APPLICATION OF ULTRA-FINE FLY ASH AS CEMENT REPLACEMENT FOR SUSTAINABLE CONCRETE WITH OPTIMAL PACKING DESIGN

Patricia Kara De Maeijer (1), Bart Craeye (1)(2), Hadi Kazemi-Kamyab (3), Ruben Snellings (3) and Michel Loots (4)

(1) Energy & Materials in Infrastructure & Buildings (EMIB), Faculty of Applied Engineering, University of Antwerp, Belgium

(2) Durable Building in Team (DUBiT), Department of Industrial Sciences & Technology, Odisee University College, Belgium

(3) VITO NV, Belgium

(4) Value Ash Technologies NV, Belgium

Abstract

In the present study, a proprietary 0.2 tonne/h Dusty Cloud Separation (DCS) technology prototype by Value Ash Technologies NV (Belgium) was used to obtain ultra-fine fly ash as a novel by-product. Two types of Class F fly ash were used: separated fly ash (FA1) with particle size < 9.3 µm and ultra-fine fly ash (FA2) < 4.6 µm as sub-fraction of FA1. Two types of cement were used: Portland cement CEM I 52.5 R HES (CEMI) and Blast Furnace Slag Cement CEM III/A 42.5 N LA (CEMIII). The results at paste- and mortar- levels showed that an increased fineness of the fly ash (FA2) contributes to better workability of the mix. For CEMI, the compressive strength of concrete with FA2 with 25% cement replacement was already equal to the reference mix at the age of 28 days. For CEMIII, the compressive strength of concrete mix with FA2 with 25% cement replacement was equal to the reference mix value at the age of 91 days. Regarding the durability, replacing cement with ultra-fine fly ash (FA2) had a positive influence on the chloride migration coefficient and ASR, and a negative influence on the carbonation resistance.

Keywords: concrete, ultra-fine fly ash, compressive strength, corrosion resistance, ASR

1. INTRODUCTION

Concrete is a dominant construction material that is used intensively in the last century. It is a unique material in a way that different wastes and by-products can be utilized in it as a partial substitute for the main components (cement, sand, and aggregates). Moreover, it gives a broad horizon for continuous research of its properties even though a lot of research has been already performed to substitute cement or aggregates. It is well known that partial substitution or replacement of cement, for example, allows utilizing by-products with a certain impact on concrete properties, in particular, in terms of slower compressive strength development, but in the case of slag an improvement in concrete durability. The pros and cons of the application of different by-products vary from one to another depending on the final target of concrete application. But the question is if any by-product could combine both compressive strength and durability as a positive quality? Which by-product it could be? New advanced technologies could provide a better-quality by-product for further investigation if there is a certain set of investigations done and the pattern of concrete properties is known?

In the present study ultra-fine fly ash, as a novel by-product obtained by means of Dusty Cloud Separation (DCS) technology, is investigated as a cement replacement in concrete as a part of the VASH-project (Value Ash). The aim of this project was not only focused on the development of innovative technology for ultra-fine fly ash application but also aimed for a maximum valorization of fly ash which contributed indirectly to the goal of the separation process of fly ashes. As a result, this process could be exploited internationally on a large scale in the future. The behavior of ultra-fine fly ash was investigated by the upscaling principle in cement-rich environments such as paste, mortar, and concrete. The goal was to determine the influence of fine fractions of ultra-fine fly ash on workability, mechanical properties (compressive strength), and the durability of concrete (ASR, chloride migration, and carbonation). A well-balanced concrete mix composition with ultra-fine fly ashes acting as a cement replacer was developed by means of optimal packing design algorithms.

2. MATERIALS AND METHODS

Two types of cement were used: Portland cement CEM I 52.5 R HES (CEMI) and Blast Furnace Slag Cement CEM III/A 42.5 N LA (CEMIII). Two types of Class F fly ash were used: separated fly ash (FA1) with particle size < 9.3 µm and ultra-fine fly ash (FA2) < 4.6 µm as a sub-fraction of FA1 which was obtained by a 0.2 tonne/h prototype DPS [1]. The chemical composition is shown in Table 1. The particle size distribution is shown in Fig. 1. Aggregates were used: river sand 0/4, limestone 2/6 and limestone 6/20. Superplasticizers were used: Type 1 – PCE-type (polycarboxylic ether), 30 con%; Type 2 – PCE type, 30 con%; Type 3 – PCE-type, 35 con%; Type 4 – PAE-type (polyacrylether), 30 con%.

Table 1: Chemical composition, LOI and density of cements and fly ashes [2]

Constituent	CEMI [%]	CEMIII [%]	FA1 [%]	FA2 [%]
CaO	66.9	57.8	2.7	2.7
SiO_2	17.2	22.6	53.2	53.6
Al_2O_3	3.8	6.5	26.0	26.4
Fe_2O_3	2.5	1.8	8.4	8.6
MgO	1.9	4.0	1.8	1.8
Na_2O	0.2	0.3	1.6	1.6
K_2O	1.8	1.1	3.7	3.7
Na_2O-eq	1.4	1.0	4.0	4.0
SO_3	5.3	5.1	1.1	1.0
Cl^-	0.1	0.1	-	-
LOI	0.5	2.1	4.1	4.3
ρ [kg/m^3]	2985	2990	2538	2524

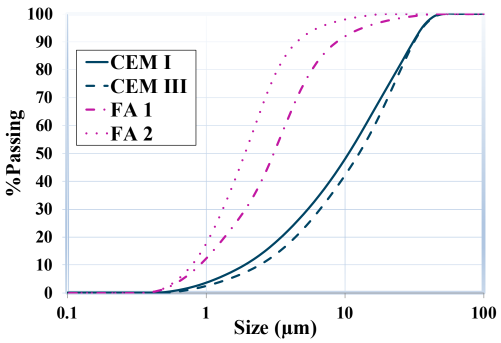


Figure 1: Particle size distribution of fly ashes and cements

2.1. Paste level

Cements were replaced with FA1 and FA2 at five levels: 0%, 15%, 25%, 35% and 50%. The workability of cement pastes was defined by mini-flow table tests in accordance with the standards EN 1015-3 based on determining the consistency of mortars. The mini-flow test setup consisted of a truncated stainless-steel cone (h=60 mm, d_{base}=100 mm, d_{top}=70 mm) placed on a flat, smooth base plate with a diameter of 300 mm. Each paste mix consisted of 500 g of binder (cement with or without fly ash, depending on the replacement level) and 225 g of water. The water/binder factor was always 0.45. Superplasticizer was added in varying amounts to reach the flow diameter in the range of 250-300 mm.

2.2. Mortar level

The mortar compositions were prepared using an automatic mortar mixer in accordance with standard EN 196-1:2016. After 24h the prisms were demolded and placed underwater at a temperature of 20±2°C. The mortar specimens' composition consisted of cement, fly ash, normalized sand and superplasticizer. The choice and dosage of superplasticizer was based on the best flowability of pastes. Mini-slump tests were performed according to the standard EN 12350-2. The mini-slump test setup consisted of a truncated cone (h = 150 mm, d_{base} = 100 mm, d_{top} = 60 mm) placed on a flat, smooth base plate with a diameter of 300 mm. The flexural strength of the hardened mortar prisms (40x40x160 mm) was determined by performing a three-point bending test in accordance with standard EN 196-1:2016. The flexural strength was determined at the age of 28 days after production. The compressive strength tests were carried out at the age of 28 days in accordance with EN 196-1:2016.

2.3. Concrete level

The concrete mix compositions with optimal packing design were partly obtained with the help of software Excel Tool Mix Design (v 1.01) offered by Betonica and optimized in a manual manner by validating the reference mix experimentally. It was decided to produce eight different concrete mixes. The concrete mix compositions are shown in Table 2.

Table 2: Concrete mix compositions with CEM I and CEM III [2]

	CEM REF (kg/m³)	CEM FA1-15% (kg/m³)	CEM FA2-25% (kg/m³)	CEM FA1+FA2-25% (kg/m³)
CEM I 52.5 R /	360	306	270	270
CEM III/A 42.5N				
FA1	-	54	-	36
FA2	-	-	90	54
River sand 0/4	471 / *514*	471 / *514*	471 / *514*	471 / *514*
Limestone 2/6	663 / *641*	663 / *641*	663 / *641*	663 / *641*
Limestone 6/20	755 / *733*	755 / *733*	755 / *733*	755 / *733*
Water	162	162	162	162
Superplasticizer	1.2 / *0.9*	1.2 / *0.9*	1.2 / *0.9*	1.2 / *0.9*
W/B-factor	0.45	0.45	0.45	0.45

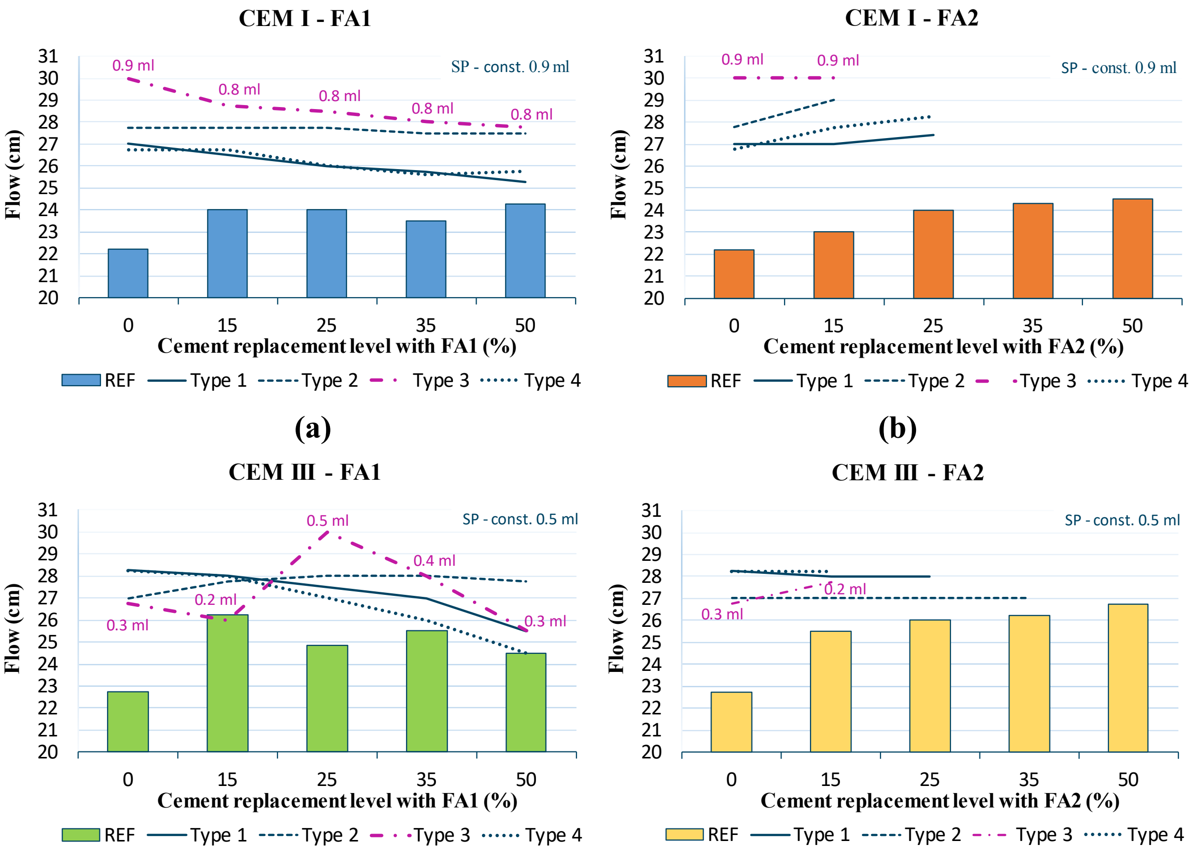
Cube and cylinder samples were produced per mix according to EN 206:2013+A1:2016. After demolding, the specimens were cured in a water bath at a temperature of 20±2°C until the age of testing. The slump test was performed in accordance with standard EN 12350-2. The target was to achieve a slump class S3-S4, which should ensure a sufficiently consistent concrete. The flow test was performed to determine the consistency in accordance with standard EN 12350-5. The volumetric mass (density) of the fresh concrete was determined according to the standard EN 12350-6. The air content of fresh concrete was determined with the pressure gauge method according to standard EN 12350-7. The compressive strength of the concrete specimens was determined at the age of 28, 57 and 91 days using an automatic hydraulic press in accordance with standards EN 12390-3 and EN 12390-4.

The ASR test was performed by following RILEM TC 219-ACS AAR-2 test method. The mortar bar specimens with dimensions 25x25x285 mm were cast in prismatic molds and cured for 28 days in a sealed inox container stored in a climatic chamber at 80±2°C for a period of 28 days. In total eight mortars identical to cement replacement levels in the concrete mix composition were prepared. The mortars were mixed in accordance with the mixing procedure EN 196-1:2016. The mortar workability was measured by a flow table test according to EN 12350-2 and a superplasticizer was added to the mortar mixes to achieve the required flow of 205-220 mm. The chloride migration was determined by the chloride migration test according to the NordTest standardized method NT Build 492. Resistance to carbonation was measured on: (1) specimens stored outside protected from rain/snow and exposed to the environment for 13 months and (2) specimens stored for 11 months outside and 2 months in an accelerated laboratory chamber where they were exposed to an environment with 1% CO_2 at a temperature of 20 ± 2 °C and relative humidity of 60 ± 10%. The carbonation depth was measured according to EN 14630 by spraying phenolphthalein (1%) over the axially split specimens.

3. RESULTS AND DISCUSSIONS

3.1. Paste level

The results of the slump [2] and the flow tests (Fig. 2) showed that the more cement is replaced with ultra-fine fly ash, the better is the workability in case of the reference mixes without superplasticizer for both cement types. Superplasticizer (Type 1) made pastes more viscous with an increasing cement replacement. Superplasticizer (Type 2) at some point didn’t have any effect / or had a slight effect on the flowability of the pastes with increasing fly ash amount. Superplasticizer (Type 3) gave a very good flowability and required a smaller dosage in comparison to other superplasticizers which had a constant dosage for all cement replacement levels. It can be seen in Fig. 2 that superplasticizer (Type 3) dosage varied depending on the target flowability, when the rest of superplasticizers (SP) had a constant value. Superplasticizer (Type 4) in combination with FA1 made the pastes more viscous, and in combination with FA2 more flowable.



(a) (b)

(c) (d)

Figure 2: The flowability of the pastes with increasing fly ash amount

Selecting the best suitable superplasticizer, the cost of materials can be limited, which is highly important on a large-scale production. Based on the obtained results, it can be seen that superplasticizer (Type 3) is compatible with both cement types and a lower dosage of it is required. This advantage enables the use of less superplasticizer or the reduction of the water/binder factor, the latter having a favorable effect on the strength and durability of concrete. Also, the results showed that the ultra-fine fly ash (FA2) did have a positive influence on the flowability. FA1, as a slightly coarser ultra-fine fly ash, didn’t have such a positive effect on the flowability of the pastes. The higher fineness of the FA2 appeared to have a positive effect on the slump and the flow of the pastes.

3.2. Mortar level

The results of flexural and compressive strength for mortar samples are shown in Fig. 3.

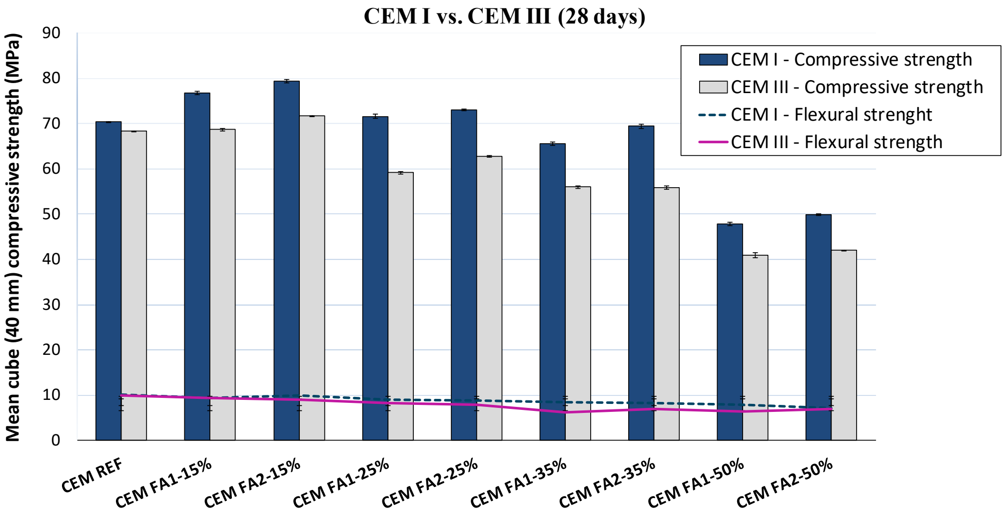


Figure 3: Flexural and compressive strength for mortar samples at the age of 28 days

CEMI – mixes compared to CEMIII – mixes showed a similar but slightly different pattern of flexural strength evolution. At the age of 28 days, the mix CEMI FA2-15% obtained 10% higher compressive strength in comparison to CEMI REF and CEMIII FA2-15% - almost equal compressive strength in comparison to CEMIII REF. The general conclusion from the tests at the mortar-level is that in terms of compressive strength the optimal replacement level of cement with fly ash varies between 15% and 35%, and higher results were achieved with ultra-fine fly ash FA2. The optimum replacement level of cement for mixes with FA2 could be within 15-35% (CEMI) and 15% (CEMIII).

3.3. Concrete level

The results of compressive strength for concrete mixes are shown in Fig. 4.With cement replacement level increase, the slump increased too and concrete mixes had a higher flowability. That was quite good correlated with observations during experiments at the paste level. Concrete with CEMI FA2-25% had a greater slump value than CEMI REF [2]. This indicated that the use of fly ash with a higher fineness (FA2) results in better workability. The densities of the compacted concrete specimens were relatively constant, around 2400 kg/m^3. Concrete mixes with FA contained a lower amount of air content in comparison to reference mix: for CEMI FA that difference was lower for 0.4-0.5% and CEMIII FA – for 0.8-1.1%. The air content decreased with an increasing replacement level, which was confirmed by literature [3].

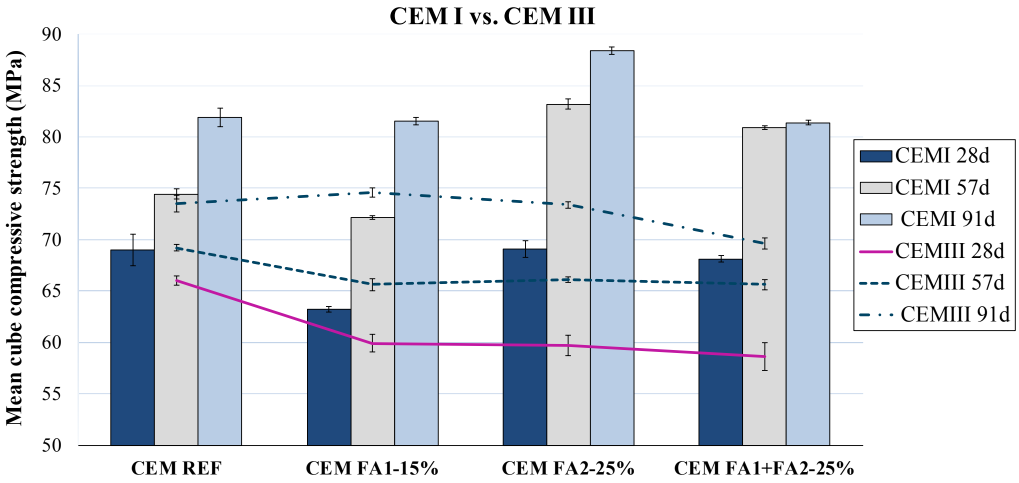


Figure 4: Compressive strength development of concrete mixes

At the age of 28 days, the two concrete mixes with 25% cement replacement (CEMI FA2-25% and CEMI FA1+FA2-25%) approached the reference mix compressive strength value (~70 MPa). From this, it can be inferred that a higher fineness results in a higher pozzolanic reactivity and the reference compressive strength is reached at the age of 28 days and not at the later ages like for conventional fly ash as mentioned in literature [4]. It is known that the pozzolanic activity of fly ash depends upon many parameters such as fineness, amorphous content, chemical and mineralogical composition, and the unburned carbon content or loss on ignition of the fly ash [5]. In an earlier study on the same fly ashes, it was shown that both FA1 and FA2 were enriched in the amorphous phase compared to medium and coarse fractions resulting from post-processing. However, it was concluded from reactivity modeling that at least for early age reactivity fineness was a predominant factor when considering fractions of the same initial fly ash [6]. This is explained by only partial reaction of the fly ash at an early age, resulting in the total amorphous fraction not being a limiting factor, while at the same time the composition of the glassy phase is usually homogeneous over different fly ash size fractions. Concrete mix CEMI FA2-25% obtained compressive strength 7.8% higher in comparison to CEMI REF value at the age of 91 days. The equal compressive strength value to CEMI REF was obtained for CEMI FA1-15% and CEMI FA1+FA2-25% at the age of 91 days.

It was observed that at the age of 28 days the combination of CEMIII with fly ashes gave lower results in comparison to the reference mix. Considering that there is less Portland cement clinker in CEM III producing $Ca(OH)_2$ is needed for the pozzolanic reaction of fly ash, lower results in comparison to concrete mixes with CEMI and fly ashes were noticed. An increase of compressive strength was observed only at the age of 91 days when concrete mix CEMIII FA1-15% reached the value of the reference mix of 74 MPa and CEMIII FA2-25% of 73 MPa. The fineness of the fly ash and the replacement percentage did not affect much compressive strength of the concrete with CEMIII.

ASR expansion tests showed that replacement by ultra-fine fly ash strongly reduced expansion. After 28 days of immersion in the NaOH-solution, the expansion of CEMI REF was significantly greater than the expansion of CEMIII REF, more specifically four times higher. This expansion difference was due to the larger amount of alkalis in CEMI (Portland cement) than in CEMIII. It can be concluded that the choice of cement is an important factor in limiting the expansion and consequently preventing harmful ASR. The replacement of 25% cement by FA2 was the most optimal to control the expansion after 28 days of immersion. For the mixes with CEMIII, the replacement of 25% cement by the combination of FA1 (10%) and FA2 (15%) performed best [2]. It can be concluded that 25% was the most effective replacement level to limit the risk of harmful ASR. The results for the CEMI- and CEMIII-mixes did not clearly show that the fineness of fly ash influenced the resistance to ASR.

Chloride migration was considerably higher for reference concrete with CEMI. While in the case of fly ash concrete compositions, the migration coefficient was greater for CEMIII (Al_2O_3 – 6.5%) than for CEMI (Al_2O_3 – 3.8%). Concrete specimens with FA2 had a lower chloride migration coefficient (Fig. 5). This was due to the fineness of fly ash that ensured a denser packing. Replacing cement with fly ash was the most effective for CEMI and replacing this cement with 25% FA2.

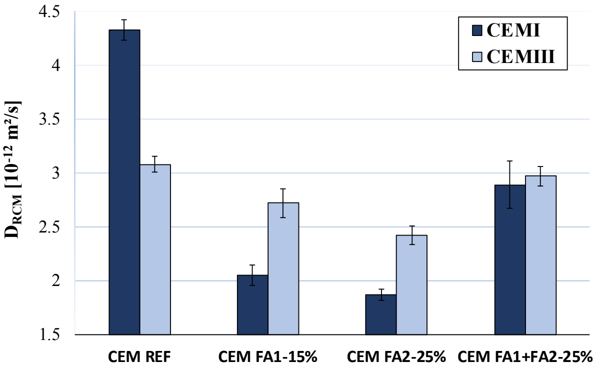


Figure 5: Chloride migration test results

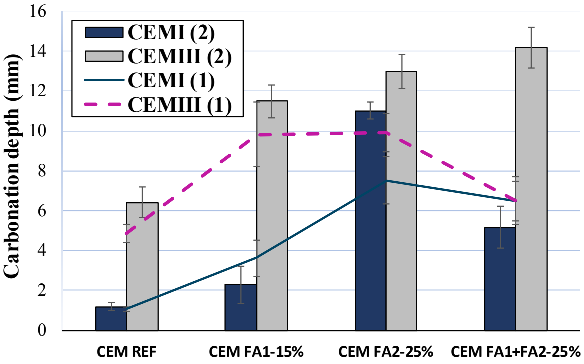


Figure 6: Carbonation test results

It was concluded that carbonation depth was greater for CEMIII compared to CEMI (CEMI - 66.9% CaO and CEMIII - 57.8% CaO). The carbonation depth increased with the increase of the replacement percentage for various concrete compositions (Fig. 6). The finer fly ash also resulted in a greater carbonation depth. The only exception was for CEMI FA2-25%. In terms of concrete microstructure, mainly the $Ca(OH)_2$ content of the cement and to a lesser extent, the pore structure affects the carbonation resistance. The pozzolanic reaction of FA consumes $Ca(OH)_2$, and therefore, also reduces the cement carbonation resistance. The use of FA as a cement component requires careful consideration in the design of concrete mixes and effective curing to produce FA concrete of similar carbonation resistance to reference concrete.

4. CONCLUSIONS

The results at the paste- and mortar- level showed that an increased fineness of the fly ash (FA2) contributed to better workability of the mix. The post-processing of FA into finer fraction by means of DCS technology increased the reactivity of FA and enhanced mechanical properties of concrete. For CEMI, the compressive strength of concrete with FA2 with 25% cement replacement was already equal to the reference mix at the age of 28 days. For CEMIII, the compressive strength of concrete mix with FA2 with 25% cement replacement reached reference mix compressive strength at the age of 91 days. Regarding the durability, replacing cement with ultra-fine fly ash (FA2) had a positive influence on the chloride migration coefficient and ASR, and a negative influence on the carbonation resistance.

ACKNOWLEDGEMENTS

This work received funding by the VLAIO-MIP program as part of the “VASH – Value ash – classification of fly ashes into valuable fractions” project under grant agreement HBC.2016.0387. The authors would like to thank Willemen Infra NV for providing the cement and aggregates, UAntwerp Mechanics Workshop Team for preparing the setup for ASR and chloride migration experiments, UGent for the performance of accelerated carbonation test. The authors would like to thank master students Lucas Vissers, Cedric van der Waal and Daan van Keijzerswaard for their contribution to the experimental program and specimen preparation/testing.

REFERENCES

[1] Loots M., Snellings R., Maul A., Van den Abeele L. ‘Feasibility study report FLAME’, 2017, www.valueash.com.

[2] Kara De Maeijer, P., Craeye, B., Snellings, R., Kazemi-Kamyab, H., Loots, M., Janssens, K., Nuyts, G. ‘Effect of ultra-fine fly ash on concrete performance and durability’, *Constr. Build. Mater.*, **263** (2020) 120493. 10.1016/j.conbuildmat.2020.120493

[3] Jolicoeur, C., To, T. C., Benoit, E., Hill, R., Zhang, Z., Page, M. ‘Fly ash-carbon effects on concrete air entrainment: fundamental studies on their origin and chemical mitigation’, *In Proc. World of Coal Ash (WOCA2009) Conference*, 4-7 May 2009, Lexington, USA.

[4] Chindaprasirt, P., Jaturapitakkul, C., Sinsiri, T. ‘Effect of fly ash fineness on compressive strength and pore size of blended cement paste’, *Cem. Concr. Compos.*, **27** (4) (2005) 425–428.

[5] Skibsted J., Snellings R. ‘Reactivity of supplementary cementitious materials (SCMs) in cement blends’, *Cem. Concr. Res.* **124** (2019) 105799. 10.1016/j.cemconres.2019.105799

[6] Snellings, R., Kazemi-Kamyab, H., Joseph, S., Nielsen, P., Loots, M., Van den Abeele, L. ‘Pozzolanic reactivity of size-classified siliceous fly ashes’, *In Proc. 2nd International Conference of Sustainable Building Materials*, 12-15 August 2019, Eindhoven, The Netherlands, p. 1-18.