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Mixture design and early age investigations of more sustainable UHPC

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This paper deals with the possibility to make the Ultra-High Performance Concrete (UHPC) as an environmentally friendly, through cement replacement with Blast Furnace Slag (BFS) and considering its cost and its early age performance. Thereby, a preliminary investigation is carried out, to design an UHPC with local materials and where Silica Fume (SF) is partially replaced with crushed quartz. The results showed that, from a mixture standpoint: i) the use of high energy mixer is necessary to ensure a homogeneous and workable mixture; ii) the polycarboxylate superplasticizer with chemical structure of acrylic polymer (ACP₁) and saturation dosage of 1.8% gives better workability for UHPC, compared to other six superplasticizers; iii) despite its negative effect on slump flow, Grey Silica Fume (silicium) ensures better compressive strength at early age, than Light one (zirconium). Results showed also that for 30% of cement replacement, the nucleation effect of BFS particles prevails and induces an acceleration of setting and hydration reaction of cement. For BFS contents of 50 and 80%, the dilution effect is dominating, which decelerates the setting and hydration reaction and decreases the peak of heat flow. BFS addition also affects the strength development. At 3 days, the strengths of the blended mixtures of UHPC with 50 and 80% of BFS were decreased by 26 and 66% respectively, while in contrast, there was a slight increase in the strength (+3%) with 30% of BFS compared to the reference mixture (UHPC₁). For UHPC containing 80% of BFS, the use of chemical activator of potassium hydroxide, with a concentration of [KOH]₃, causes slag's dissolution and reaction, which in turn improves the compressive strength by 42% and 11%, at 3 and 7 days, respectively.

1. Introduction and scientific background

Developed in last decade, Ultra High Performance Concrete (UHPC) represents a revolutionary concrete type, characterized by the absence of coarse aggregates, a dense and homogeneous microstructure [1–6] and a self-compactness [7–9]. UHPC has high

packing density and the use of fibers result in ultra-high mechanical and durability performances [6,10–22]. From a composition point of view, UHPC is a mixture of several powders and has a large amount of cement (900–1100 kg/m³), which raises largely the cost of manufacture and releases high heat of hydration, considered as a source of shrinkage risks [19,22]. This quantity of cement in UHPC is circa three times the cement content of ordinary concrete, which results in the larger emission of CO₂. Therefore, the production of UHPC with low CO₂ emissions represents a main challenge to make this concrete more sustainable. It is a question of promoting alter-

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native binders allowing a significant decrease of greenhouse gas. In such binders, clinker is replaced with mineral admixtures [6,19,21,23,24], during the grinding or directly in the mixer. However, their incorporation in UHPC should be optimized in order to ensure its mechanical and durability properties, without affecting its workability and early age performance [6,9,25–27]. Indeed, the mineral admixtures can contribute to improving the long term performances of concrete, but decrease the rate of early strength development, particularly for high replacement volumes of cement [28,29]. This effect could be different in the case of UHPCs, known by their complex cementitious system (low water-to-binder ratio, high superplasticizer dosage, reactive powders) and depends greatly on used by-product (Silica fume, Fly Ash and Blast Furnace Slag). As commonly known, Blast Furnace Slag (BFS) has hydraulic properties although its slow reaction [30]. At an early age, BFS particles act as nucleation sites and accelerate the hydration reaction of cement [31,32]. BFS is also known by its environmental and economical virtue [33]. It reduces the heat of hydration and enhances the long-term strength and durability of concrete [19,34]. The high specific area of BFS particles could intensify the contact zone between the hardened cement paste and the aggregate by their physical filling role. Thereby, BFS improves the packing density of the UHPC as its fineness is between those of cement and silica fume (SF). All the grains are carefully chosen to fulfill a perfect grain size distribution, thus the density is enlarged and the UHPC efficiency is increased [6,35–37].

Otherwise, the slag blending slows the concrete setting time, as the primary rate of slag reaction is slower than that of cement [29]. The degree of set retardation relies on the composition, fineness, and amount of slag blended, aside from other factors like the water-to-binder ratio (w/b), the kind and content of chemical admixtures [38,39]. BFS is a potential hydraulic mineral admixture, and its hydration reaction can be divided into two parts. In the first part that involves the early stage of the reaction, the dominant reaction is with alkali hydroxide whereas later reaction (i.e. second part) is mostly with calcium hydroxide. Primary hydration of BFS relies on the collapse and decay of the glassy slag structure by liberated $(OH)^-$ through the cement hydration and as well the alkali content in cement. The higher the collapse, the higher the hydrated phases. The quick production of an aluminosilicate shell stays impenetrable to water and hinders other reactions pending the shell is collapsed. A highly alkaline medium ($pH > 12$) is requisite to break the shell layer and resumes dissolution. Hence, the slag glass-network is quickly corroding. The BFS hydration exhausts the portlandite $Ca(OH)_2$ for producing more CSH on the surface of the slag grains. Through reaction of the slag particles, portlandite is not produced due to the fact that there is lower lime content in BFS than in cement. BFS engenders heat through the reaction, which is remarkably less than that of Portland cement in addition to the appearance of a further peak in heat flow curve. Likewise, it engenders longer setting time, dropped early strength and faster strength development at later ages [33,38].

Undoubtedly, the variation of BFS amount is an essential item that affects the setting and hydration behavior in addition to strength of UHPC blended mixtures, particularly for high BFS content. This is attributed to low slag activity at early ages with its latent reaction and dilution impact related to the reduction of cement amount. It was reported that the higher rate of slag, the higher delay of setting, the lower heat reaction degree and peak intensity, and the slower strength gain [29,40–45]. Accordingly, several researchers aimed at activating the early-age reactions of blended cement. This activation can be of thermal, mechanical or chemical origins [40,46]. The latter is generally based on alkaline activation. Sodium and potassium hydroxides (NaOH, KOH) are considered as the most popular alkaline activators despite the limited investigations on the KOH activator, for its availability and

cost. Both activators can be realized by two crucial variables including the sodium oxide content ($\%Na_2O$) and the silica modulus (SiO_2/Na_2O) of the alkaline solution [47]. When these activators are merged with slag, OH^- in the solution can destroy not only Ca–O bonds, but also a considerable number of Si–O and Al–O bonds. Due to the larger solubility of portlandite, in comparison with C–S–H, C–A–H and C–A–S–H, the former can be precipitated from the solution. An extremely fluffy coat composed of low Ca/Si ratio, C–S–H, C–A–H and C–A–S–H, which has a quite less solubility, precipitates so fast through the solution. The microstructure evolution of alkali activated slag (AAS) mixture is controlled by the quick modifications at early ages and the late evolution subsequently. This will be fully compatible with the rapid setting and lower hydration heat of AAS concrete, and the slow strength gain at later ages [48,49].

The properties of the slag and the quality and quantity of activators are very effective in determining the setting, heat and strength development characteristics of AAS concrete. The setting times of AAS concrete are shortened, the hydration is quickened, and the cumulative hydration heat is enhanced when the activator quantity is raised [48]. From a strength standpoint, there are two opposite ideas about the effectiveness of these activators on the strength of AAS concrete. The first idea reveals their activation ability with BFS to achieve a high strength while the second idea considers these alkaline compounds as supplying agents of comparatively low strength, high porosity and coarse pore structure [50,51]. The strength gain and output hydrates' formation are more rapid in alkali activated slag than in Portland cement. Higher concentrations of Si and Na in the pore solution accelerates C–S–H production at the early age of hydration [47] and improves the compressive strength of the AAS concrete.

Even if the early age properties of mortars or ordinary and high performance concretes are largely studied, those of UHPC should be more investigated, particularly in the presence of BFS and a chemical activator. The influence of the latter on the workability of UHPC, on its setting and hydration kinetic is worthwhile to investigate and needs further deepening.

In this context, the research work presented herein deals with the mixture design of eco-friendly UHPCs and the investigation of their fresh and early age properties. Accordingly, the intentions of this paper are twofold: Firstly, it intends, through a preliminary study with common technology and materials, to ensure the compatibility between the local UHPC ingredients. Secondly, analyze the effect of BFS content on fresh and early age properties of designed UHPCs in terms of workability, setting time, heat of hydration and compressive strength. Furthermore, the effect of chemical activation of BFS on the hydration mechanism and the compressive strength of UHPC at an early age will be deepened.

2. Experimental program

2.1. Used materials

Materials used in this study are of local origin (France). The cement used is a CEM I 52.5 N PM ES (Le Teil's plant). Its chemical composition is provided in Table 1. It contains 97% of clinker and 2.8% of gypsum. The mass percentages of principal constituents of main clinker phases, given by Bogue's formula are 67.8% of C_3S , 16.6% of C_2S , 4.0% of C_3A and 7.2% of C_4AF . This type of cement was chosen because of its high compressive strength as well as for its resistance in aggressive environments containing chlorides, sulfates...

In the current study, two types of mineral admixtures have been considered: Blast Furnace Slag (BFS) and Silica Fumes (SF). BFS comes from Ecocem's plant while Grey Silica Fume is commer-

Table 1
Chemical compounds (mass percentage), fineness and density of used materials.

Compounds	Portland Cement (%)	Gray silica fume (%)	Blast furnace slag (%)
CaO	65	0.3	43.9
SiO ₂	22	95	37.4
Al ₂ O ₃	2.78	-	10.9
Fe ₂ O ₃	2.42	-	0.7
K ₂ O	0.17	-	0.24
MgO	0.76	-	6.5
Na ₂ O eq	0.24	0.08	0.46
SO ₃	2.2	0.06	0.1
MnO	0.01	-	-
TiO ₂	0.17	-	0.5
Cl ⁻	<0.1	0.1	0.01
S ²⁻	<0.1	-	0.8
LOI	0.9	0.6	<1.5
Specific area (cm ² /g)	3555 [*]	250000 ^{**}	4450 [*]
Density (-)	3.17	2.24	2.9

^{*} Blaine method.

^{**} BET method.

cialized by Condensil, as S95 B DM. The main physical properties and chemical composition of the cement and the two types of mineral admixtures are given in Table 1.

Fig. 1 depicts the X-ray diffractograms of cement, Blast Furnace Slag, Grey (silicium) and White (zirconium) Silica Fumes. The figure shows the major phases of cement; C₂S and C₃S. The highest peaks of rays are observed at 2 Θ = 34.32° for C₂S and 2 Θ = 32.16° for C₃S. Besides, the XRD patterns of BFS and SF show that they have mainly an amorphous character too. The small peaks on XRD pattern of white SF represent ZrO₂. The vitreous aspect of BFS is clearly illustrated by a large halo on XRD pattern at 2 Θ = 29.60°.

Crushed Quartz (CQ), used as a partial substitution of SF, comes from Sibelco and marketed as C500 (0–20 μ m). It contains more than 99.1% of SiO₂ and its specific area and density are 10,435 cm²/g and 2.65, respectively. Quartz Sand (QS), containing more than 99% of SiO₂, comes from Sibelco and marketed as CV32 (0–500 μ m). Quartz Sand's specific area and density are 124 cm²/g

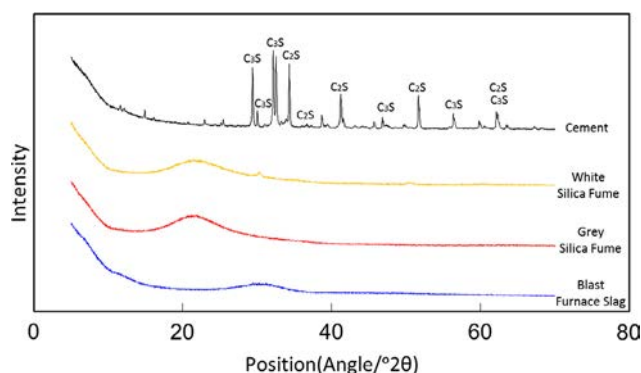


Fig. 1. X-ray diffraction (XRD) patterns of used materials.

Table 2
Basic characteristics of tested superplasticizers.

Properties	EPL	PL	PLPH1	PLPH2	ACP1	ACP2	AC
Colour	Brown	Brown	Yellow	Brown-orange	Yellow	Light brown	Amber yellow
Density (-)	1.09	1.06	1.085	1.08	1.055	1.08	1.05
Solid content	30.5	29.5	41	29.9	30.5	31	19.9

and 2.65, respectively. Tap water was used for all produced mixtures along this study.

Seven superplasticizers are investigated in this research work; Ether Polycarboxylate (EPL), Polycarboxylate (PL), two patterns of Polycarboxylate and Phosphonate (PLPH₁ and PLPH₂), two patterns of Acrylic Copolymer (ACP₁ and ACP₂), and Acrylic (AC). All cited superplasticizers are considered as high water reducers, but have different molecular structures, which govern their mechanism of action and performance, when incorporated in UHPC mixture. The characteristics of the whole superplasticizers are shown in Table 2.

To activate slag, KOH was used. When cement is substituted with BFS, KOH is added to compensate for the decrease of alkalis normally provided by cement. Thus, [KOH]₁ is the original concentration of added KOH for each mixture to provide the same [Na₂O]_{eq} if only cement is used. As the slag content changes (0%, 30%, 50%, 80%), the quantity of added KOH changes, even for the same concentration. [KOH]₁ is respectively 1.2707 kg/m³, 2.1179 kg/m³ and 3.3886 kg/m³, for 30%, 50% and 80% BFS content. The concentrations [KOH]₂, [KOH]₃ and [KOH]₄ are respectively two, three and four times [KOH]₁.

2.2. UHPC mixtures manufacturing

The basic mixture of UHPC was designed by Richard et al. [2], who eliminated the coarse aggregates to enhance the homogeneity and microstructure of concrete. Mounanga et al. [52] improved this homogeneity by incorporating crushed quartz, as partial substitution of silica fume. In Table 3, is shown their optimized mixture of UHPC. The cement was partially replaced by 25% of both silica fume and crushed quartz. Three quarters of this replacement rate were for silica fume while one quarter of this rate was for crushed quartz. In this research work, slag was incorporated, as partial substitution of cement, to improve concrete packing, by providing grains with fineness between those of cement and SF. Three levels of volume percentages have been explored (30%, 50% and 80%). SF, QS, CQ and water contents are kept constants. Superplasticizer content was adjusted to obtain the same concrete workability. This workability is measured through mini slump flow test and is fixed at 30 cm for UHPC.

Inasmuch of variety of nature, chemical and physical characteristics of the raw materials in the basic UHPC mix which shown in Table 3, compared to those used in the current study, preliminary investigations are carried out in order to design UHPC mixture with optimum and harmonic ingredients in both of their kind and quantity. These investigations deal with different parameters of mixture design; (1) the suitable mixer, (2) the more compatible superplasticizer, (3) the saturation dosage of superplasticizer, (4) the optimal water-to-binder ratio (w/b), (4) the optimal type of silica fume and (5) the optimal mixing time. To justify the sequencing of these investigations, it should be noticed that the choice of Portland cement type is accurate due to its high mechanical performance besides its high resistance to aggressive attacks. Thus, the first step of the applied approach consists of checking the compatibility of used superplasticizer with a binder (cement + silica fume + crushed quartz). Its type and dosage were chosen to reach a required concrete workability. This latter is the key parameter

Table 3
Basic UHPC mix design [52].

Content	CEM I 52.5 PM ES	QS	SF	CQ	SP	Water
Mass ratio	1	1.1	$0.25 \times 3/4$	$0.25 \times 1/4$	1.8%	0.16

for researching the minimum w/b, without compromising concrete implementation. The last step of this investigation consists on optimizing the mixture duration, using the more suitable mixer.

Regarding the mixing procedure of these constituents of UHPC, all the solid compounds are mixed for 30 s at slow speed. The superplasticizer is dissolved in net mixing water and added as a liquid solution. The net mixing water depends on the solid content of used superplasticizer type. Then the solution of water and dissolved superplasticizer is added and mixed with the powders at high speed. The mixing time depends greatly on the mixer; conventional or high energy one (see Section 3.1).

When alkaline activator (potassium hydroxide) is used, the basic solution should be prepared, some hours before, to avoid the increase of temperature, resulting from its exothermic reaction. After that, the adjusted dosage of superplasticizer is dissolved in this solution (water + dissolved KOH) before its addition to the dry components during the process of mixing. The preparation of all specimens and testing procedures were achieved in a regulated laboratory at a temperature of 20 ± 2 °C.

2.3. Testing methods

- *Workability*

A mini slump flow test is carried out on different concrete mixtures, according to EN 12350-8 [53] with small cone ($\varnothing_1 = 5$ cm, $\varnothing_2 = 10$ cm, $l = 15$ cm) as shown in Fig. 2. The test was conducted at a temperature of 20 ± 2 °C. Every result is the average of two tests.

- *Setting time*

Setting time of the UHPC mixtures was determined according to the standard specification NF P15-431 [54] using the Vicat apparatus. The test was conducted at a temperature of 20 ± 2 °C.

- *Hydration*

The hydration test consists of measuring the temperature and heat of hydration of concretes by means of semi-adiabatic calorimetry, also known as the Langavant method. This method is described in European Standard EN 196-9 [55]: a freshly made concrete (approximately 1900 g) is introduced in an insulated



Fig. 3. Semi-adiabatic calorimeters for hydration test.

flask, which is placed into calorimeter (Fig. 3) in order to quantify the heat emitted in accordance with the development of the temperature. This latter is measured with platinum resistance thermometer, and the test was conducted in a regulated room at 20 ± 2 °C.

- *Compressive strength*

For mechanical properties, fresh concrete is introduced in steel moulds, without vibration. The moulds were stored for 24 h, before demoulding. Then $4 \times 4 \times 16$ cm³ specimens were plastic-wrapped, avoiding any drying and stored in fog room at 20 °C. At 3, and 7 days, the compressive strength was measured by means of 300 kN load-machine. Every result is the average of three tests.

3. Results and discussions

3.1. Preliminary investigations and mixture design

The objective of this section is to design an UHPC, with required workability. The latter depends on used mixer, materials and superplasticizer type and dosage. These parameters have to be checked, in relation with a used binder. Then the mixing duration should be optimized.



Fig. 2. Steps of mini slump flow test.

• Suitable mixer

The first step of this work was to test a conventional mixer. The tested mixture is that designed by Mounanga et al. [52], where used cement and white silica fume were replaced with cement and gray silica fume, presented in Table 1. After 30 min of mixing, there was no cohesion between grains and the mixture is not homogeneous, for two reasons; i) the low speed of mixer and ii) the geometry of its blade. Therefore, the mixer does not produce enough energy to promote particles dispersion, and its blade does not allow high shear stress to disperse dry powders and homogenize the concrete mixture. These observations agreed with those of Parant [56] and of Cherkaoui [57]. The former concluded that the conventional mixer is not suitable with fibred UHPC: its blades agglomerate fibers and the mixing time is increased. For the latter, more than 20 min was necessary to reach the required workability of an UHPC, manufactured with white silica fume. Therefore, to avoid this problem, despite the low water-to-binder ratio, a mixer with high energy (Eirich intensive mixer) was used. It has a star-blade, a tilted drum and a high mixt speed of up to 40 m/s (opposed currents). This results in optimum dispersion of particles and high mixt homogenization, with low mixing time and despite the presence of fibers [56,58].

• Superplasticizer/binder compatibility

UHPCs are designed, not only to have high mechanical performance (low water-to-binder ratio) but also to be highly densified. Their workability should be managed to secure their on-site properties. Indeed, the rheological properties of concrete are responsible for its mechanical and durability ones on-site. In a recent study, Choi et al. [59] reported an interesting method for estimating rheological properties of UHPC; mini slump test. This simple method is applied in this section to compare different superplasticizers. As mentioned before, seven different superplasticizers, marketed in France as very high water reducers, are compared. For all superplasticizers, the same dosage of 3% (solid content, per gram of cement) is applied. This content was chosen to exceed remarkably the saturation dosage [56]. Beyond this content, the concrete workability will not be improved.

Fig. 4 shows the mini slump flow of reference concrete (without slag), with 0.14 of water-to-binder ratio, for different superplasticizers. Two families can be distinguished; the first (PL, PLPH₂ and AC) with a mini slump flow around 15 cm and the second (PLPH₁, EPL, ACP₂ and ACP₁) with a mini slump flow exceeding 25 cm. In particular, two superplasticizers provide the required workability (30 cm); ACP₁ and ACP₂.

Generally, the chemical and physical behavior of superplasticizer is dominated by length, the degree of polymerization and

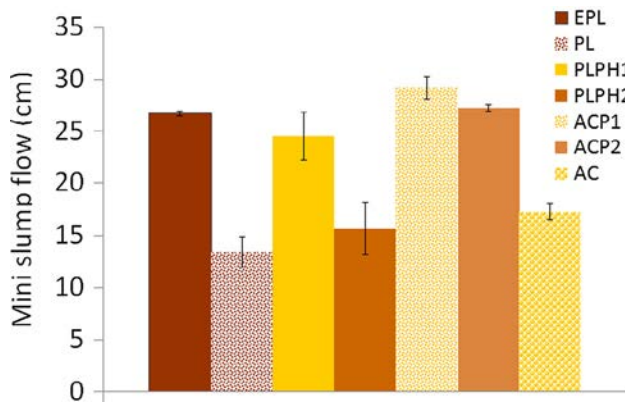


Fig. 4. Mini slump flow measurements for examined superplasticizers.

the density of graft chains [60]. Thanks to their polymer structure and polyoxyalkylene side chains, ACP₁ and ACP₂ induce better cement dispersion, which makes a steric repulsion through sets of anionic carboxylic [61]. The graft chains of the polymer molecules on the cement surface would prevent by themselves from flocculating cement grains into large and irregular agglomerates. Once the side chain density reduces, the adsorption of molecules enhances. Aside from that the molecular weight of these superplasticizers has a fundamental impact on their function due to that when the molecular weight of polymers become larger, both the adsorption and workability are relatively increased [62]. Consequently, the shorter the major chain and the lengthy and further plentiful the side chains, the larger and extra enduring workability [63,64].

To choose between both superplasticizers (ACP₁ and ACP₂), these latter were examined at the same dosage of 3% in terms of the mini slump flow with w/b of 0.12 and 0.14, and of the 7-days compressive strength with w/b of 0.14 as shown in Table 4.

For a water-to-binder ratio of 0.14, ACP₁ gives the higher slump flow, which results in best dispersion of binder particles and then better homogeneity and packing. This explains the improve of UHPC compressive strength (at 7 days), in comparison with UHPC based on ACP₂. This difference was more important for the lower water-to-binder ratio. In fact, for w/b of 0.12, ACP₂ does not allow any cohesion between particles, and the measured slump flow is zero. With ACP₁, and despite the decrease of workability, the manufacturing of UHPC was possible. This superplasticizer is marketed as Sika Viscocrete Krono 20 HE.

• Saturation dosage of superplasticizer

The assessment of saturation dosage of the superplasticizer ACP₁ must be carried out by examining the wide range of dosages between 0.5 and 5%, as demonstrated in Fig. 5. At each dosage, the workability should be checked by measuring mini slump flow. Different tests are carried out on samples with a water-to-binder ratio of 0.14.

Firstly, it can be seen that beyond a content of 3% of superplasticizer, there was not an improvement of concrete workability, which confirms the choice of this dosage to compare all superplasticizers. Secondly, it was found that the saturation point of the superplasticizer ACP₁ is 1.8%. This content relies on the active substances (i.e., solid content) in the superplasticizer that maintain the required mini slump flow of 30 ± 1 cm. The solid content of ACP₁ is about 41% which is located within the empirical range of 30–45% for the effective superplasticizers in the UHPC [65].

• Water-to-binder ratio

In order to improve the UHPC mixture with accepted properties, it is substantial to explore optimal w/b. Water-to-binder ratio and workability of UHPC has so far closed linkage due to that the flowability of the binder paste is quite impacted by the mixing water quantity. Therefore, the w/b was tested within the range of 0.10–0.18 so as to choose the optimum value as shown in Fig. 6.

For high water-to-binder ratios (0.18 and 0.16), the slump flow of concrete exceeds 37 cm. As packing density and workability are intimately attached, the high workability of concrete could increase the volume of capillary pores, which results in compres-

Table 4
Comparison between ACP₁ and ACP₂.

SP	Mini slump flow (cm) at w/b = 0.12	Mini slump flow (cm) at w/b = 0.14	7-Days compressive strength (MPa)
ACP ₁	20	30	120
ACP ₂	0	27	113

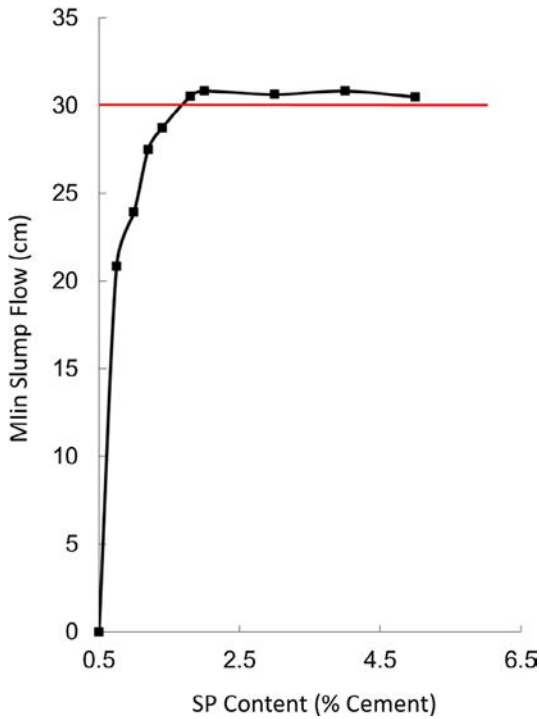


Fig. 5. Assessment of saturation dosage for superplasticizer ACP₁.

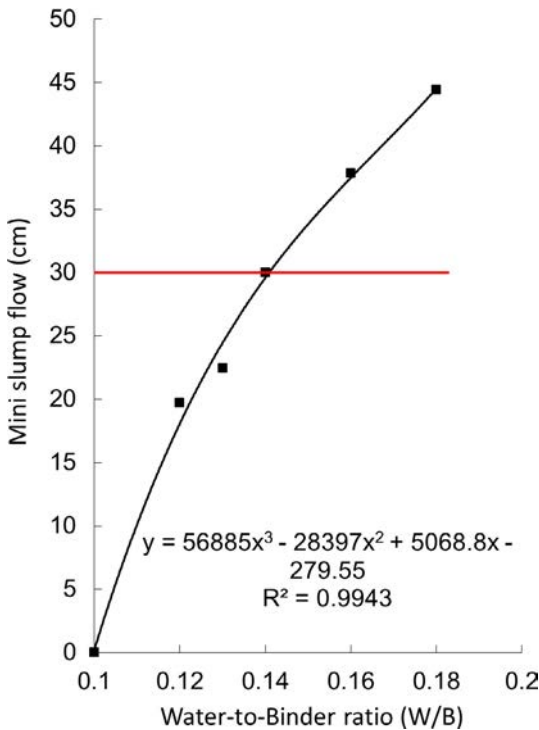


Fig. 6. Assessment of the optimum w/b for reference UHPC.

Table 5
Comparison between gray and white silica fumes.

Silica fume	Mini slump flow (cm)	7-Days compressive strength (MPa)
Light gray silica fume	29 ± 0.8	119 ± 1.8
White silica fume	33 ± 1.0	113 ± 2.1

%1.8 = 1ACP; 0.14 = b/w.

• Type of silica fume

Two silica fumes were tested for comparison. The first one is silicium SF with 95% ±3 of SiO₂ and a specific area of 25.0 m²/g (see Table 1) whereas the second is zirconium SF with 86% of SiO₂ and a specific area of 22.4 m²/g. The physical and chemical characteristics of the first type were shown in Table 1. Both silica fumes are compared through workability and 7-days compressive for SF-to-cement mass ratio of 25% × 3/4 (the other quarter is crushed quartz), the water-to-binder ratio of 0.14 and with 1.8% of ACP1. Results are presented in Table 5.

The chemical composition of silica fume, its specific area and its degree of agglomeration has a remarkable effect on the workability of UHPC mixtures and their mechanical properties [2]. In particular, the amount of carbon and alkali impurities has a great effect on superplasticizer adsorption and then on concrete fluidity [35,67].

As indicated by its color, the gray silicium SF contains more carbon than the white zirconium one. Carbon adsorbs the superplasticizers and hinders adsorption to gray SF particles, which results in workability decrease by 12%. This result agreed with that of Coppola et al. [68]; an increase by 29% of the water-to-binder ratio of gray-silica-fume UHPC was necessary to reach the same flow table of UHPC based on white one. They explained this difference by the high dispersibility of white silica fume, even in the absence of superplasticizer, compared to gray one. Although its negative effect on UHPC workability, gray SF improves its 7-day-compressive strength by 5%, in comparison with white SF. The high reactivity of gray SF and its high specific area explain this result. Indeed, gray SF consumes more portlandite, which promotes the development of more strong C-S-H and improves the bond between cement and quartz sand. Aside from that, at early age, the physical filler effect prevails, while the pozzolanic one dominates in the long term. This results in microstructure refinement and compressive strength increase [69,70]. In contrast, the white type has lower pozzolanic reaction, which decelerates the compressive strength development at an early age. In fact, there are not enough hydration products to bridge various particles together. Therefore, several particles were still disconnected and could move readily.

These obtained results agreed with those of Šerelis et al. [66] and Coppola et al. [68]. The former showed the high amount of portlandite consumed by SF particles with high specific area, reflecting their reactivity and the second present the delay in compressive strength development when white silica fume is used.

Despite its negative effect on UHPC concrete workability, in comparison with white SF, gray SF is more reactive and has a better effect on early age compressive strength. As the research objective is to develop a more sustainable UHPC, with high content of BFS, the risk is the drop of early age mechanical properties of UHPC. In addition, the white SF is no longer produced in France, and its use should increase the environmental footprint of concrete, due to its important delivery distance. For these reasons, gray SF is retained for this study.

• Optimum mixing time

The mixing time is a basic parameter for obtaining a steady and workable UHPC, and inasmuch of its extreme prominence, it

sive strength decrease [27]. Thereby, and to obtain a slump flow of 30 cm, the water-to-binder ratio was decreased to 0.14 (w/c = 0.175). For the latter, the matrix packing density is optimum, and the mixture does not exhibit any bleeding or segregation. For lower water-to binder ratio, the slump drops greatly, and the matrix packing is not ensured. This should affect negatively the properties of UHPC [65,66].

Table 6
Examined mixing times.

Mixing time (min)	Mini slump flow (cm)
3.5	30 ± 1
4.5	31
5.0	31

should be assessed accurately to avoid the high consumption of mixer energy as possible without changing the flowability of the produced UHPC mixture. The wide range of mixing times depends on several variables such as mixer quality, mixing procedure, batch size, the level of mixer filling, temperature, etc [65,71].

In this section, the reference concrete, designed previously is tested and three mixing times are compared, for a required concrete workability of 30 cm. For all tests, the mixing of dry powders lasts 0.5 min, at low speed. The obtained results of total mixing time, presented in Table 6, confirm that: i) 3.5 min is enough to produce an UHPC with 30 cm of mini slump flow and ii) beyond this mixing time, there is any improvement of concrete workability.

3.2. Workability

The workability of UHPC is measured through mini slump flow test. This simple method that could be used in laboratory and on-site, is applied in this section to estimate the necessary content of superplasticizer for bended-cement UHPC, to achieve the same workability of reference one (UHPC₁). Every result is the average of two tests. Even if for all blended-cement UHPC, the required SP dosage to reach 30 cm-slump flow does not exceed that of reference concrete (SP = 1.8%), concrete behaves differently. Their behavior depends greatly on BFS content. For UHPC₂, the substitution of 30% of cement, induces a drop of SP content (-58%), necessary to achieve the mini slump flow of UHPC₁. Two phenomena, occurring simultaneously, explain this drop: i) the decrease in the amount of C₃A available to absorb and consume admixture and ii) the improve of packing and then the particles' cohesion and viscosity. Indeed, decreasing the cement content decreases the C₃A amount, and the admixture is absorbed onto the silicate phases of the clinker and onto the slag particles [62]. In addition, the presence of Blast furnace slag particles makes the mixture more cohesive and decreases bleeding water and segregation. Kim et al. [27], Palacios et al. [62] and Yu et al. [26] observed an increase in fluidity of slag-blended cement, in comparison with ordinary one. The former measured, for the same SP dosage, an enhancement in slump flow by 9% and 16%, when slag content is respectively 15% and 30%, and the latter showed that cement needs more super-plasticizer (+40%) to reach a certain slump flow, compared to the binder with BFS. The obtained results agreed also with those of Boukendakdji et al. [72] and Bani Ardalan et al. [73], who

Table 7
UHPCs mix proportions.

Components (kg/m ³)	UHPC ₁ (C:BFS = 100:0)	UHPC ₂ (C:BFS = 70:30)	UHPC ₃ (C:BFS = 50:50)	UHPC ₄ (C:BFS = 20:80)	UHPC ₄ [KOH] ₃ (C:BFS = 20:80)
CEM I 52.5	977.00	683.90	488.50	195.40	195.40
PM ES					
SF	183.00	183.00	183.00	183.00	183.00
CQ	61.00	61.00	61.00	61.00	61.00
BFS	-	268.10	446.90	715.00	715.00
QS	1075.00	1075.00	1075.00	1075.00	1075.00
SP	25.31	10.54	22.49	25.31	25.31
SP (%)	1.80	0.75	1.60	1.80	1.80
W	145.63	160.39	148.44	145.63	140.65
KOH	-	-	-	-	10.17

measured respectively an increase of slump flow and a decrease of superplasticizer dosage with increasing BFS content.

For UHPC₃ and UHPC₄ and despite the increase of BFS content, the required SP dosage to achieve the mini slump flow of reference concrete is respectively 2.13 and 2.4 times that of UHPC₂; the lubrication effect of BFS and the fluidizing one of superplasticizer seem mitigated by the water demand of BFS particles. Indeed, BFS particles enhance matrix packing and promote cohesion, which improves the rheological behavior of concrete in a fresh state. In addition, the decrease of cement content decreases the amount of C₃A, which induces an increase of slump flow. This explanation was supported by Alonso and Puertas [74] and Palacios et al. [62]. The former emphasized on the affinity and reactivity of C₃A with superplasticizer admixture. The second explained that SP admixture is absorbed onto BFS particles when the amount of cement and then that of C₃A decrease.

On the other hand, BFS particles have high specific area and absorb more water, which allows particles free movement and results in a decrease of workability [25]. This phenomenon counterbalances that of lubrication.

When KOH is added, the SP content was kept constant, but the mixing period of UHPC₄-[KOH]₃ was extended by 30 s, compared to that of UHPC₄. This observation is in accordance with those of Puertas et al. [75], who concluded that increasing mixing time is possible to avoid fast setting and improve the workability of chemically activated slag-concrete. In fact, even in the first minutes, chemical activator could affect the smooth sliding planes and reduces the lubrication effect of BFS particles. In addition, the dissolution of KOH increases the liquid-to-solid ratio of basic solution, growths its density and thus diminishes the mini slump flow of concrete [76].

Afterword the preliminary investigation and the optimization of Superplasticizer content in order to obtain the required workability, the outcome UHPC mixtures are presented in Table 7.

3.3. Setting time

The rate of setting of cementitious materials results from chemical and physical behaviors, in relation with the initial porosity of mixture and the binder reactivity. Indeed, an important quantity of hydrates is necessary, when the matrix is initially porous, to reach the percolation threshold [77]. These formed hydrates depend greatly on binder reactivity. In this case, the initial porosity is kept constant for all concretes, as water-to-binder and water-to-solid volume ratios are unchanged. Indeed, the only variables in studied mixtures are the contents of SP and BFS, which is incorporated as volume substitution of cement. Thereby, the measured setting time period is mostly governed by early age reactivity of binder.

Table 8 summarizes the obtained results of setting time for all studied mixtures. As shown, the effect of BFS on setting time depends on its content, and the dosage of superplasticizer.

Table 8
Vicat setting times of studied UHPCs.

Concrete mixture	Initial setting time (min)	Initial setting time (min)	Setting time period (min)
UHPC ₁	330	420	90
UHPC ₂	150	180	30
UHPC ₃	450	510	60
UHPC ₄	750	930	180
UHPC ₄ -[KOH] ₃	660	690	30

For UHPC₂ (BFS content of 30% and SP dosage of 0.75%), the initial and final setting are accelerated respectively by 2.2 and 2.3 times, in comparison with those of reference concrete. The setting time period is also decreased by 3 times when 30% of BFS are incorporated. Two parameters explain this behavior difference:

- The superplasticizer dosage: UHPC₁ contains two times more SP than UHPC₂, which participates largely in decelerating simultaneously initial and final setting times of the former;
- The presence of slag: BFS accelerates the hydration of CEM I and shortens the setting time period (three times) of concrete. This result is in accordance with those of Mounanga et al. [29]. Indeed, these authors did not observe any modification of initial setting time of mortars containing 25% and 50% of BFS. However, the setting time period of the second was shortened by 30%, compared to that of reference mortar.

In the presence of BFS, there is more water available to the reaction of CEM I. This phenomenon, explained by dilution effect, is counterbalanced by the acceleration of cement hydration [29,78]. Indeed, BFS particles act as nucleation sites for the formation of calcium hydroxide. This behavior is attributed to their high specific area, in comparison with that of cement (+ 25%) and has a physical origin, as reported by Cyr et al. [79]. In fact, their results on mineral admixtures, particularly inert ones, highlighted that the presence of fine particles with the high specific area could activate the cement hydration by heterogeneous nucleation [79,80]. For the same authors, the physical effect of the fine particles is dominating at an early age, causing an acceleration of hydration and setting of cement matrix.

For UHPC₃, SP content is 1.6%, 11% lower than that of UHPC₁. Thus, the delay of initial setting is attributed to BFS; its content is of 50%. As shown, with high BFS content, the dilution effect dominates that of hydration acceleration, which results in deceleration of initial setting of UHPC₃ by 36%, in comparison with UHPC₁. Once setting initiated, the physical effect of BFS particles, by heterogeneous nucleation of formed hydrates occurs. This results in an acceleration in setting and reduces its period. The latter is 1.5 times lower than that of UHPC₁.

With very high BFS content (80%), the early-age concrete behavior is different. Indeed, its initial and final setting times are respectively increased by 2.27 and 2 times, in comparison with those of UHPC₁. The dilution phenomenon governs the hydration, and setting process and cement particles are suspension materials. Indeed, the water-to-cement ratio is 5 times more in UHPC₄ than in UHPC₁. Consequently, 930 min were necessary to reach the final setting and setting time period was 180 min for UHPC₄. To remediate this delay, KOH was added, in order to provide necessary alkalis for BFS reaction. The effect of BFS particles would be of physical and chemical origins. Comparing setting time results of UHPC₄ and UHPC₄-[KOH]₃ exhibited clearly the great effect of KOH in accelerating setting: initial and final setting times decreased respectively by 12% and 25.8%. The addition of chemical activator causes the dissolution of the glassy structure of BFS and promotes its reaction, which

results in decreasing the effect of dilution, by decreasing liquid-to-solid ratio. This phenomenon is more pronounced, once the setting is initiated. Thus, setting period of UHPC₄-[KOH]₃ is reduced respectively by 6 and 3 times, in comparison with that of UHPC₄ and UHPC₁.

3.4. Hydration

Fig. 7 gives the variation of the reaction heat for the UHPC mixtures while the reaction heat flow measured for these mixtures was presented in Fig. 8. Also, Table 9 summarizes the main measured and normalized characteristics values of the semi-adiabatic hydration curves, where t_{max} is the time of maximum heat flow and I_{max} is the maximum intensity of heat flow.

As observed, the maximal heat reaction and heat flow peak of UHPC₁ are respectively 161 J/g of the binder and 6.43 mW/g of the binder, and the time to reach the maximum reaction heat is 1572 min. This result highlights the great difference between a semi-adiabatic and an isothermal test. For the latter, the heat flow is low, in comparison with the former. Mounanga et al. [52] tested an UHPC with similar composition (ERPC₄) in isothermal conditions and measured a heat flow of 0.52 mW/g. This peak appears after 3324 min.

The replacement of cement with slag results in a reduction of produced reaction heat and in the magnitude of the peak of heat flow. A great decrease of temperature is also measured, when BFS content increased; the maximal temperature is 67.4 °C, 66.5 °C, 54.1 °C, 37.2 °C and 41.4 °C, respectively for UHPC₁, UHPC₂, UHPC₃, UHPC₄ and UHPC₄-[KOH]₃. This is related to the dilution effect of slag and its slow reaction. The latter releases less heat

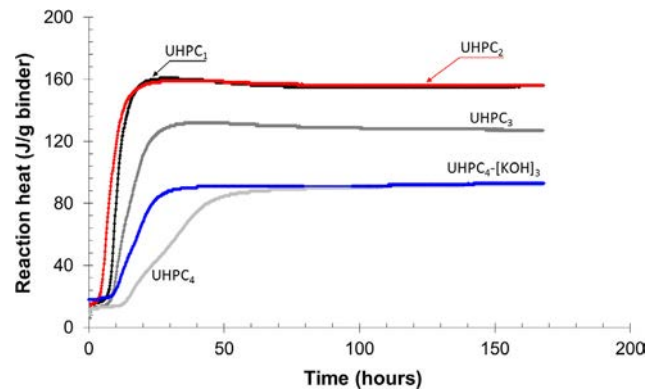


Fig. 7. Reaction heat of studied UHPC mixtures.

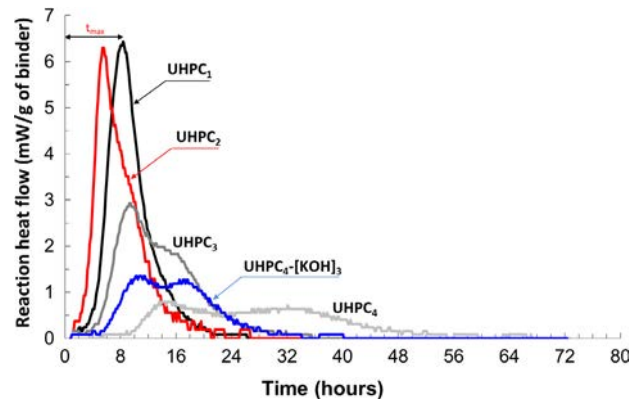


Fig. 8. Reaction heat flow of studied UHPC mixtures.

Table 9
Hydration characteristics of UHPC mixtures.

Mixtures	Reaction heat		Maximum Temperature Measured Value (°C)	Time of maximum heat flow- t_{max}		Maximum intensity of heat flow- I_{max}	
	Measured value Q_{max} (J/g binder)	Time of maximum reaction heat (min)		Measured value t_{max} (min)	Normalized value $\frac{t_{max}}{t_{max}(UHPC1)}$ (-)	Measured value I_{max} (mW/g of binder)	Normalized value $\frac{I_{max}}{I_{max}(UHPC1)}$ (-)
UHPC ₁	161	1572	67.4	502	1	6.43	1
UHPC ₂	159	1595	66.5	335	0.67	6.30	0.98
UHPC ₃	132	2109	54.1	569	1.13	2.94	0.46
UHPC ₄	91	3241	37.2	900	1.79	0.79	0.12
UHPC ₄ -[KOH] ₃	91	2401	41.4	651	1.30	1.35	0.21

than that of Portland cement [29,40–43,42,78]. The influence of low BFS content on hydration seems rather low and profile of hydration characteristics of the UHPC₂ (30% slag) shows a closed behavior to that of UHPC₁ as exhibited in Figs. 7 and 8. The maximal heat reaction and heat flow peak of UHPC₂ are respectively 159 J/g of binder and 6.3 mW/g of the binder and the time of maximum reaction heat is 1595 min. The kinetic of early hydration is different, when 30% of cement is replaced with BFS. In the presence of BFS particles, the peak of heat flow appears 167 min before that of Portland cement, even if the time to reach the maximum reaction heat is quite the same.

To better explain this phenomenon, the following reasons should be considered: i) the superplasticizer inhibits the dissolution of anhydrous cement particles, which decelerates the hydration reaction. This phenomenon results from the complexation of Ca²⁺ ions by the superplasticizer and the adsorption of the polymer on the anhydrous grain surfaces [81]; ii) the lower water content of UHPC and its high solid one decrease the free water in cementitious system [26], which results in restriction of Ca²⁺ and OH⁻ diffusion. Hence, pozzolanic reaction of SF is postponed, and the early hydration is decelerated. Both reasons explain the delay in initial and final setting and in the apparition of the peak of heat flow for UHPC₁, in comparison with UHPC₂. Otherwise, even if the superplasticizer participates largely in the hydration kinetic of UHPCs, prevailing on other parameters, the presence of low content of BFS in UHPC₂ contributes in the acceleration of binder hydration. This behavior is attributed to the physical effect of BFS particles. They promote the reaction of cement by heterogeneous nucleation, thanks to their fineness [79]. This results in acceleration of cement reaction. Thereby, the alkalis, provided by cement, and subsequently, portlandite increases the pozzolanic reaction of SF and BFS [42,82]. The higher portlandite amount, the more enhanced hydraulic/pozzolanic reaction of BFS, which jointly provides further emitted heat.

For 50% and 80% of cement substitution, the reaction heat decreased by 18% and 43%, and the maximal magnitudes are reached after 2109 min and 3241 min for UHPC₃ and UHPC₄ sequentially. The lesser pozzolanic and hydraulic activity of BFS is basically linked with its potential to dissolve and to react with portlandite so as to produce further hydrated products through the pozzolanic reaction. This phenomenon depends on BFS content; more the BFS content, higher the dilution effect. Hence, the heat reaction decreases and postpones the hydration acceleration. Indeed, two peaks appear: the first peak (2.94 mW/g for UHPC₃ and 0.79 mW/g for UHPC₄) is related to cement reaction and the second one is related to BFS phases hydration. The peaks appear at 600 and 960 min for UHPC₃ and at 900 and 1920 min for UHPC₄ respectively. The first peak is created on account of hydration of C₃A from the cement that melts and reacts with both of the Ca²⁺ and SO₄²⁻ ions existing in the liquid phase to produce ettringite. As well it is attached with the decay of calcium silicate phases. The height of the second peak was less, so it exhibits as a shoulder. It is named

as “silicate peak” which is characterized by fast growth and a slow reduction of the heat-flow rate, relying on the slag proportion. The fast hydration of C₃S is related to the development of second-phase C–S–H (i.e., C–S–A–H) and the precipitation of portlandite [40,82]. As both concretes contain the same or less superplasticizer content than UHPC₁, the slow behavior is attributed to the low cement content, which limits the rate of portlandite.

As shown in Table 9, the maximal reaction heat measured on UHPC₄ and UHPC₄-[KOH]₃ is 91 J/g. The chemical activator accelerates hydration reaction and decreases by 26% the time to reach the maximal heat reaction. The heat released at once upon touch between the slag and the activator is backed to wetting and dissolution of slag grains and production of melted silicate classes [83]. The hydration operation was affected by the sodium amount and, the larger Na₂O was connected to advanced hydration levels. A significant number of Si–O and Al–O bonds in the slag glass structure was destroyed, resulting in acceleration of dissolution of Si and Al ions that is followed by precipitation of less-solubility calcium silicate, calcium aluminate and magnesium aluminate hydrates because of excessed ionic amounts in the liquid state. So the slag hydration is highly hurried as a result of an increase of pH to 12 for the liquid phase plus the ettringite production [84]. The same effect is noticed in Fig. 8, showing the earlier apparition of both peaks, in comparison to UHPC₄. The first peak, related to the cement reaction appears 240 min earlier. It results in the destruction of slag bonds Ca–O, Mg–O, Si–O–Si, Al–O–Al, and Al–O–Si. The second peak, related to BFS reaction is more pronounced and is accelerated by 960 min. It occurs on account of the production of a Si–Al layer all over the surface of slag particles and, eventually, the generation of the hydration products promptly after the ionic amounts in the pore solution amounts to the critical rate impeding more reaction [85].

The obtained results confirm those of needle test and show the role of BFS particles and chemical activator on the early age hydration of binder.

3.5. Compressive strength

Figs. 9–11 provide the test results on early age compressive strength of different studied UHPCs at 3, and 7 days. Every result is the average of three tests.

Compared to UHPC₁ mixture, it is exhibited that a volume substitution of 30% of cement by BFS (UHPC₂) results in the same strength of UHPC₁ at 3 days and as well slightly increases the strength at 7 days. Two various physical mechanisms are responsible for this improvement in strength: The first is the particle size distribution influence and the second being heterogeneous nucleation. When there is a blend of silica fume and BFS in the mixture both the mechanisms are supposed to occur. Indeed, the filler impact indicates to the modification of primary porosity which enable in turn be connected to UHPC₂ density. Heterogeneous nucleation is likely the influence correlated with each of fineness

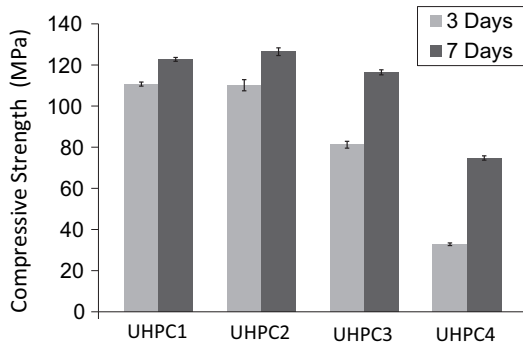


Fig. 9. Compressive strength of UHPC mixtures at 3 and 7 days.

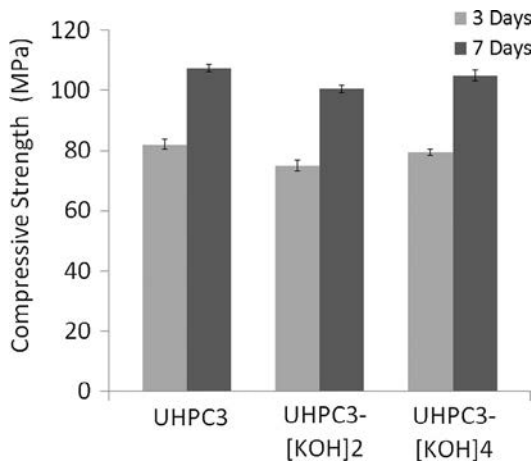


Fig. 10. Compressive strength of UHPC₃ with activated slag by different concentrations at 3 and 7 days.

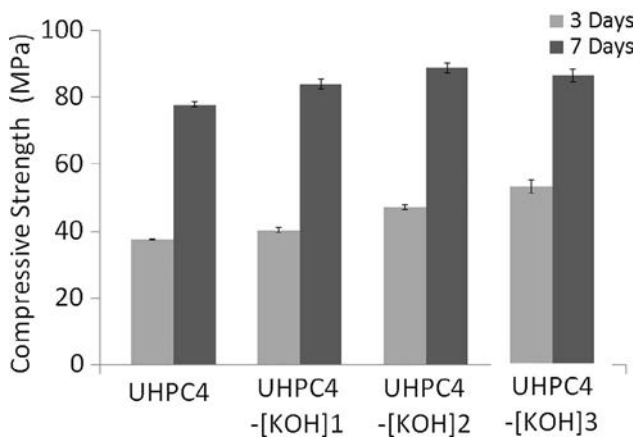


Fig. 11. Compressive strength of UHPC₄ with activated slag by different concentrations at 3 and 7 days.

and slag proportion used and provides a chemical activation of cement hydration. In another meaning, it points to the nucleation of hydrates on mineral particles that aids in catalyzing the nucleation and lowers the energy impediment [19,44]. This phenomenon induces ongoing cement hydration and promotes portlandite formation. Thereby, pozzolanic reaction of BFS is accelerated, which generates new C-S-H. The latter fill the pore structure and improves the compressive strength of UHPC. In addition, the high superplasticizer content of UHPC₁ inhibits cement reaction and the generation of C-S-H gel. These C-S-H are

particularly of low density, at an early age. Hence, the microstructure of UHPC₁ may be less dense than that of UHPC₂ [26].

The obtained results agreed with those of Yang et al. [21], who tested an UHPC with 35% of BFS. They measured a compressive strength of 100 MPa at 7 days. The difference could be explained by the high water-to-binder ratio of their UHPC (0.15) in comparison with UHPC₂ (0.14). For high contents of BFS (50% and 80%), there is a remarkable drop in the strength at 3 and 7 days. Compressive strength decrease is 26 and 12% for UHPC₃ and 66 and 37% for UHPC₄, at 3 and 7 days, respectively. Since slag hydrates more slowly than Portland cement, the early rate of strength development of slag concretes is slower, the higher slag content the slower strength development. Indeed, with high BFS content, the dilution effect dominates the hydration reaction kinetic. This is in accordance with obtained results of setting and hydration reaction, which indicate that the increase of BFS content decreases the heat of reaction and delays the hydrates development. Therefore, the generation of portlandite is restricted and BFS reaction is postponed, which results in the decrease of mechanical performance of UHPC. The obtained results agreed with those of Yazıcı et al. [19], who measured an increase of 22% in the compressive strength of UHPC at 28 days, when 60% of cement is substituted with BFS.

From Fig. 10, it is noted that alkaline activation does not improve the compressive strength of UHPC₃. Indeed, for a BFS content of 50%, the added basic solution of KOH doesn't increase greatly pH, which should promote the hydration of slag and the formation of hydrates.

As shown in Fig. 11, the compressive strength of UHPC₄ at 3 days increases by approximately 7%, 25% and 42%, for [KOH]₁, [KOH]₂ and [KOH]₃, respectively. The addition of KOH in UHPC₄, with concentration [KOH]₃ (i.e., UHPC₄-[KOH]₃), improves the compressive strength by 42 and 11% at 3 and 7 days, sequentially. For a high concentration of KOH, the pH of alkaline solution increases, which destroys the constraints of Si-O and Al-O, and consequently facilitates the dissolution of the slag glass structure. As a result, the hydration promotes, and the strength boosts. The obtained results agreed with those of setting time and hydration.

4. Conclusions

This original paper dealt with the mixture design and early age investigations of more sustainable ultra-high performance concrete (UHPC). The following conclusions can be drawn:

- The use of high energy mixer is of great interest for UHPC. Its blade's form and high mixt speed result in homogeneous and workable concrete, despite the low water-to-binder ratio (0.14) and short mixing duration (3.5 min);
- The polycarboxylate superplasticizer, ACP₁, by its chemical skeleton of acrylic copolymer ensures the best workability of UHPC. Thanks to its short backbone with carboxyl groups and its long side chains, ACP₁ is adsorbed on binder particles, ensuring the water reduction and improving concrete workability by steric hindrance;
- Thanks to its high carbon content, its high absorption and reactivity, gray silica fume (silicium) improves early age compressive strength of UHPC, in comparison with white one (zirconium). The latter ensures better workability;
- In UHPC, the substitution of 30% of cement by Blast Furnace Slag (BFS) improves its density packing, increases its workability, accelerates its setting duration and promotes the cement hydration, which increases the compressive strength of UHPC at an early age. Indeed, the dilution effect related to the reduction of cement content occurs with the heterogeneous nucleation one related to the fineness of BFS particles; the first

makes more water available for cement reaction (more slump flow or less superplasticizer dosage for the same workability) and the second increases the cement hydration and enhances UHPC's mechanical properties.

- For cement replacement with 50% or 80% of BFS, dilution effect is dominating, binder particles are very dispersed and more time is necessary for the occurring of hydration reaction and setting initiation. The production of portlandite is restricted, and BSF reaction is postponed. This results in a drop of compressive strength at an early age.
- The presence of potassium hydroxide solution (KOH), with high concentration, supplies sufficient alkalis, which increases pH, promotes the dissolution of slag glass structure and its reaction. This results in hydration reaction acceleration, setting duration reduction and compressive strength improvement.

In conclusion, an UHPC was designed and optimized using local materials. The replacement of 30% of cement with BFS improves slightly the compressive strength at early age and decreases by two times the superplasticizer content, without any activation. This decreases the environmental footprint of developed UHPC.

With high BFS content, a drop of compressive strength at early age is observed, and a chemical activation reduces this drop. However, a high concentration of KOH is necessary to compensate for the decrease of compressive strength, which affects drastically the workability of concrete. Therefore, further researches are necessary to investigate other modes of activation, which improve the compressive strength of blended UHPC, and ensure its required workability.

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