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Freezing and de-icing salt resistance of blast furnace slag concretes

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Abstract

This paper presents the results on investigations made into a concrete containing cement rich in granulated blast furnace slag (57%). Whereas slag cement concretes have proved successful in structures subjected to chemical attack, their use in structures subjected to freezing and de-icing salt attack is a problem of numerous investigations. The results concerning water/cement ratio and air content in concrete mixtures are presented in this paper. The effect of polypropylene microfibre addition to the concrete was also analysed. The research shows that air entraining the concrete mix up to the level of 5–6% guarantees obtaining high resistance to the action of de-icing agents, even at relatively high values of water/cement ratio. Apart the air content, the addition of microfibre to the concrete mixture was highly effective. For these samples scaling was the lowest. Phase composition investigations confirm that calcite and aragonite (as the carbonation products) were present on the surface of concrete.

Keywords: Slag cement; Freezing and thawing; Scaling resistance; De-icing salt; Phase composition

1. Introduction

Concrete used for the construction of road and footpath pavement, apart from the ordinary resistance to cyclical freezing and thawing, must also be resistant to the effects of de-icing agents. In many European countries the problem of concrete resistance to freezing and thawing in the conditions where de-icing agents are used is of key importance.

The resistance of concrete to the effects of de-icing agents is significantly dependent on the kind of cement used.

In many countries there is a general agreement on the fact that keeping the value of the water/cement ratio at a level below 0.45 [1] and using a concrete air content of 4–6% [2] are necessary for high resistance to the effects of de-icing agents.

Such philosophy is presented also in a new European Standard EN 206 (Concrete-Part 1: Specification, performance, production and conformity). According to this standard, the recommendations for concrete surfaces exposed to direct spray containing de-icing agents and freezing are: $w/c \leqslant 0.45$, strength class—C 30/37, minimum cement content—340 kg/m^3, minimum air content—4.0%.

However, there are big discrepancies between the opinions of various authors on the resistance of concrete made of slag cement to the effects of de-icing agents. Many test results show that for blast-furnace cement concretes even with low w/c ratio ($\leqslant 0.45$) and high content of air the freeze-de-icing salt resistance is not sufficient [3,4].

In general, research results indicate that concrete mixes using slag cement have a lower number of air pores [5,6] while some authors have also observed lower effectiveness of air-entraining agents in fresh concrete and the effectiveness of air voids in the hardened concrete [7–9]. On these grounds some authors observed a markedly lower resistance of slag cement concrete in comparison with Portland cement concrete.

However, there are authors who have obtained completely different results. Among those, Wiebenga [10] noticed that after an initial quick scaling of slag cement concrete, that type of concrete had a greater resistance than OPC concrete (Fig. 1).

The initially faster scaling of slag cement concrete may be explained, among other factors, by the carbonation of the weak and porous surface layer of concrete.

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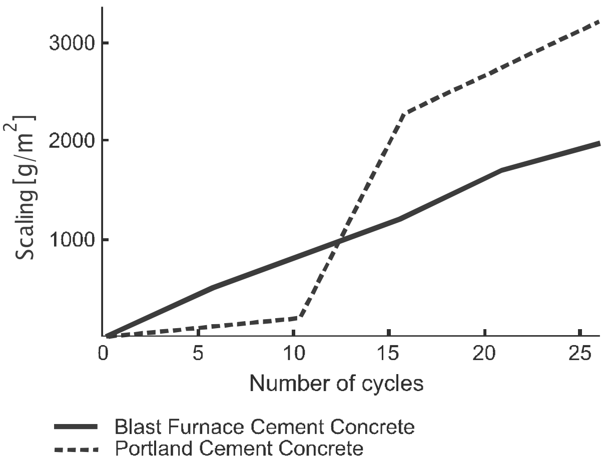

Fig. 1. Loss of mass in freezes thaws de-icing salt cycles for Portland cement concrete and blast-furnace slag cement concrete with 300 kg/m^3 cement [8].

Some authors suggest that the reason for that phenomenon in the surface layer is the re-crystallisation of calcium carbonate [5]. The surface layer of slag cement concrete has been found to contain (beside calcite) also metastable calcium carbonates (aragonite and vaterite) soluble in NaCl. Following the action of de-icing agents only weakly crystallised calcite was found [11]. A positive influence of microfibre addition on the de-icers action is also reported in some papers [5,11,12].

The author's experience in studying the characteristics of binding agents containing granulated blast-furnace slag indicate that the problem of the slag used (its chemical and mineralogical composition) should also be taken into consideration [13].

In the assessment of the freeze-de-icing salt resistance of concretes made of cements containing granulated blast-furnace slag a number of questions is still unanswered. It is well visible in many national standard regulations—in many countries (for example: Austria and Germany) new recommendations for constructions exposed to the de-icing salts action are different from EN 206-1. In German standard DIN 1045-2 concretes with $w/c \leqslant 0.5$ are recommended for such constructions; in Austrian standard ÖNORM B 4710-1 it can be even 0.55.

The subject of research carried out by the author was to identify the effect of air entraining and addition of polypropylene fibres on the resistance of slag cement concrete with w/c ratio over 0.45 to the action of de-icing agents. The resistance of 30 MPa class concrete after an initial 28 day period of curing in natural conditions was studied.

2. Characteristics of raw materials used in the study

In this study the industrial slag cement CEM III/A 32.5 (according to EN 197-1) was used (57% of gbfs content).

Table 1 presents the strength characteristics and chemical composition of the cement.

Sand, fractionated gravels 2–8 and 8–16 mm, and crushed basalt aggregate of the 8–16 mm fraction was also used in the study. Table 2 presents the characteristics of the sand and gravel aggregates used in the preparation of concrete mixes. The crushed basalt aggregate was a single-sized aggregate (8–16 mm).

3. Admixtures

The following chemical admixtures were used in the study:

- air-entraining admixture (active main substance: synthetic (anion) tensides),
- superplastisizer (major active substance: SMF).

Fibrillated polypropylene fibres (length 19 mm) were also used as the addition to the part of the concrete samples.

3.1. Proportioning of the concrete mixtures

The concrete mix compositions were proportioned using the experiment/calculation method. Four concrete mixtures were prepared, of which 150 mm cubic samples were formed. In accordance with the technical requirements for the concrete work conducted, the mixes prepared had a consistency, which allowed their pumping (slump ca. 15 cm).

The air entraining of the concrete mixes was achieved using the air-entraining admixture. In order to improve the consistency of the mixes, superplastisizer was used in three of them (in the control mixture, no superplastisizer and no air-entraining agent were used).

Table 1
Cement characteristics

Cement type	Bending strength (MPa)		Compression strength (MPa)	
	After 7 days	After 28 days	After 7 days	After 28 days
CEM III/A 32.5	6.61	9.65	22.5	47.7
Chemical composition	$CaO = 51.20\%$ $Fe_2O_3 = 1.81\%$	$SiO_2 = 31.67\%$ $SO_3 = 3.40\%$	$Al_2O_3 = 5.97\%$ $LOI = 0.6\%$	$MgO = 4.20\%$ $Na_2O = 0.76\%$

Table 2
Sand and gravel characteristics

Fraction type (mm)	Fraction share (%)		
	Sand 0–2 mm	Gravel 2–8 mm	Gravel 8–16 mm
8–16	–	–	77.4
4–8	–	50.5	16.9
2–4	0.9	29.6	2.8
1–2	8.0	10.3	0.8
0.5–1	33.5	5.0	0.5
0.25–0.5	45.8	3.4	0.6
0.125–0.25	10.3	0.9	0.5
0.0–0.125	1.5	0.3	0.5

The influence of aggregate type on the properties of concrete was also studied. In concrete C partial replacement of gravel by crushed basalt have been done. The compositions of the concrete mixtures are shown in Table 3.

Fig. 2 presents a cumulative grain size curve of the combined aggregates.

Table 3
Concrete mix compositions

Ingredient	Ingredient share (kg/m^3)			
	A	B	C	D
Cement: CEM III/A 32.5	369	360	366	368
Water	213	180	186	187
Sand	492	480	487	486
Gravel 2–8 mm	468	457	464	467
Gravel 8–16 mm	761	742	395	394
Basalt aggregate 8–16 mm	–	–	394	393
Superplastisizer	–	2.88	2.88	2.88
Air-entraining agent	–	0.36	0.30	0.30
Polypropylene fibres	–	–	–	0.90
w/c	0.58	0.50	0.51	0.51

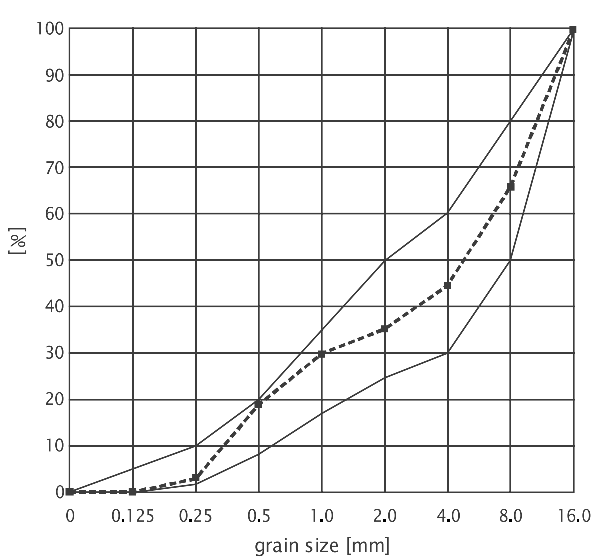

Fig. 2. Cumulative grading curve of the aggregate composition of the concrete mixtures.

The prepared concretes were cured over 28 days at 20±1 °C and RH >90%.

4. Results

The air content and slump of fresh concrete mixes were measured. After 7, 14 and 28 days of curing the compressive strengths were studied.

Before starting the study of resistance to the action of de-icing agents, the density and water absorption of the concretes were measured.

The physical characteristics of the concrete mixes and hardened concrete samples are presented in Table 4.

During the study, the effectiveness of the use of the air-entraining admixture was observed. For the control sample (A), relatively low air content was obtained (1.1%) which is typical for concretes containing slag cements. But, satisfactory air content for samples B, C and D was obtained by relatively high dosage of air-entraining admixture. It was ca two times more then for typical OPC concretes with similar air content. The concrete exhibited good rate of strength increase: ≈17–20 MPa as soon as after 7 days of curing and 35.5 to almost 40 MPa after 28 days of curing.

The low water absorption of the concretes prepared is also worth noting. Even for concrete A, with a relatively high w/c ratio (0.58), the absorption did not exceed 3.9%.

The influence of aggregate type on the properties of the concretes is not significant. Practically no differences between concrete B and C (partial replacement of gravel by basalt) were observed.

4.1. Resistance to the de-icing agents

The study of concrete resistance to the effects of de-icing agents was conducted in accordance with the one of RILEM recommended method [14].

A 3% solution of NaCl was used. The samples were frozen at a temperature of -20 ± 2 °C. After each freezing/thawing cycle a visual macroscopic assessment of samples was conducted, while at the end of the

Table 4
Physical characteristics of fresh concrete mixes and hardened concrete

Properties	Concrete type			
	A	B	C	D
Slump (cm)	15.5	15.5	15.0	14.5
Air content (%)	1.1	6.2	5.0	5.1
Apparent density (kg/m^3)	2330	2219	2292	2280
Absorption (% mass)	3.9	3.4	3.1	3.3
Compression strength (MPa)				
7 days	19.3	17.0	20.9	19.8
14 days	28.8	23.5	28.1	27.6
28 days	38.3	35.5	39.3	37.8

Table 5
Concrete resistance to the action of de-icing agents

	Concrete type			
	A	B	C	D
No. of freeze/thaw cycles	14	50	50	50
Degree of surface damage	4	2	2	1
Weight loss (kg/m^2)	10.5	1.1	1.6	0.7

50 cycles the loss of mass was also established. Six samples for each type of concrete were tested and average results were calculated. Table 5 presents the results of observations and measurements conducted for different concrete types.

The results show significantly high influence of air content and polypropylene fibres addition on the concrete resistance to the action of de-icers.

Concrete A without air-entraining agent showed such a serious damage as early as after 14 cycles of freezing and thawing that the experiment was stopped. However, the introduction of air-entraining agent (concretes B and C) definitely improved concrete resistance.

For the B concrete (air content = 6.2%) the surface damage after 50 cycles was relatively small (1.1 kg/m^2). A decrease in the air content to the level of 5.0% (concrete C) brought about a certain increase in damage, but it still had a relatively high resistance.

It should also be emphasised that in the case of concretes B and C scaling occurred only during the approximately first 15 cycles. In the case of a greater number of freezing/thawing cycles practically no progress in the degradation of the surface was observed.

Especially interesting results were found for the concrete containing polypropylene fibre (D). After 50 freeze/thaw cycles only very limited scaling (0.7 kg/m^2) was observed.

5. Study of the phase composition

The XRD technique was used to study the phase composition of the surface layer of control concrete (A). Fig. 3 presents the XRD diffraction pattern of sample A.

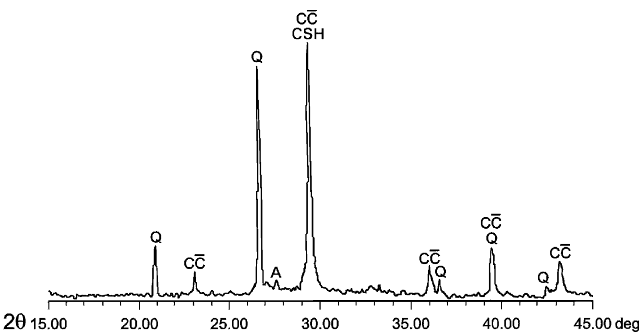

Fig. 3. Diffraction pattern of the surface layer of blast-furnace slag cement concrete.

It can easily be seen that apart from some inclusions of quartz (from the aggregate) the sample contains calcite ($C\overline{C}$) as dominating phase. Traces of aragonite (A) were also present.

6. Conclusions

A significant influence of air-entraining agent and synthetic micro-fibres addition on the resistance of slag cement concrete—to the effect of de-icing salts action have been proved in this work.

Slag cement concretes without air-entraining admixture show significantly lower air content than typical OPC concrete. The tests showed that effectiveness of air-entraining agent in fresh concrete mix was much lower for slag cement concrete than for OPC concrete. For the same air content the dosage of air-entraining admixture should be even two times higher than for OPC concrete.

Low water absorption of slag cement concrete (3.1–3.9%) did not influence significantly the resistance to de-icing agent action.

The influence of the aggregate type (replacement of gravel by basalt) on the de-icing agent action was not observed.

Phase composition observations (XRD) of concrete surface confirmed Stark [5] results and showed the presence of metastable aragonite in this layer.

The research shows that the air entraining of the concrete mix up to the level of 5–6% gives high resistance to the action of de-icing agents, even at a relatively high value of the w/c ratio.

Apart from the air content, the addition of polypropylene fibres to the concrete mixtures was highly effective. For these samples scaling was the lowest.

In the light of the results thus produced it seems that high resistance of slag concretes to the action of de-icing salts can be achieved also for concretes with w/c ratio higher than 0.45.

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