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High-volume fly ash paste for developing ultra-high performance concrete (UHPC)

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Abstract

Ultra-high performance concrete is a kind of high-tech composite material which shows superb characteristics such as self-compactness, compressive strength higher than 150 MPa, and exceptional durability performances compared to other kinds of concrete. In this research, compared to known commercially available UHPCs, a type of UHPC paste with greener pozzolans was developed. In this regard, cement and silica fume, as two main constituents of the prevalent UHPC compositions and particularly with high cost and environmental impacts, were replaced by fly ash as a waste material. It was found that the highest fluidity and strength could be achieved with 13% and 16% of fly ash substitution, respectively. Furthermore, ultra-fine fly ash with mean particle size of 4.48 μm showed its applicability to be used in UHPC with 20 wt.% cement substitution resulting in a paste with 153 MPa compressive strength and 37.5 cm flow diameter. Moreover, addition of at least 5% silica fume seems to be a prerequisite regarding strength gain of UHPC paste. Metakaolin as another pozzolanic material was studied. Although it improved the paste strength, it demonstrated lower fluidity and showed its inability to be applied in UHPC with required high workability.

Keywords: Ultra high performance concrete (UHPC); ultra-fine fly ash; eco-efficient; self-compacting; metakaolin; silica fume.

1. Introduction

Ultra-high performance concrete (UHPC) is a kind of high-tech composite material which shows superb characteristics such as self-compactness, compressive strength higher than 150 MPa and exceptional durability performances compared to other types of concrete. This new composite material consists of an optimized gradation of granular ingredients, water/binder ratio less than 20 wt.% and a high content of steel fibre [1,2]. One of the first compositions for UHPC, designated as *reactive powder concrete*, contains 25% of silica fume (SF) of the cement weight [3]. Lately, in order to develop more sustainable and eco-efficient UHPC, various pozzolanic materials have been studied as cement replacement since with low water/binder ratio in UHPC just 50% to 60% of cement could be hydrated at the age of 90 days and the rest remain as micro-filler [4]. Furthermore, with a water/binder of 0.18 and SF/cement of 0.3 only 15% of silica fume has the ability to be included in the pozzolanic reactions [5]. It has been also investigated that the degree of pozzolanic reaction of supplementary cementitious materials is highly dependent on their mean particle size [6]. Various pozzolanic materials have been studied since now for the aim of cement replacement. Silica fume is the most famous pozzolanic material particularly for developing UHPC with 25-32 wt.% of cement [7,8]. This material plays three important roles in UHPC: a) as micro-filler, with a mean particle size less than 1 μm, to fill the gaps between coarser

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particles such as cement, b) rheology modifier, due to its glassy and spherical particles and finally c) C-S-H producer through reaction with $Ca(OH)_2$ from cement hydration [3]. With respect to these benefits and particularly highest reactivity of SF compared with other pozzolanic materials, having around 90% of vitreous SiO_2, its high price makes it as a non-desired material in a sustainable context. The other pozzolanic material is metakaolin (MK) which develops high pozzolanic activity however degrading workability [9]. The other disadvantage of MK is its high embodied CO_2 generated for the production of one ton of MK, normally around 330 kg/ton compared to values of 14 and 4 kg/ton for silica fume and fly ash respectively [10,11]. On the other hand, the advantage of metakaolin is its faster strength development along with its lower drying shrinkage rather than plain cement and silica fume concrete [12]. The other pozzolanic material which is of great interest is fly ash (FA), available in huge quantities worldwide as a waste material with very low cost and environmental impacts since its application prevents the massive landfills with this waste material from thermal power plants. It was found that in concrete with 45%-55% cement replacement by fly ash, just 20% reacts in the pozzolanic reaction and the rest remains as filler [4,13]. It was also studied that by restraining the mean particle size of fly ash from 20 μm to 8 μm, its activity increases leading to higher compressive strength [14]. The present research aims at development of an eco-efficient UHPC paste with high content of ultra-fine fly ash, as partial replacement of cement and silica fume, and also adding some contributions to the UHPC research.

2. Materials

Type I Portland cement (CEM I 42.5R according to EN 197-1 [15]) and metakaolin with 9.3 μm and 8 μm, respectively, of average particle size were used. Silica fume from Elkem Microsilica® MS 940-U with an average particle size of 0.15 μm and an original fly ash (O-FA) provided from Pego thermal power unit, Portuguese coal based one, with 8.55 μm of average particle size were also used in this research. Some physical properties and chemical analysis of the materials are reported in Table 1. A commercial superplasticizer (SP), MasterGlenium SKY 526®, with 30% solid content was also used. The SP (Table 2), a carboxylic ether polymer based, consists of a brown liquid with properties according to the definitions and requirements of Standard EN 934-2, established for European concrete admixtures.

Table 1. Chemical (wt.%) and physical characterization of cement.

Components	CEM 42.5R	MS 940-U	MK	FA
SiO_2	19.79	> 90.00	50.50	48.02
Al_2O_3	4.37	–	42.60	29.59
Fe_2O_3	3.52	–	2.28	4.48
CaO	63.09	–	0.16	4.65
MgO	1.67	–	0.22	1.44
SO_3	2.82	–	0.04	0.49
Cl^-	0.04	–	–	–
Loss on ignition	3.01	< 3.0	–	3.0
Blaine surface area (cm^2/g)	4228	150000-300000	–	3848
Density (g/cm^3)	3.1	2.2 - 2.3	2.3	2.4

Table 2. Technical characteristics of Superplasticizer MasterGlenium SKY 526®.

Relative density at 20ºC (g/cm^3)	1.07±0.02
pH	6.0±1.0
Cl^- (%)	≤ 0.1
Solid content (%)	30

2.1. Fly ash preparation

Two different methods were applied to decrease the grain size of the original fly ash (O-FA): dry milling and wet milling (Fig. 1). The first one consists of milling fly ash for 30 min (FA D-30) in a container with 15 balls (2 cm in diameter) which results in an ultra-fine fly ash with 4.48 μm of average particle size. The second method consists of fly ash milling as a water suspension with 1.4 g/cm^3 of density. In this process almost 30% of the milling container volume was filled with balls with diameters of 2 to 3.5 cm (Fig. 1) and the mill was operated in different time intervals: 60, 240 and 360 min, named as FA W-60, FA W-240 and FA W-360, respectively. The particle size of cement and fly ash with different grinding time were also analysed. The results are presented in Fig. 2. As it can be seen, the wet grinding process isn’t as efficient as the dry one since the mean particle size remains around 6 μm after 360 min of milling. Figs. 3 and 4 were obtained by scanning electron microscopy (SEM – Hitachi SU1510) and show the particle shape of O-FA and FA D-30. It is also clear that the finer particles preserve their own original spherical shape and just the coarser particles are crashed into finer ones.

Fig. 1. Wet milling machine and the balls' dimensions used.

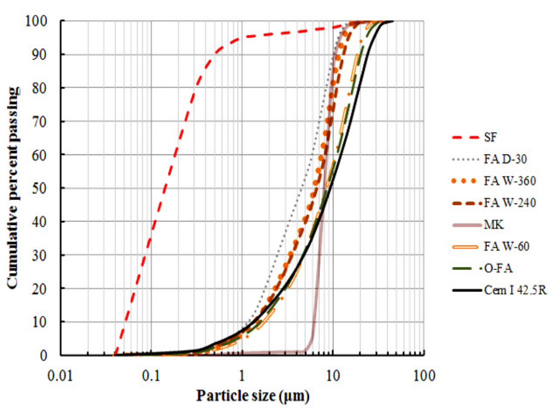

Fig. 2. Cumulative particle size distribution (from left: SF, FA D-30, FA W-360, FA W-240, MK, FA W-60, O-FA and Cement I 42.5R with average particle size of 0.15, 4.48, 6.19, 6.61,8, 8.5, 8.55 and 9.3 µm, respectively).

3. Paste Development

The fluidity and compressive strength are two of the most important UHPC paste properties and its adjustment should be carefully developed. In this regard, the effects of O-FA, FA D-30, FA W-360, metakaolin and silica fume were studied based on the apparatus described in ASTM C 230/C230M-03 flow table test for Hydraulic Cement [16]. Before starting the mixtures, the enhanced fly ash FA W-360 was dried in oven at 100ºC until constant weight and then cooled during 24h at room temperature.

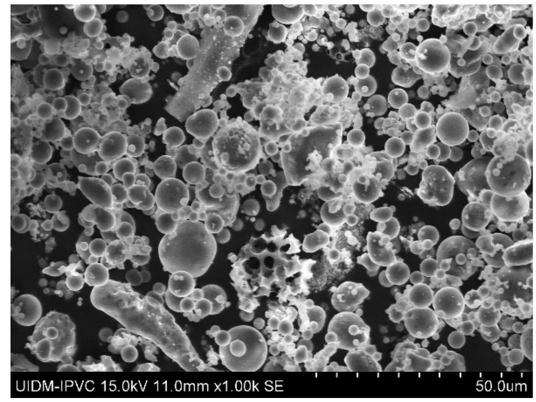

Fig. 3. Low magnified SEM image of O-FA particles.

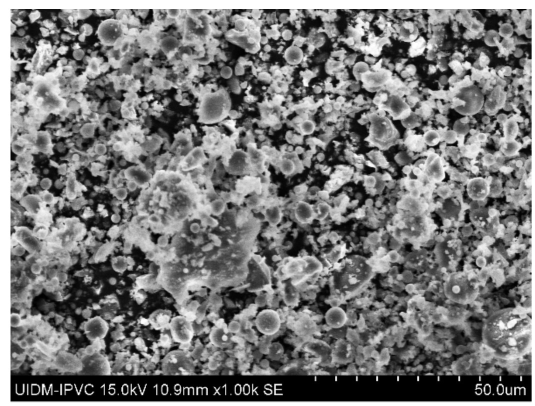

Fig. 4. Low magnified SEM image of FA D-30 particles.

In the first step, cement was mixed with 10%, 15%, 20%, 25%, 30% and 35% of O-FA by weight. For all these pastes water to binder ratio of 18 wt.% and SP to binder ratio of 2.5 wt.% were used. All the compositions in this study are presented in Table 3.

Table 3. Weight of added pozzolans in terms of ratio to cement weight.

Mixture	Cement	O-FA	FA D-30	FA W-360	MK	SF
O-FA 0%	1	0	0	0	0	0
O-FA 10%	1	0.1	0	0	0	0
O-FA 15%	1	0.15	0	0	0	0
O-FA 20%	1	0.2	0	0	0	0
O-FA 25%	1	0.25	0	0	0	0
O-FA 30%	1	0.3	0	0	0	0
O-FA 35%	1	0.35	0	0	0	0
FA W-360 20%	1	0	0	0.2	0	0
FA D-30 20%	1	0	0.2	0	0	0
FA D-30 25%	1	0	0.25	0	0	0
FA D-30 30%	1	0	0.3	0	0	0
FA D-30 25%+MK 2.5%	1	0	0.25	0	0.025	0
FA D-30 25%+MK 5%	1	0	0.25	0	0.05	0
FA D-30 25%+SF 5%	1	0	0.25	0	0	0.05

After mixing the dry powders during 3 min, 70% of water was added and after 3 min of mixing the SP was introduced and mixed during 6 extra min. Afterwards, the rest of the water was added and the mixture was continuously mixed for further 6 min. After the total mixing time (18 min), the flow table was carefully dampened and the paste placed in the conical mould. Then, the paste was cut to a plane surface and the mould was lifted up. When no more spreading was observed, without stroking the table, the measurement of two perpendicular diameters was taken and the average of the two readings was registered as the paste final flow. After the final flow determination, the paste was replaced in the mixer, mixed by hand and moulded in three cubes of 5x5x5 cm. The samples were demoulded after 24h and immersed in water at 20ºC until evaluating their compressive strength after 28 days. With this method the optimum percentage of O-FA regarding fluidity and compressive strength was obtained. This test was also repeated with FA W-360 and FA D-30, with the optimum percentage of O-FA, in order to study their effects on fresh paste consistency as well as its compressive strength.

Fig. 5. Flow-table test procedure.

4. Results and Discussion

As can be seen in Fig. 6, the best addition percentage of the original fly ash (O-FA), with 8.55 μm of average particle size, to cement concerning compressive strength is 15 wt.% of cement while 20% of it brings highest fluidity (143 MPa and 33 cm, respectively). However, its fluidity is still 0.5 cm lower than the plain mixture without any fly ash. The main reason regarding the fluidity improvement by increasing FA content from 10% to 20% could be attributed to its spherical particles shape (see Fig. 3) with better sliding effect rather than angular cement particles. By increasing the fly ash content to 35 wt.%, both strength and fluidity of paste decrease by around 10% and 12% of their corresponding maximums to 128 MPa and 29.1 cm, respectively.

In the next step FA W-360 with 6.19 μm of average particle size was used instead of O-FA. It was interesting to observe that not only the compressive strength increased (to around 5% compared to 20% FA), but also the fluidity was increased even more than the best of FA (7.6% to a flow with 35.5 cm, respectively). This phenomenon can take great importance in the UHPC workability when very low water/binder ratio is tried. Fluidity and compressive strength were even more improved with replacement of FA D-30 by FA and FA W-360 to a maximum of 153 MPa and 37.5 cm of strength and fluidity respectively, for 25% of FA D-30 addition to cement which is equivalent to 20% cement replacement. The reason why fluidity is directly dependent on the fly ash particle size is the sphericity of its fine particles and their glassy surface as well, even after crushing, which offers easier particles sliding between each other when incorporated on the cement paste (see Figs. 3 and 4). Compressive strength improvement could be attributed to the higher reactivity of finer FA particles which could promote a better distribution in the paste and react with higher percentage of cement particles resulting in higher C-S-H development as well as higher packing density of the paste, since these finer particles are able to fill the voids between coarser cement particles, developing a uniform distribution of the compressive stress.

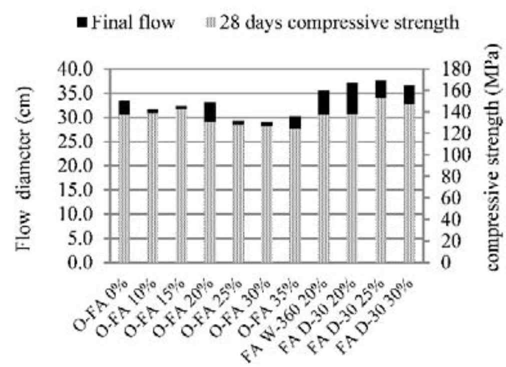

Fig. 6. Strength and fluidity of paste composed of O-FA, FA W-360 and FA D-30 in different percentages.

Since the best amount of fly ash added proved to be 25 wt.% of cement in the FA D-30 state, the final part of the present research was made with this fixed quantity of FA and with incorporation of the two other pozzolanic materials, metakaolin and silica fume. The aim was to study their effects on the paste rheology and on the compressive strength. As can be seen (Fig. 7), the fluidity reduces by 4% and 12.8% for 2.5% and 5% of added MK, respectively, compared to the mixture of cement with just 25% FA D-30. However, the obtained results show also that the compressive strength of the mixture containing 5% metakaolin is 1.7% higher than FA D-30 25%.

Two compositions could be selected regarding the greatest cement replacement, the fluidity and the compressive strength at the same time. The first one is 25% of FA D-30 plus 5% of Elkem® micro silica which gives approximately 154.4 MPa of compressive strength and 36 cm fluidity. The second one is the mixture with 30% of FA D-30 with 147 MPa and 36.5 cm of compressive strength and fluidity, respectively.

As expected, the former one develops higher strength and the later one shows higher fluidity. On the other hand, metakaolin seems to be an unsuitable material for self-compacting UHPC. However, compressive strength of the mixture containing 5% MK is greater than the mixture having 5% silica fume, its fluidity is 9% less than that. This undesired effect of MK could be attributed to its gap-graded particle size distribution (Fig. 2) and its angular particle shape as well [9,17].

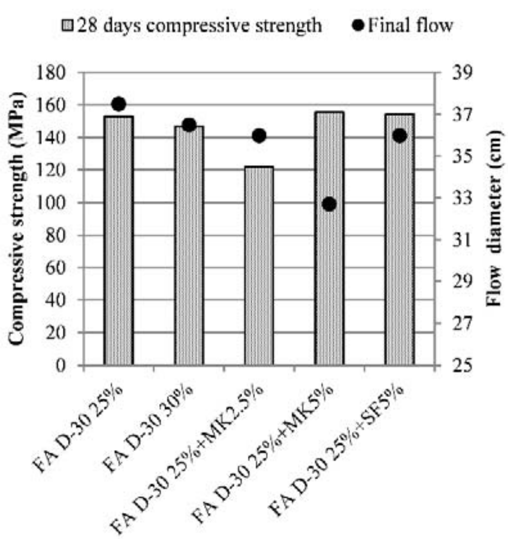

Fig. 6. Comparison of different pastes including 25% FA D-30, 30% FA D-30, 2.5% MK+25% FA D-30, 5% MK+25% FA D-30 and 5% silica fume+25% FA D-30.

5. Conclusions

A greener paste with 25% of ultra-fine fly ash and just 5% of silica fume was developed in this research with the aim of UHPC development. This kind of composition brings normally higher cost-efficiency and environmental efficiency in construction industry due to silica fume and cement substitution by fly ash as an industrial waste. Cement and silica fume play an important role in the price and eco-efficiency of UHPC with respect to their high price and environmental impacts. The compressive strength and fluidity of the proposed paste show its applicability for UHPC development. The results also demonstrated that the particle size of pozzolanic materials plays a significant role in fluidity as well as in strength of UHPC paste. In this regard, 25% ultra-fine fly ash with 4.48 µm of average particle size, improved the aforementioned characteristics compared to the paste containing 25% of original fly ash with 8.55 µm of average particle size. Furthermore, metakaolin showed inability to be applied in UHPC since it reduces fluidity mainly because of its angular particles and high water absorption as concluded in some other recent research works [9,17]. It was also observed that around 5% silica fume can reduce workability to some limited level but improve strength gain of the paste due to its higher pozzolanic reactivity.

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