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SURFACE SCALING RESISTANCE OF CONCRETE MODIFIED WITH BITUMINOUS ADDITION

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Abstract. Deterioration of concrete due to surface scaling is a very serious durability problem faced by the construction industry in cold environments. The experimental results of resistance to scaling due to cyclic freezing and thawing in the presence of 3 % NaCl solution (de-icing agent) of not air-entrained concrete with and without bituminous addition are presented and discussed in the paper. The results have been analysed using the analysis of variance and regression to verify the effect of addition content, number of freeze-thaw cycles and the sort of cement on concrete ability to scaling. The statistical analysis showed that the bituminous addition significantly improves the scaling resistance of Portland cement concrete.

Keywords: concrete, de-icers, freeze-thaw resistance, scaling, bituminous addition, analysis of variance, regression.

1. Introduction

The exposed surfaces of concrete structures are subjected to the attack of deleterious agents such as temperature, sun, moisture, chlorides, carbon dioxide, etc, which cause the rapid deterioration of concrete structure. Cyclic freezing and thawing is a particular problem for concrete structures exposed to chlorides, such as: marine structures, particularly in splash and tidal zones, parking garages, in the areas exposed to de-icing salts and highway structures, such as bridge decks and other elevated roadways. Surface scaling due to freezing in the presence of de-icer salts is a much more complex problem than frost induced internal cracking. The complexity of the phenomenon is related to the fact the deterioration affects the very surface layer of concrete [1–4]. Therefore it is vital to focus attention on those properties of the concrete near the exposed surface, which allow the ingress of deleterious agents.

The need to extend concrete durability has led to the use of several admixtures and modifications to the concrete composite.

The modification of the concrete with bituminous addition, introduced during mix preparation, is an effective method of concrete protection against damaging influence of the corrosion causing media as well as the freezing in the presence of de-icing salts. The application of bituminous additions leads to the formation of hydrophobic coating on the walls of fine pores and capillaries and makes chlorides and other agents penetration difficult and limits their contact with hardened cement paste [5, 6].

In the cause considered the composition of bituminous addition – the asphalt solution in high-boiling organic solvent – does not disturb cement hydration process, makes the concrete batch homogenisation possible and allows obtaining the concrete containing even up to 20 % of addition related to cement mass, laid out evenly in the hardened paste [7, 8].

The current investigation was carried out with the primary objective to assess the long-term performance of the concrete containing bituminous addition in a freeze/thaw with chloride exposure regime.

2. Experimental investigation

2.1. Materials

The tests were carried out for fine-grained concrete. All tested concrete mixes were characterised by identically plastic consistence, which demanded the correction of water amount each time. The addition of bituminous paste was included in the batch of concrete by suitable reduction of aggregate amounts. Two sorts of Portland cement recommended for bridges and highway structures were used: the sulphate resistant CEM I 42.5 HSR NA (C1), and moderate sulphate resistant CEM I 42.5 MSR NA (C2). The mineral compositions of cements used are presented in Table 1. The cement content in tested concretes was constant (450 kg/m^3).

The fine aggregate used was quartz sand, the coarse aggregate - basalt grit. The bituminous addition – industrial asphalt solution in high-boiling organic solvent –

Table 1. Composition of cements used

Cement	Content in mass, %					
	C_3S	C_2S	C_3A	C_4AF	Na_2O_{eq}	SO_3
CEM I 42.5 HSR NA (**C1**)	61,3	14,6	2,1	15,6	0,49	2,33
CEM I 42.5 MSR NA (**C2**)	59,7	15,5	7,8	10,5	0,54	1,79

was a modifying component. The concrete mix compositions are given in Table 2.

The tests were carried out on specimens prepared of mixtures with two different values of addition content as well as on the unmodified control specimens. The analysis of the previous test results, described in details in [7, 8], shows the possibilities of composite properties forming towards obtaining the advantageous applicable qualities. The content of the bituminous paste related to cement mass (p/c ratio), determined by previous test results, was 0,11, 0,13 for cement C1 and 0,095, 0,11 for cement C2. A water to cement ratio in the tested concretes ranged from 0,355 to 0,395 (dependably on the bituminous paste content).

2.2. Test specimens preparation

The concrete resistance to scaling due to cyclic freezing and thawing with de-icing salt saturation was determined according to standard [9] (the Borås method). It is the most severe method of frost resistance test [1, 2]. The behaviour of concrete under field exposure conditions is simulated, the type of deterioration is found in real structures and the test results evaluation is quantitative.

The bituminous paste of plastic consistence was added to the dry mix of cement and aggregate. After homogenisation of dry components in mixer the water was added. The test specimens were cast and compacted on a vibrating table in 150 mm cube moulds. After 24 hours of curing, the specimens were removed from the mould and stored for 6 days in tap water, and for next 14 days – in the climatic chamber (20 °C, 65 % RH).

Every series was composed of 3 cubes. After 21 days a 50 mm thick specimen was sawn from each cube perpendicular to the top surface, so that the saw cut for the freeze surface was located in the centre of the cube. The rubber sheet was glued to all surfaces of the specimen except for the test surface. The edge of the rubber sheet reached 20 mm above the test surface. Then all surfaces of the specimen except for the test surface were thermally insulated. Top specimen surface was saturated with demineralised water during 72 hours. Immediately before the specimens were placed in the freezing chamber, the demineralised water was replaced with 3 % NaCl solution. The freezing medium was prevented from evaporating by applying a flat polyethylene sheet, as shown in Fig 1.

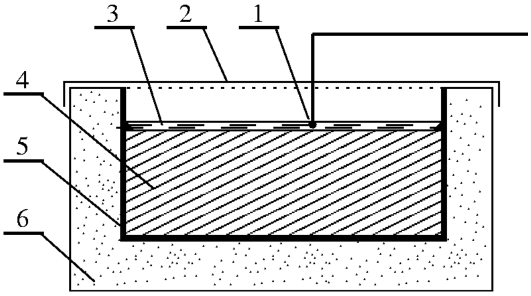

Fig 1. The test specimen used for freeze-thaw test: 1 – temperature measuring device; 2 – polyethylene sheet; 3 – freezing medium; 4 – specimen; 5 – rubber sheet; 6 – thermal insulation

2.3. Test procedure

In freezing chamber with temperature and time controlled refrigerating and heating system, the specimens were subjected to repeated freezing and thawing. During the test cycle, the temperature in freezing medium fell within the graph shown in Fig 2.

Every 7 days NaCl solution was exchanged. The material that had scaled from the test surface was collected and dried to constant weight. The amount of thescaled material per unit area after n cycles m_n was calculated for each measuring occasion and each specimen.

Table 2. Compositions and the selected properties of the concrete tested

Cement sort	p/c	w/c	Components, kg/m^3					Concrete density, kg/m^3	Water absorbability, %
			Cement	Bituminous addition	Sand 0–2 mm	Grit 4–8 mm	Water		
C1	0,0	0,395	450	–	806	988	178	2374	4,28
	0,095	0,380	450	42	760	940	171	2317	1,87
	0,11	0,370	450	49	758	936	166	2304	1,91
C2	0,0	0,395	450	–	806	988	178	2380	4,33
	0,11	0,370	450	49	758	936	166	2327	1,92
	0,13	0,355	450	58	754	930	160	2310	2,02

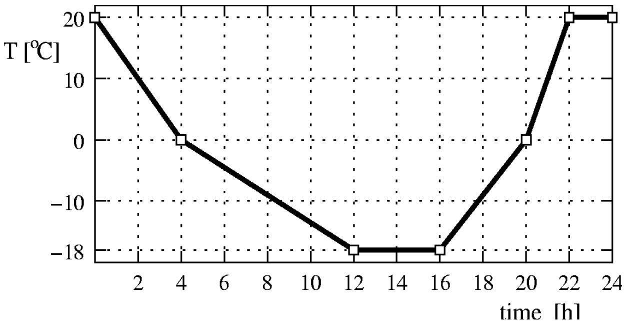

Fig 2. The time-temperature cycle in the freezing medium

The mean mass of scaled material after 28, 56 and 112 cycles is used for evaluating the scaling resistance, according to criteria presented in Table 3. In the case of concrete with addition improving frost resistance, the number of freeze-thaw cycles may exceed 112.

Table 3. Criteria of the scaling resistance evaluation

Scaling resistance	Requirements
Very good	$m_{56} < 0{,}10$ kg/m^2
Good	$m_{56} < 0{,}20$ kg/m^2 or $m_{56} < 0{,}50$ kg/m^2 and $m_{56}/m_{28} < 2$ or $m_{112} < 0{,}50$ kg/m^2
Admissible	$m_{56} < 1{,}00$ kg/m^2 and $m_{56}/m_{28} < 2$ or $m_{112} < 1{,}00$ kg/m^2
Inadmissible	$m_{56} > 1{,}00$ kg/m^2 and $m_{56}/m_{28} > 2$ or $m_{112} > 1{,}00$ kg/m^2

The concrete specimens with bituminous addition were subjected to 252 freeze-thaw cycles. The testing of the specimens without addition was terminated after 126 cycles because of severe damages, making further investigation impossible.

3. Analysis of test results

The scaling resistance evaluation of the tested concrete is presented in Table 4, and the test results are given in Fig 3.

As shown in Table 4, only the frost resistance of concrete with bituminous addition, evaluated according to the criteria of Table 3, was very good.

It may be seen from Fig 3 that the concrete with bituminous addition showed significantly more improved resistance to cyclic freezing and thawing in the presence of 3 % NaCl than unmodified concrete (Fig 3). In the range from 40 to 80 cycles the increase in mass of scaling for unmodified concretes was stabilised but exceeded tenfold respective value for modified concretes made with both sorts of cement.

For unmodified concretes, after 80 freeze/thaw cycles, a sudden increase in scaling was observed and after 126 cycles the mass of scaling reached 2,77 kg/m^2 (cement C1) and 1,57 kg/m^2 (cement C2). In the case of the concretes containing bituminous addition, made with the same cements, the mass of scaled material was respectively ~18 and 16 times smaller.

In the case of the cement C1 concretes with bituminous addition the mass of scaling dependence on addition content was observed. Moreover, the mass of scaling was greater for p/c = 0,13 than for p/c = 0,11. At the same time for the cement C2 concretes with bituminous addition, the increase in mass of scaling was 2 times smaller and was independent of p/c value in tested range.

The effects of number of cycles n (factor A), p/c value (factor B) and cement sort (factor C – qualitative) on mass of scaling residue m (variable Y) have been studied using the method of analysis of variance. In this analysis both the basic effects and the higher order interactions are analysed. For statistical interpretation of regression and analysis of variance it is assumed that the data is normally distributed.

For each sample, consisting of three replicates, the mean value Y_{ijk} and the variance S^2_{ijk} were calculated.

Before the proper analysis the Cochran's G test was used as the homogeneity test. The results of scaling residue measurements for 6 concrete mixes after 14, 42, 70, 98 and 126 freeze-thaw cycles were taken into account. The test showed that for 30 means and the degrees of freedom df = 2, the calculated value is equal to:

$$G_{ijk\,\max} = S^2_{ijk\,\max} / \Sigma S^2_{ijk} = 0{,}0174/0{,}0972 = 0{,}1790, \quad (1)$$

for level of significance α = 0,05, is less than $G_{0.05,2,30}$ = 0,1980 [10], thus the compared variances are homogeneous and the test results are reproducible. The analysis of variance was carried out in compliance with proce-

Table 4. Evaluation of concrete resistance to cyclic freezing and thawing with de-icing agent

Cement sort	p/c	Mean mass of scaling after n cycles, kg/m^2			Scaling resistance according to criteria – Table 3
		m_{28}	m_{56}	m_{112}	
C1	0,0	0,535	0,702	1,741	Admissible
	0,11	0,051	0,061	0,092	Very good
	0,13	0,077	0,100	0,178	Very good
C2	0,0	0,174	0,251	0,925	Admissible
	0,095	0,054	0,074	0,087	Very good
	0,11	0,057	0,073	0,095	Very good

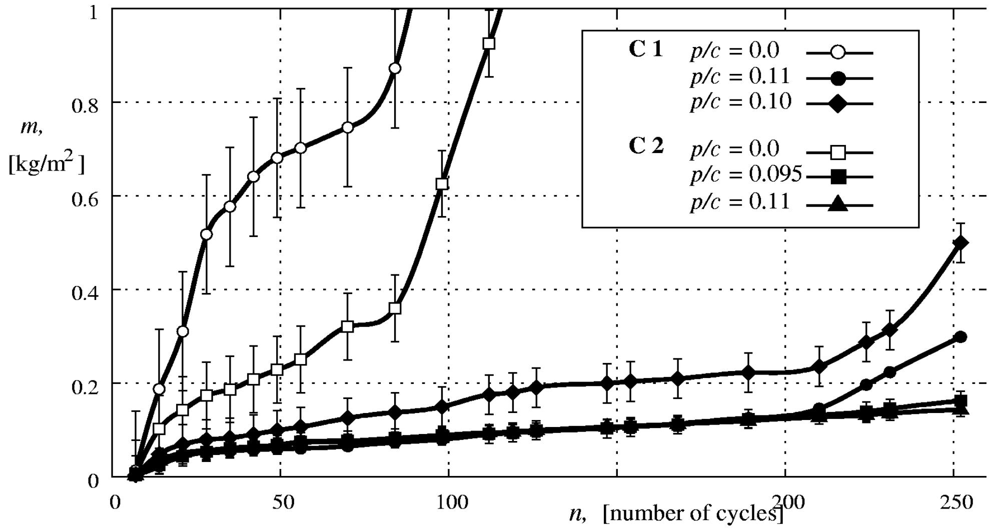

Fig 3. Mean mass of scaling residue *m* vs freeze–thaw cycles number *n* as well as *p/c* value (vertical bars represent the range of accuracy)

dure given in [10]. The results of the analysis are given in Table 5.

The F-Fisher test [10] was used to verify the hypothesis that the A, B and C factors had a significant effect on concrete resistance to scaling. The influence of the individual factor or the interaction is recognized as significant if

$$F_{\exp} > F_{tab} = F_{\alpha, f_1, f_2}, \qquad (2)$$

where: $\alpha = 0{,}05$ – level of significance, f_1, and f_2 – degrees of freedom.

As a result of analysis of variance, it has been found that individual factors and the first-order interactions as well as the second-order interaction have significant effect on the mass of scaling due to cyclic freezing and thawing. The percentage fraction of factors and interactions influence h was calculated (Table 5).

The ranges of accuracy (Fig 3) for individual curves were calculated according to formula:

$$\Delta_i = \pm t\sqrt{S_i^2/n}, \qquad 3)$$

where t = 1,96 – the value of argument of Laplace's function for confidence level P = 0,95 [10], S_i^2 – mean variance for individual curve, n = 3 – number of replicates.

For predicting concrete resistance to scaling, mathematical model describing the increase in mass of scaling m (function $\hat{Y}$) in dependence on selected factors was developed. Only the effect of the quantitative factors was taken into account: *p/c* ratio (factor X_1) and the number of cycles n (factor X_2), separately for each cement sort.

For mathematical model elaboration significant for practice factor's levels were selected:

- factor X_1: 0,11, 0,13 (for cement C1); 0,095, 0,11 (for cement C2),
- factor X_2: 14, 49, 84, 119, 154, 189, 224 cycles.

Table 5. Analysis of variance results

Source of variation	Sums of squares	Degrees of freedom	Mean squares	F_{exp}	F_{tab}	η (%)
Factor A	$S_A^2 = 5{,}841$	4	1,460	449,86	2,52	19,08
Factor B	$S_B^2 = 11{,}744$	2	5,872	1809,00	3,15	38,36
A and B	$S_{AB}^2 = 9{,}393$	8	1,174	361,72	2,10	30,68
Factor C	$S_C^2 = 0{,}922$	1	0,922	284,14	4,00	3,01
A and C	$S_{AC}^2 = 0{,}391$	4	0,098	30,10	2,52	1,28
B and C	$S_{BC}^2 = 1{,}496$	2	0,748	230,45	3,15	4,28
A and B and C	$S_{ABC}^2 = 0{,}637$	8	0,080	24,52	2,10	2,08
Error	$S_Z^2 = 0{,}195$	60	0,003	–	–	0,64

As a function describing the increase in mass of scaling due to cyclic freezing and thawing the orthogonal polynomial was assumed. The values of regression equation's coefficients were determined using the least square method. The calculations were conducted using the Data Analysis Programs | STAT [11]. The values of factor X_2 were divided by 250 to facilitate the calculation.

The relationship for the cement C1 concrete has been obtained as:

$$\hat{Y}1 = -0{,}5828X_2 + 6{,}6820X_1X_2 + 0{,}0287, \qquad (4)$$

for the cement C2 concrete:

$$\hat{Y}2 = 0{,}1469X_2 - 0{,}3081X_1X_2 + 0{,}0371. \qquad (5)$$

The adequacy of the relationships obtained was tested using the F-Fisher test. The experimental F-value for concretes made with cement C1 is equal $F_{exp1} = 0{,}92$ and for concretes made with cement C2 – $F_{exp2} = 0{,}86$. The critical F-value, for a = 0,05 and degrees of freedom $f_1 = N - d^* = 14 - 3 = 11$ and $f_2 = N\ (n–1) = 14(3–1) = 28$, is equal $F_{crit} = 2{,}15$. The degrees of freedom were calculated considering: N – number of variances – 14, d^* - number of relationship coefficients - 3 and n – number of replicates – 3. The experimental values F_{exp} are less than the critical value F_{crit}; thus the relationships obtained can be estimated as good fitted.

4. Interpretation

In order to make the test results interpretation easier, the relationships (4) and (5) were presented graphically in the form of isolines (Fig 4).

The analysis of relation $m = f(p/c,\ n)$ (Fig 4a) for cement C1 concrete showed significant difference in the increase of surface scaling due to cycling freezing and thawing for different *p/c* values. For *p/c* = 0,11, during the test (between 14 and 224 cycle) the *m* value increase amounted 0,14 kg/m^2, whereas for p/c = 0,13 the mass of scaled material reached 0,24 kg/m^2, it means almost 1,7 times greater value. It may be seen from Fig 4a that the mass of scaling increases together with p/c value increase. Thus, the change in *p/c* value from 0,11 to 0,13 causes the straying from the optimum value.

The analysis of the same relation for cement C2 concrete (Fig 4b) showed that the increase in *m* value, during 210 test cycles, for *p/c* = 0,095 and *p/c* = 0,11 reached 0,098 kg/m^2 and 0,095, respectively. The increase in *p/c* value caused slight decrease in mass of scaling. Thus, the values of *p/c* ~ 0,11 are closed to optimum value.

Developed statistical models can serve as a useful tool for optimising and predicting concrete ability to scaling according to *p/c* value (in range tested) and the number of freeze/thaw cycles.

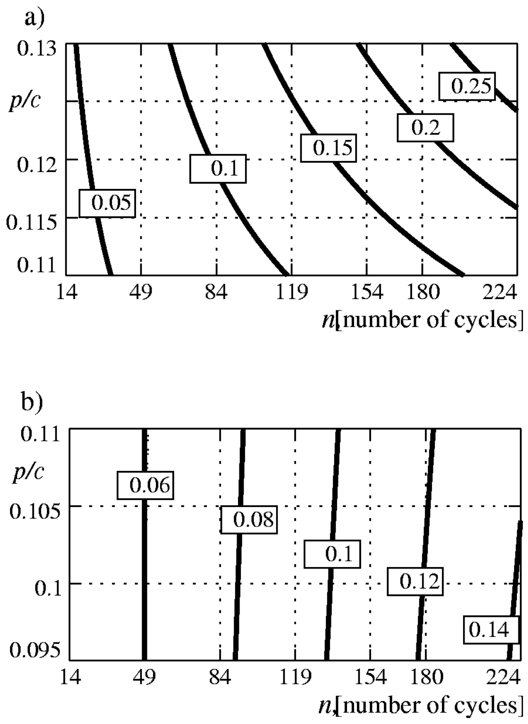

Fig 4. Isolines of scaling residue $\hat{Y}$ (m, kg/m^2) versus X_1 (p/c values) as well as the number of freeze/thaw cycles X_2 (n): a) for cement C1 concretes; b) for cement C2 concretes

5. Conclusions

1. The concrete made with cements tested, contained bituminous addition, showed significantly more improved resistance to cyclic freezing and thawing in the presence of 3 % NaCl than control plain concrete. After 126 freeze/thaw cycles the mean mass of material, which scaled from the test surface of modified concrete was ~18 times (cement C1) and ~16 times (cement C2) smaller than the mass of scaled material – for concrete without addition.
2. The sort of cement, the bituminous addition content (expressed in *p/c* ratio) as well as the number of cycles have significant effect on the mass of scaled material. The *p/c* value and the number of cycles have the greatest influence expressed in the percentage fraction, 38 % and 19 % respectively. The influence of the sort of cement was the smallest one.

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