Influence Of Selected Activation Methods On The Waterproofness And Freeze Thaw Resistance Of Concretes Having High Dosage Of SCM's

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Abstract—Use of fly ash, as well as other supplementary cementitious materials (SCM´s) in large volumes can bring both technological and economic benefits for concrete industry. In this study, waterproofness and freeze-thaw resistance of concrete having high dosage of SCM´s were experimentally investigated. In the binder mix, fly ash was intended as a basic SCM, being 60% of the cement amount. In concrete technology, concrete having this amount is considered as "high volume fly ash concrete". Then, with constant amount of FA, ground granulated blast furnace slag and silica fume were added in specific amounts while cement content was reduced accordingly. Because of extremely high amount of SCM´s, three methods of activation were applied for improvement the properties of concrete: reduction of water to binder ratio, addition of chemical activator (sodium sulphate) and adjustment of fly ash granularity by grinding. This work is aimed on the comparison of those methods in terms of their influence on both the waterproofness and freeze-thaw resistance (using de-icing salts) of concrete.

The reduction in w/b ratio was found as the most effective activation among the tested methods. The best waterproofness (lowest depth of penetration of water) as well as the best freeze-thaw resistance (lowest scaling) has been achieved by mixtures having reduced w/b ratio from 0.55 to 0.47.

Keywords—SCM's; fly ash; ground granulated blast furnace slag; silica fume; waterproofness; freeze-thaw resistance using de-icing salts

I. INTRODUCTION

Historically, fly ash has been used in concrete at levels ranging from 15 to 25 % by mass of the cementitious material. The actual amount used varies widely depending on the application, the properties of the fly ash, specification limits, and the geographic location and climate. Higher levels (30 to 50 %) have been used in massive structures to control the temperature rise. In recent decades, research has demonstrated that high dosage levels (40 to 60 %) can be used in structural applications, producing concrete with good mechanical properties and durability [1]. The principal factors affecting the durability of concrete can be the environmental conditions, aggregate type, dosage of aggregate, the concrete strength, the mixture proportioning, the use of special cement, the use of SCM's, and water/binder ratio. Two others important factors have an effect on durability of concrete: surface finishing and curing conditions [2], [3]. Concrete containing high volume of Class F fly ash exhibited excellent mechanical properties, good durability with regard to repeated freezing and thawing, very low permeability to chloride ions, and showed no adverse expansion when reactive aggregates incorporated into concrete [4], [5].

In general, the resistance of a reinforced concrete structure to corrosion, alkali aggregate expansion, sulfate and other forms of chemical attack depends on the waterproofness of the concrete. The waterproofness is greatly influenced by the amount of mixing water, type and amount of supplementary cementitious materials, cutting and cracking resistance of concrete. High-volume fly ash concrete mixtures, when properly cured, are able to provide excellent waterproofness and durability [6].

It has been testified that using fly ash in concrete as cement replacing material causes better mechanical properties and durability of concrete structure. With the progress of the pozzolanic reaction, a gradual decrease occurs in both the size of the capillary pores and the crystalline hydration products on the transition zone, thereby reducing its thickness and eliminating the weak link in the concrete microstructure [7].

Concrete can be resistant to cyclic freezing and thawing provided it has sufficient strength and an adequate air-void system, and the aggregates are frost resistant. However a number of laboratory studies have shown that concrete containing fly ash may be less resistant to scaling when subjected to freezing and thawing in the presence of deicing salts. Based on a review of published data the following observations have been made [8], [9]:

- scaling increases as the w/c increases,
- scaling generally increases with fly ash content, especially at high levels of replacement.

According to [8], [9], fly ash concrete is likely to provide satisfactory scaling performance, provided w/c does not exceed 0.45 and the level of fly ash does not exceed 20 to 30 %. This, of course, assumes an adequate air void system is present in the concrete and that proper construction practices are adhered, too. High volume fly ash concrete invariably performs poorly in laboratory scaling tests even when the w/c is maintained at very low values. Testing using various curing regimes, including different curing compounds, showed severe scaling (mass loss < 4 kg/m^2 and visual ratings 5) for concrete with high levels of fly ash (58 %) and low w/c (0.32) regardless of curing compounds did improve the performance to some degree.

The advantages of using cement additions in concrete are, mainly, the improved concrete properties in fresh and hardened states, and economical and ecological benefits. The achievement of these advantages becomes to be more important for concrete proportioning when concrete comply with trends of high amounts of cementitious materials. However, the selection of additions needs more attention due to their different properties: initial reactions of fly ash, ground granulated blast furnace slag and natural pozzolans are slower than that of Portland cement, which causes a slower rate of strength development and a longer curing period. The strength development of slag is more rapid than that of fly ashes. Silica fume due to its high surface area, increases water and superplasticizer demand for a certain consistency [10], [11]. However, silica fume works positively in cement concretes due to extremely high reactivity, so it affects properties of hardened concrete in positive way in the end.

To improve the properties of high volume fly ash concrete, various methods of its activation are presented in [12], [13], [14], [15], [16]. It has been observed in many studies that lowering water/cement ratio leads to improve mechanical properties and overall durability. Grinding can increase the reactivity of fly ash to some extent. Grinding, however, is an energy intensive process and needs complicated facilities. Spherical fly ash particles are broken during grinding, which will result in higher water demand for a given workability and thus somewhat offsets the improvements in reactivity due to grinding. The use of chemical activator can significantly accelerate the pozzolanic reactions between fly ash and lime, and increase the strength development rate and ultimate strength of hardened materials containing fly ash. Chemical activator can be easily added into concrete mixtures during the concrete mixing process.

Presented experiment was aimed on the verification of both the waterproofness and freeze-thaw resistance of concretes having high dosage of SCM´s, while 3 variations of binder mixture (FA; FA + GGBFS and FA + GGBFS + SF), as well as 3 methods of binder activation: reduction of water to binder (w/b) ratio, addition of chemical activator (sodium sulphate) and adjustment of fly ash granularity (by grinding) were applied.

Those methods were chosen for verification of effectiveness of typical methods of binder activation in the case of high amount of SCM´s and their influence on specific properties of hardened concrete (waterproofness and freeze-thaw resistance using de-icing salts).

II. Experimental Program

A. *Materials*

For concrete mixes, following materials were used:

- Portland cement CEM I 42,5 R
- Natural aggregates (0/4, 4/8 and 8/16 fractions)
- Fly ash of F type (FA)
- Ground granulated blast furnace slag (GGBFS)
- Silica fume (SF)
- Polycarboxilate type plasticizer
- Sodium sulphate (Na_2SO_4)

Basic characterization - chemical composition of binder materials is shown in

Table I.

For finer granularity of fly ash, thus enhancement its reactivity, it was ground by ball planetary mill for 1 hour. Results of granulometric analysis before and after grinding expressed as d(0.1), d(0.5) and d(0.9) are given in Table II. Exact granulometric curves are shown in *Fig. 1* for origin fly ash and in *Fig. 2* for ground fly ash. By milling the FA, its particle size of grains above 100 μm was reduced. By d(0.9) parameter, 90% of the particles before milling are of size 94,76 μm, while 90% of the particles after milling are of size 63,94 μm.

TABLE I CHEMICAL COMPOSITION OF BINDER MATERIALS

Cementitious materials	Content of oxides [%]						
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	SO_3
Cement	19.87	4.00	3.18	64.36	4.61	0.32	2.60
FA	47.36	21.62	7.14	3.82	1.76	1.67	-
GGBFS	41.28	6.30	0.40	35.98	12.85	0.54	1.07
SF	97.00	1.10	1.50	0.70	-	-	-

TABLE II RESULTS OF GRANULOMETRIC ANALYSIS

Granulometric parameters	Particle size [μm]	
	Origin	*Ground*
d(0.1)	3.10	2.79
d(0.5)	19.12	14.42
d(0.9)	94.76	63.94

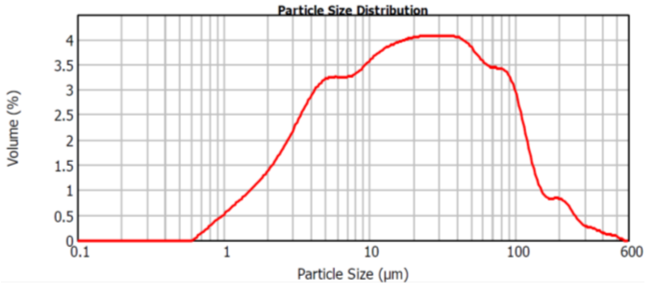

Fig. 1 Grading curve of origin fly ash

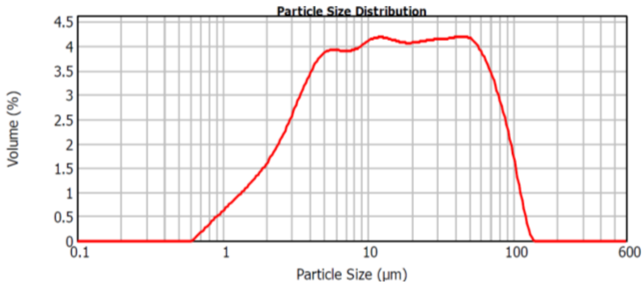

Fig. 2 Grading curve of ground fly ash

B. *Concrete Mixtures*

Eleven different mixes were tested in this study. Control concrete mixture (CM) does not contain any additives. Basic concrete mixes with high dosage of SCM´s (M1-3-B) were prepared in 3 variations of binder containing fly ash in constant amount (60 % of binder mass), then GGBFS and SF in specific amounts (M2 and M3), while cement content was reduced accordingly. Thus, mixture M3 contains the biggest amount of SCM´s (80%) and lowest amount of cement (20%). CM and M1-3-B were produced with w/b = 0.55. Next, the same mixes were prepared using three methods of binder activation:

- reduction of water/binder ratio (from 0.55 to 0.47) – mixtures M1-3-0.47.
- chemical activation by sodium sulphate (Na_2SO_4) - mixtures M1-3-NS.
- adjustment of fly ash granularity (by laboratory grinding) – mixture M1 only: M1-GFA.

Principle of concrete mixtures composition as for variables is shown in TABLE III. Amount of aggregates was constant in all mixtures. Also, all concrete mixes were prepared keeping the same workability: slump class S4 (160 – 200 mm by slump test) through optimization of plasticizer dosage.

TABLE III PRINCIPLE OF MIXTURES COMPOSITION

Mixture	C [%]	FA [%]	GGBFS [%]	SF [%]	Na_2SO_4 [%]	w/b -
CM	100	-	-	-	-	0.55
M1- B	40	60	-	-	-	0.55
M2- B	25	60	15	-	-	0.55
M3- B	20	60	10	10	-	0.55
M1-0.47	40	60	-	-	-	0.47
M2-0.47	25	60	15	-	-	0.47
M3-0.47	20	60	10	10	-	0.47
M1-NS	40	60	-	-	3.0	0.55
M2-NS	25	60	15	-	3,0	0.55
M3-NS	20	60	10	10	3,0	0.55
M1-GFA	40	60	-	-	-	0.55

C. *Test Methods*

For waterproofness and freeze-thaw resistance testing, the cube specimens (150 mm) were made. Testing procedures was carried out after 28 days of curing under relative humidity > 95 % and temperature 20 ± 1° C.

- Waterproofness

Testing the waterproofness (depth of penetration of water under pressure) of concrete was performed according to EN 12390 – 8 [17]. Waterproofness test was performed for 72 ± 2 hours, while water pressure of 500 ± 50 kPa was applied. Then sample is split in half and water penetration can be clearly seen. Limit value for water penetration is 50 mm – criteria given by technical standard EN 206 – 1 [16].

- Freeze thaw resistance

Freeze-thaw resistance of concrete using de-icing salt is only required for concretes of exposure class XF2 and XF4 in accordance to [16] or it can be defined by individual requirements. This test was performed according to national technical standard STN 73 1326 [19], by automatic freeze-thaw cycling in temperature range +20 to -15 °C. The test surface of the samples was immersed in 3% NaCl solution to replicate the effect of de-icing salt. Mass of scaled material was weighted after 25 and 50 cycles of freezing and thawing. According to technical standard, the degree of concrete surface damage is classified by [19] and is given in TABLE IV.

TABLE IV DEGREE OF SURFACE DAMAGE

Degree of surface damage	ρ_a [g/m²]
1 – no damaged	< 50
2 – slightly damaged	< 500
3 – damaged	< 1000
4 – heavily damaged	< 3000
5 – disintegrated	> 3000

Parameter ρ_a is calculated by formula (1):

$$\rho_a = \frac{\sum m}{A} \quad (g/m^2) \qquad (1)$$

where: ρ_a is scaling (g/m²)
m is the mass of scaled material (g)
A is the surface area of sample (m²)

III. RESULTS AND DISCUSSION

A. *Waterproofness*

Results of testing the waterproofness of concrete with high volume of SCM's are shown in TABLE V. The lowest depth of penetration of water has been achieved by M3-0.47 - concrete mixture having biggest amount of SCM´s together with reduced water/binder ratio. The highest depth of penetration of water has been achieved by M2-NS – chemically activated concrete mixture containing FA and GGBFS. Only following mixtures meet the limit for water penetration (max. 50 mm): the control mixture CM, the M2-B, the M3-0.47 and M1-NS.

The highest depth of penetration of water has been achieved by M2-NS – chemical activated concrete mixture.

TABLE V RESULTS OF WATERPROOFNESS OF TESTED CONCRETE MIXTURES

Mixture	Depth of penetration of water under pressure [mm]
CM	47
M1- B	67
M2- B	47
M3- B	78
M1-0.47	67
M2-0.47	72
M3-0.47	25
M1-NS	29
M2-NS	97
M3-NS	63
M1-GFA	55

Results of testing the waterproofness of concrete with high volume of SCM's in graphical form are shown in *Fig. 3*.

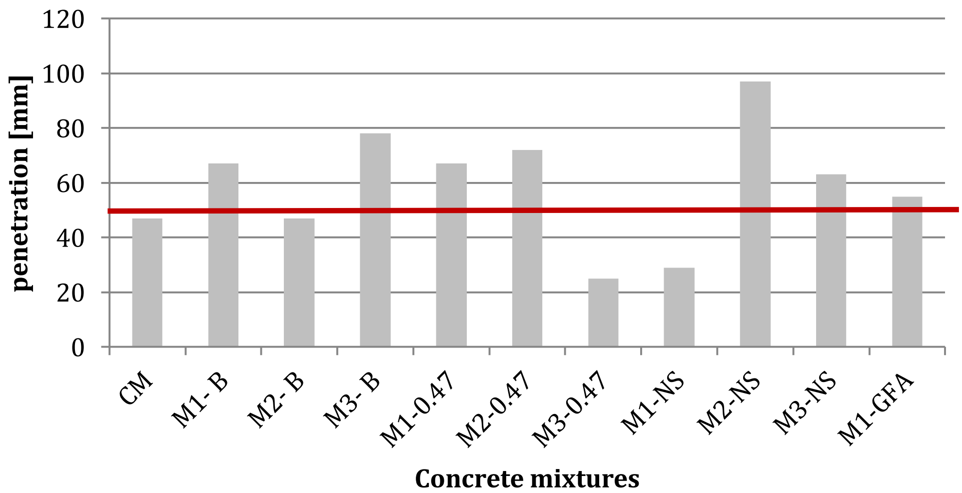

Fig. 3 Results of waterproofness of tested concrete mixtures

Looking at the *Fig. 3*, generally negative effect of high amount of SCM´s on the waterproofness of concrete can be assumed. Activation approach seems to be poorly useful comparing CM as well; reduction of w/b ratio was effective only in the case of M3 (FA+GGBFS+SF), while chemical activation was effective in mixture M1 (FA only).

Analysis of activation methods for individual binder types:

- comparing basic mixture containing fly ash only (M1-B), positive effect can be attributed to both the chemical activation (M1-NS) and grinding the fly ash (N1-GFA).
- comparing basic mixture containing FA+GGBFS (M2-B), neither reduction of w/b (M2-0.47)

nor chemical activation (M2-NS) had positive effect on the waterproofness.

- comparing basic mixture containing FA+GGBFS+SF (M3-B), positive effect can be attributed to both the reduction of w/b (M3-0.47) and chemical activation (M3-NS).

B. Freeze-Thaw Resistance

Results of testing the freeze-thaw resistance of concrete with high volume SCM's, are shown in TABLE VI. The best freeze-thaw resistance among modified concrete mixtures has been achieved by M1-0.47 - concrete mixture with lower water/binder ratio and fly ash only. In this case reduction of water/binder ratio has positive influence on freeze-thaw resistance.

TABLE VI CUMULATIVE SCALING AFTER FREEZE-THAW CYCLES

Mixture	Cumulative scaling [g/m^2]	
	25 cycles	***50 cycles***
CM	44.5	120.2
M1- B	4 053.5	3 083.6
M2- B	5 414.0	31 083.4
M3- B	6 291.5	17 561.9
M1-0.47	1 236.4	4 554.1
M2-0.47	3 994.5	8 724.3
M3-0.47	7 536.3	12 163.0
M1-NS	4 798.8	9 490.8
M2-NS	1 231.0	27 704.3
M3-NS	7 576.3	24 927.5
M1-GFA	4 241.2	21 828.8

Results of testing the freeze-thaw resistance of concrete with high volume SCM's in graphical form are shown in *Fig. 4*.

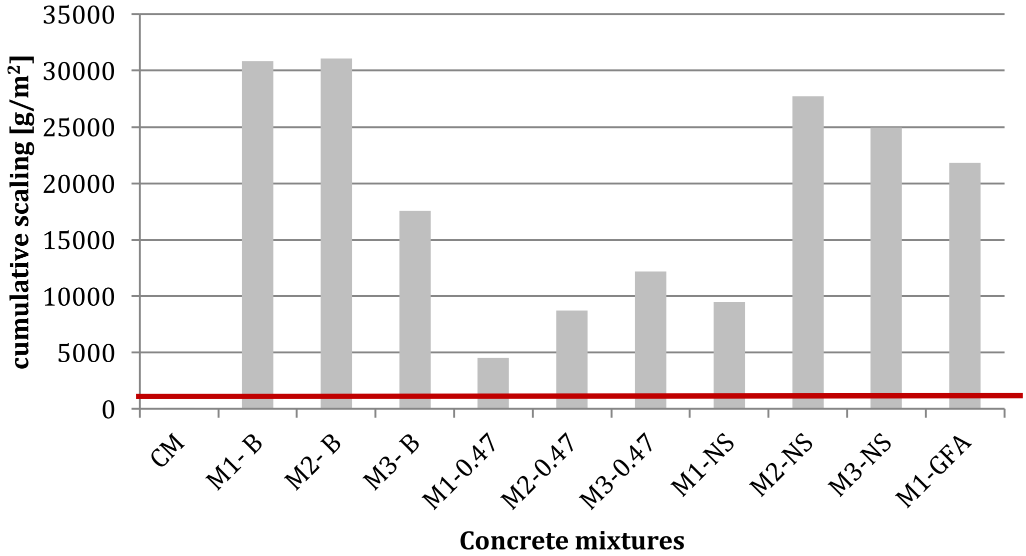

Fig. 4 Results of freeze-thaw resistance of tested concrete mixture

Looking at the *Fig. 4*, generally negative effect of high amount of SCM´s on the freeze-thaw resistance of concrete can be assumed. Activation approach seems to be poorly useful comparing CM as well; no any activated mixture has better (lower) depth of penetration of water than CM. It is the only mixture complying standard limit given for exposure class XF 2, as shown in figure 4; this exposure class was selected here as an example for evaluation by standard criterion.

Analysis of activation methods for individual binder types:

- comparing basic mixture containing fly ash only (M1-B), positive effect can be attributed to all activation methods: reduction of w/b (M1-0.47), chemical activation (M1-NS) and grinding the fly ash (N1-GFA). The most effective is reduction of w/b.

- comparing basic mixture containing FA+GGBFS (M2-B), both the reduction of w/b (M2-0.47) and chemical activation (M2-NS) had positive effect on the freeze-thaw resistance

- comparing basic mixture containing FA+GGBFS+SF (M3-B), positive effect can be attributed to the reduction of w/b (M3-0.47), not to chemical activation (M3-NS)

To improve the freeze-thaw resistance, reduction of water/binder ratio appears to be the best method in this study. Anyway, all concrete mixtures except of CM achieved the degree of surface damage 5 – disintegrated.

IV. Conclusion

Experiments have been performed to investigate the waterproofness and freeze-thaw resistance of high volume additives concrete. Three different methods to improve properties of concrete was compared and evaluated. The following conclusions can be drawn from this study:

- Extremely high volume of SCM´s up to 80% of cement amount generally worsens both the waterproofness and freeze-thaw resistance of concretes.

- Sporadic satisfactory results were observed in the case of waterproofness: mixture M3 (FA+GGBFS+SF) prepared by reduction of w/b in and mixture M1 (FA) prepared by chemical activation.

- Mixtures with lowest amount of cement and highest amount of SCM´s (M3) do not show always the worst results as would be expected, most likely due to efficiency of silica fume.

- Among tested activation methods, the best one for concrete containing high volume of SCM´s seems to be the reduction of water/binder ratio.

Concretes having high volume of additives are generally not suitable for environment where waterproofness and freeze-thaw resistance is required. On the other side, some of presented approaches are promising for further improving by optimization of concrete composition together with tailored activation method. Air entraining admixture can be used to improve air-void system, as well as selection of high quality fly ash and greater reduction in fly ash granularity to improve pozzolanic reaction can be mentioned here as some idea.

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