable for producing UHPC with lower CO_2 emissions.

To assess the embodied CO_2 emissions of the current concrete mixtures, the calculation approach presented by Yang et al. [32] in accordance with the lifecycle assessment (LCA) procedure specified in the ISO 14040 series was employed. Because of the lack of lifecycle inventory (LCI) formulated considering the local situation, CO_2 inventories studied by King [33] and Shi et al. [34] were taken for all the ingredients of concrete, as summarized in Table 6. The CO_2 footprints emitted during the heat curing process of concrete and transportation of each ingredient were not considered in this assessment because of the absence of the available data in the local condition. Thus, it should be noted that the current system boundary was from cradle to gates taken in each ingredient at the material phase.

Table 6. Embodied e-CO_2 of the raw materials used to calculate the CO_2 emissions of high-volume fly ash (HVFA) UHPC [33,34]. Unit: CO_2-kg/kg

Cement	FA	SF	Quart Sand	Water	SP
0.83	0.009	0.028	0.01	0	0.72

Figure 10 presents the effect of FA content on the embodied CO_2 emission of UHPC cured at the standard condition. As commonly known, concrete with lower *W/B* possessed a higher embodied CO_2 emission because of the increase in binder content. The increase in FA content significantly reduces the CO_2 emission of UHPC because the CO_2 inventory of FA is only 0.009 CO_2-kg/kg, giving a considerably lower value than that of cement. Increase of FA from 0% to 20%, 30%, 50%, 70% of binder led to the reduction of the embodied CO_2 emission in the values of 200, 300, 500, 700 kg/m^3 in average correspondingly. When 50% of the cement content was replaced by FA, the embodied CO_2 emission for UHPC mixture reduced up to approximately 50%, which is comparable to the CO_2

emission calculated from the conventional concrete [32] with the compressive strength not exceeding 50 MPa. Consequently, the use of FA to partially replace cement is favorable for producing UHPC with low CO_2 emission.

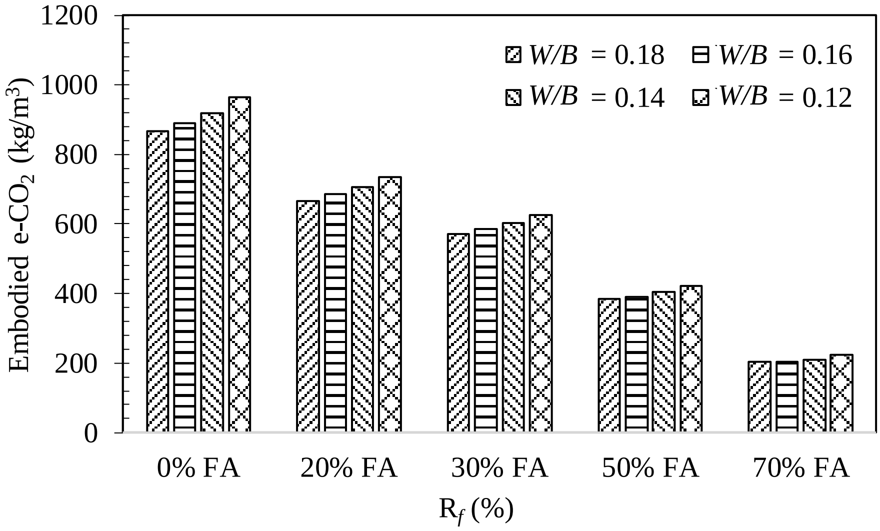


Figure 10. Embodied CO_2 emissions of UHPC with different FA contents under different curing conditions.

Regarding the heat curing condition, with the CO_2 emission of 2.49 kg $CO_2/(m^3 \cdot h)$ for heat curing [34] and the total heating time of 54 h including the constant temperature time of 48 h and the time for gradual heating of 6 h, the calculated CO_2 of heat curing was 54 h × 2.49 kg/($m^3 \cdot$h) = 134.46 kg/m^3. This value was added for the CO_2 emissions of all samples applied the standard curing condition.

6. Conclusions

Based on the experimental results, the following conclusions can be drawn regarding material characterization and methods used:

(1) The ratio of compressive strength under the heat curing condition and the standard curing $(f'_c)_H/(f'_c)_S$ slightly increased as the heat curing age increased up to 2 days, beyond which it was insignificantly affected by the heat curing age, where $(f'_c)_H$ is 28-day compressive strength of UHPC at different heat curing ages and $(f'_c)_S$ is that of the counterpart UHPC specimen cured under standard condition. This confirms that 2-day heat curing is sufficient for UHPC to gain high strength.

(2) At the same heat curing age, higher values of $(f'_c)_H/(f'_c)_S$ were observed for UHPC mixtures with more contents of fly ash and lower water-to-binder ratio (*W/B*). The higher content of fly ash used with the higher values $(f'_c)_H/(f'_c)_S$ was gained with time of heat curing age, particularly UHPC using 70% fly ash content.

(3) The preference of the addition of fly ash for enhancing the compressive strength of UHPC requires the early heat curing procedure which can be recommended as at least 2 days under 90 °C hot water. The strength gain rate of UHPC cured under heat curing condition was insignificantly affected by fly ash contents, indicating that the rates at 3 days ranged between 0.92 and 0.99 for all the specimens. Overall, the compressive strength of UHPC with fly ash under heat curing condition mostly reached its 28-day strength at just 3 days. The FA content can be increased up to 50% for UHPC with early heat curing while considering a comparable value to the compressive strength of UHPC without FA and cured under standard curing condition.

(4) For predicting the compressive strength development of UHPC mixtures cured under heat curing condition, the *fib* 2010 model gives underestimation at early ages and overestimation at long-term ages, irrespectively of fly ash contents. The predictions obtained from the proposed models are in good agreement with test results measured at different ages. Thus, the proposed models have a good potential to assess reliably the compressive strength development of UHPC (with different fly ash contents (up to 70% fly ash content)) and cured under different conditions.

(5) The model is applicable to HVFA UHPC with a time from 3 to 180 days incorporating 0%–70% class F fly ash, cement type I, *W/B* from 0.12 to 0.18 by mass, compressive strength from 80 to 165 MPa, curing under standard condition and heat treatment.

(6) The CO_2 emission of UHPC mixtures decreased in proportion to FA content, indicating that a 50% reduction can be obtained with the cement replacement of 50% FA.

Author Contributions: Methodology: P.S.D., N.V.T., L.T.T., N.C.T., C.V.H., and J.-H.M.; modeling: J.-H.M.; validation: P.S.D. and N.V.T.; writing—original draft preparation: P.S.D., N.V.T., N.C.T., V.H.C. and J.-H.M.; writing—review and editing: J.-H.M., L.T.T. and N.V.T.; project administration: N.V.T. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the National University of Civil Engineering, Vietnam, under grant number 220-2018/DHXD-TD.

Conflicts of Interest: The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results.

References

1. AFGC-SETRA. *Ultra High Performance Fibre-Reinforced Concretes*; AFGC: Paris, France, 2002.
2. Buitelaar, P. *Ultra High Performance Concrete: Developments and Applications during 25 Years*; International Symposium on UHPC: Kassel, Germany, 2004.
3. Collepardi, M. *Innovative Concretes for Civil Engineering Structures: SCC, HPC and RPC*; Workshop on New Technologies and Materials in Civil Engineering: Milan, Italy, 2003; pp. 1–8.
4. ASTM C 1856-2017. *Standard Practice for Fabricating and Testing Specimens of Ultra-High Performance Concrete*; ASTM International: West Conshohocken, PA, USA, 2017; p. 4.
5. Richard, P.; Cheyrezy, M.H. Reactive Powder concretes with high ductility and 200–800 MPa compressive strength. In *Concrete Technology: Past, Present and Future, Proceedings of the V. Mohan Malhotra Symposium*; Mehta, P.K., Ed.; Detroit: Victoria Wieczorek, MI, USA, 1994; pp. 507–518. Available online: https://www.concrete.org/publications/internationalconcreteabstractsportal.aspx?m=details&ID=4536 (accessed on 24 September 2020).
6. Schmidt, M.; Fehling, E. Ultra-High-Performance Concrete: Research, Development and Application in Europe. In Proceedings of the Seventh International Symposium on the Utilization of High-Strength/High-Performance Concrete, Washington, DC, USA, 20–24 June 2005.
7. Nguyen, V.T. Rice Husk Ash as a Mineral Admixture for Ultra High Performance Concrete. Ph.D. Thesis, Delft University of Technology, Delft, The Netherlands, 2011; p. 165.
8. Richard, P.; Cheyrezy, M.H. Composition of Reactive Powder Concretes. *Cem. Concr. Res.* **1995**, *25*, 1501–1511. [CrossRef]
9. Van Tuan, N.; Ye, G.; Van Breugel, K.; Fraaij, A.L.; Bui, D.D. The Study of Using Rice Husk Ash to Produce Ultra High Performance Concrete. *Constr. Build. Mater.* **2011**, *25*, 2030–2035. [CrossRef]
10. Thắng, N.C.; Thắng, N.T.; Hanh, P.H.; Tuấn, N.V.; Lâm, N.T. Ultra High Performance Concrete Using a Combination of Silicafume and Ground Granulated Blast-furnace Slag in Vietnam. In Proceedings of the International Conference on Sustainable Built Environment for Now and the Future, Hanoi, Vietnam, 26–27 March 2013; pp. 303–309.
11. Thang, N.C.; Van Tuan, N.; Yang, K.-H.; Phung, Q.T. Effect of Zeolite on Shrinkage and Crack Resistance of High-Performance Cement-Based Concrete. *Materials* **2020**, *13*, 3773. [CrossRef] [PubMed]
12. Voo, Y.L.; Fosterb, S.J. Characteristics of Ultra-High Performance 'Ductile' Concrete and Its Impact on Sustainable Construction. *IES J. Part A Civ. Struct. Eng.* **2010**, *3*, 168–187. [CrossRef]

13. Pham, S.D.; Le, T.T.; Nguyen, C.T. Sustainable Development of Ultra High Performance Concrete Mixture Using High Volume of Fly Ash in Vietnam. In Proceedings of the the 2nd International Conference on UHPC Materials and Structures (UHPC2018-China), Fuzhou, China, 7–10 November 2019; pp. 161–170.
14. Yazıcı, H. The Effect of Curing Conditions on Compressive Strength of Ultra High Strength Concrete with High Volume Mineral Admixtures. *Build. Environ.* **2007**, *42*, 2083–2089. [CrossRef]
15. Nguyen, T.N.; Bui, T.S.; Do, M.N. An Experimental Study of Reusing Coal Ash for Base Course of Road Pavement in Viet Nam. *Electron. J. Geotech. Eng.* **2019**, *24*, 945–960.
16. Ibrahim, M.A.; Farhat, M.; Issa, M.A.; Hasse, J.A. Effect of Material Constituents on Mechanical and Fracture Mechanics Properties of Ultra-High-Performance Concrete. *ACI Mater. J.* **2017**, *114*, 453–465. [CrossRef]
17. Aghdasi, P.; Heid, A.E.; Chao, S.H. Developing Ultra-High-Performance Fiber-Reinforced Concrete for Large-Scale Structural Applications. *ACI Mater. J.* **2016**, *113*, 559–570. [CrossRef]
18. Mehta, P.K.; Malhotra, V. *High Performance, High Volume Fly Ash Concrete for Building Sustainable and Durable Structures*, 3rd ed.; ACAA: Indianapolis, IN, USA, 2008.
19. Carey, A.S.; Howard, I.L.; Scott, D.A.; Moser, R.D.; Shannon, J.; Knizley, A. Impact of Materials, Proportioning, and Curing on Ultra-High-Performance Concrete Properties. *ACI Mater. J.* **2020**, *117*, 213–222. [CrossRef]
20. Le, T.T. Ultra Performance Fibre Reinforced Concrete Paving Flags. Ph.D. Thesis, University of Liverpool, Liverpool, UK, 2008; p. 387.
21. Vietnamese Standard TCVN 2682:2009. *Portland Cements—Specifications*, 5th ed.; Vietnam Standards and Quality Institute (VSQI): Hanoi, Vietnam, 2009.
22. ASTM C 618-19. *Standard Specification for Coal Fly Ash and Raw or Calcined Natural Pozzolan for Use in Concrete*; ASTM International: West Conshohocken, PA, USA, 2019. [CrossRef]
23. De Larrard, F. *Concrete Mixture Proportioning*; A scientific approach, Modern Concrete Technology Series; E&FN SPON: London, UK, 1999.
24. ASTM C 109M-2020. *Standard Test Method for Compressive Strength of Hydraulic Cement Mortars*; ASTM International: West Conshohocken, PA, USA, 2020. [CrossRef]
25. Soutsos, M.; Millard, S.G.; Karaiskos, K. Mix Design, Mechanical Properties and Impact Resistance of Reactive Powder Concrete (RPC). In Proceedings of the International Workshop on High Performance Fiber Reinforced Cementitious Composites in Structural Applications, RILEM, Honolulu, HI, USA, 23–26 May 2005.
26. Cheyrezy, M.; Maret, V.; Frouin, L. Microstructural Analysis of RPC (Reactive Powder Concrete). *Cem. Concr. Res.* **1995**, *25*, 1491–1500. [CrossRef]
27. Comité Euro-International du Beton. *Fib Model Code for Concrete Structures 2010*; International Federation for Structural Concrete (FIB): Lausanne, Switzerland, 2010. [CrossRef]
28. Verbeck, G.J.; Helmuth, R.A. Structures and Physical Properties of Cement Paste. In Proceedings of the Fifth International Symposium on the Chemistry of Cement, Tokyo, Japan, 7–11 October 1968; pp. 1–32.
29. Mindess, S.; Young, J.F. *Concrete*; Prentice-Hall: Upper Saddle River, NJ, USA, 1981; p. 671.
30. Breugel, K.V. Simulation of Hydration and Formation of Structure in Hardening Cement-Based Materials. Ph.D. Thesis, Delft University of Technology, Delft, The Netherlands, 1991.
31. Benhelal, E.; Zahedi, G.; Shamsaei, E.; Bahadori, A. Global Strategies and Potentials to Curb CO_2 Emissions in Cement Industry. *J. Clean. Prod.* **2013**, *51*, 142–161. [CrossRef]
32. Yang, K.-H.; Jung, Y.-B.; Cho, M.-S.; Tae, S.-H. Effect of Supplementary Cementitious Materials on Reduction of CO_2 Emissions from Concrete. *J. Clean. Prod.* **2015**, *103*, 774–783. [CrossRef]
33. King, D. The Effect of Silica Fume on the Properties of Concrete as Defined in Concrete in Society Report 74, Cementitious Materials, In Proceedings of the 37th Our World in Concrete & Structures, Singapore, 29–31 August 2012.
34. Shi, Y.; Long, G.; Ma, C.; Xie, Y.; He, J. Design and Preparation of Ultra-High Performance Concrete with Low Environmental Impact. *J. Clean. Prod.* **2019**, *214*, 633–643. [CrossRef]