ISSN 1330-3651
UDC/UDK 691.32 : 620.17

CONCRETE RESISTANCE TO FREEZING AND THAWING EFFECTS

Ana Hranilović Trubić, Dunja Mikulić, Srđan Uzelac

Preliminary notes

Concrete durability is a capacity of concrete to resist the changes of its properties. Concrete structures should be designed and performed in the way that, under expected environmental conditions, their safety and usability hold over the structure's lifetime with minimal repair and maintenance costs. Long-life concrete must be resistant to destruction when exposed to agressive environment like, among other things, the freezing effect with or without deicing salt. Direct testing methods in Croatia so far have not provided for timely information about the required concrete resistance to the freezing and thawing effects. The aim of this paper is the analysis of the air voids parameters in fresh concrete and the proving of the concrete resistance to the freezing and thawing effects already in fresh concrete. Thirty nine (39) concrete mixtures have been prepared and all the concrete's physical and mechanical properties have been tested. Mixtures are prepared with two cement types and five types of air entraining admixtures out of which one is selected and used. The assessment of concrete resistance obtained in fresh concrete is compared with assessments obtained in hardened concrete. By means of an air pores analyzer, it is proved that it is possible to make necessary corrections of the concrete composition in the mixing stage and avoid additional costs of repair works. With a proper pre-selection of concrete components by the "AVA method", a reliable perception of the resistance to freezing in fresh concrete is possible already during mixing. Also, checking by the microscopic method in hardened concrete has significantly reduced time necessary for the execution of preliminary testing by the alternating freezing and thawing cycles.

Key words: *hardened concrete, fresh concrete, thawing, freezing, air voids, spacing factor, specific surface*

Otpornost betona na djelovanje smrzavanja i odmrzavanja

Prethodno priopćenje

Betonske konstrukcije trebaju biti projektirane i izvedene tako da pod očekivanim uvjetima okoliša očuvaju sigurnost i uporabljivost s minimalnim troškovima održavanja. Dugotrajni betoni moraju biti otporni na razaranje kada su izloženi agresivnom djelovanju okoliša, među ostalima djelovanju smrzavanja s ili bez soli za odmrzavanje. Cilj ovoga rada je analiza zračnih pora u svježem betonu i dokazivanje otpornosti betona na djelovanje smrzavanja i odmrzavanja već na svježem betonu. Napravljeno je trideset i devet mješavina betona i ispitana su fizička i mehanička svojstva. Mješavine su pripremljene s dvije vrste cementa i jednom vrstom aeranta. Rezultati ispitivanja otpornosti betona na smrzavanje i odmrzavanje na svježem betonu uspoređeni su s rezultatima dobivenim na očvrslom betonu. Upotrebom analizatora zračnih pora moguće je izvršiti potrebne korekcije sastava betona u fazi spravljanja te izbjeći naknadne troškove sanacijskih radova. Pravilnim odabirom sastojaka betona "AVA metodom" omogućena je pouzdana spoznaja o otpornosti betona na smrzavanje na svježem betonu već tijekom spravljanja. Također, provjerom mikroskopskom analizom na očvrslom betonu bitno se smanjuje vrijeme potrebno za provedbu prethodnih ispitivanja.

Ključne riječi: *očvrsli beton, svježi beton, odmrzavanje, smrzavanje, zračne pore, faktor razmaka, specifična površina*

1 Introduction
Uvod

The problem of the concrete structures' durability, particularly reinforced concrete structures, is today the basic, almost existential problem in concrete construction industry.

Concrete is found in the conditions of very low but also very high temperatures. Concrete is often used in the freezing and thawing conditions. During these cycles concrete can significantly expand and shrink which is caused by a change of liquid and solid water states in the concrete's microstructure. The material expanding and shrinking processes may fatigue the concrete microstructure in time and result in the destruction and final collapse of material.

The freezing and thawing cycles are one of the factors which contribute to the premature concrete damage (Figure 1 and 2).

Until recently, the only method for the assessment of a total air voids system in concrete was the concrete sampling after hardening. Since the concrete sample is usually taken at least seven days after placing, the results are obtained too late to do any changes in a concrete mix.

The analysis of the fresh concrete air voids ("AVA method") is a method which can be used for a precise assessment of the fresh concrete air voids system. The concrete sample is usually obtained in situ. With results

Figure 1 / Slika 1.

Figure 2 / Slika 2.

obtained in less than an hour (usually in 30 minutes), the concrete quality control adjustments during concrete mixing can be made. This is necessary for the improvement of the distance between voids and thus increasing the durability in the freezing and thawing processes.

The aim of this paper is the analysis of the air voids parameters in fresh concrete and the proving of the concrete resistance to the freezing and thawing effects with or without deicing salt already in fresh concrete. The results of concrete resistance to freezing and thawing obtained in fresh concrete are compared to the results obtained in hardened concrete (by a microscopic analysis and the alternative freezing and thawing cycles).

1.1 Regulations
Regulativa

The spacing factor as a criterion for the resistance determination of concrete exposed to the aggressive environmental impact is for the first time mentioned in the technical regulation for concrete structures (TPBK, Official Gazette 101/2005) contrary to the former PBAB (1987) (Table 1 and 2).

Table 1 / Tablica .1

Class mark	Environment description	Standard HRN U.M1.016:1977
XF1	Moderate water saturation without deicing salt	At least 100 cycles
XF3	High water saturation without deicing salt	At least 200 cycles

Table 2 / Tablica 2.

Class mark	Environment description	Standard HRN CEN/TS 12390-9:2006
XF2	Moderate water saturation with deicing salts	28 cycles
XF4	High water saturation with deicing salts or sea water	56 cycles

1.2 Voids in concrete
Pore u betonu

In the moment of cement and water mixing a formation of the system of voids takes place.

In concrete, we distinguish closed or isolated voids and open (passable and baggy) voids (Figure 3). The formation of the voids system is affected by the w/c ratio, type and characteristics of cement, its activity and particles' dispersion and conditions of hydration development, the degree of pro-reaction and presence of different additives, especially the air entrained agents.

The air entrained agents are chemical additives which enable air entrainment into concrete and creation of numerous tiny air voids incorporated within the cement composite. This helps to increased workability of a fresh mass and consequently, better freezing resistance.

During mixing of concrete components, two main processes take place. The first one is the air entrainment by a whirl created by mixing ad then the entrained air is dispersed and broken into tinier voids by the action of shared forces. The second process is related to aggregate which acts as a so called "three-dimensional sieve" by which air voids are entrained and retained within aggregate particles and it is very significant for the air voids distribution. Concrete without added air entrained agent has a certain content of entrained air which is called "trapped air". Air voids entrained within the plastic cement composite without added air entrained agent isolate from the fresh mass to the greatest extent (voids join together and rise to the surface).

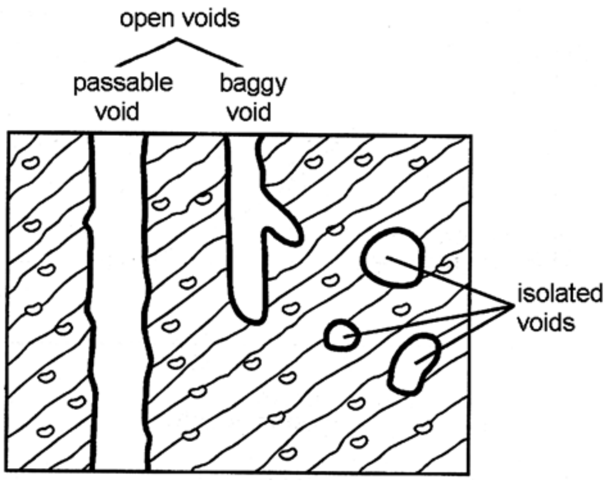

Figure 3 Schematic presentation of void types in hardened cement paste [3]
Slika 3. Shematski prikaz tipova pora u očvrsloj cementnoj pasti [3]

According to size, voids can be classified as presented in Table 3.

Table 3 / Tablica 3.

Size of voids	Voids orientational Ř
Void gel (micro-cracks)	2 nm
Capillary voids	50 nm
Entrained air voids	0,05 mm
Micro-craks	0,2 mm
Craks	0,5 mm
Cavities	1,0 mm

Quantity and size of air voids are affected by: nature and quantity of an air entrained agent, nature and size of the constituents in the air entrained agent, concrete composition, aggregate, quantity of finely dispersed material, temperature, chemical composition of cement, method and duration of a mixing process, fresh concrete consistency, method and degree of a compaction during the concrete placing.

1.3 Concrete structure
Struktura betona

Concrete has a heterogeneous structure which can be observed at three levels: macro, meso and micro level. At the macro level, concrete is a homogeneous material with macroscopic properties, a composite of aggregate and air voids in a cement paste. At the meso level, the sferic cavities are visible entrained by the air entrained agent of 50 to 100

Table 4 / Tablica 4.

Degree of damage	Mass loss, mg/mm^2	Max. depth of damage, mm	Visual description	Assessment criterion
0 - without scaling	0	0	No changes at surface	Resistant
1 - poor scaling	0,2	1	Damage of fine mort	Resistant
2 - mid scaling	0,5	4	Damaged surface, observed individual aggregate grains	Non-resistant
3 - extensive scaling	1,0	10	Observed aggregate grains over the whole surface	Non-resistant

µm ratio. At the micro level, it can be observed that the structure of calcium-silicate-hydrate is not homogeneous, in some areas it is dense and in others highly porous.

The destruction of concrete caused by freezing increases water volume by 9 %. Water which freezes in voids (where a critical saturation of 90 % is achieved) squeezes part of non-freezed water out to the non-freezed surrounding area. If distributed voids are close enough that water may expand (spacing factor <0,2 mm), the pressure which is destructing concrete will not occur. If water freezes in larger voids, created ice has less free energy from non-freezed water in the neighboring smaller voids, potentials are created and non-freezed water diffuses towards formed ice and the pressure is created.

1.4 Testing methods
Ispitne metode

1.4.1 Most frequently used testing methods for concrete resistance to freezing and thawing in the Republic of Croatia
Najčešće korištene metode ispitivanja betona na djelovanje mraza i soli u Republici Hrvatskoj

Methods for the testing of concrete resistance to freezing effect with or without deicing salt may be direct where testing is performed by the alternate freezing and thawing cycles according to the stipulated standards, or indirect performed by measurement of the air voids system (total air content, spacing factor, specific surface). So far, mainly direct testings (HRN U.M1.055:1984) have been performed in Croatia and in rare cases indirect (HRN U.M1.056:1977).

HRN U.M1.055:1984 – Testing of the concrete surface resistance to frost and deicing salts impact. The testing is performed on three samples of 150 × 150 × 150 mm. The testing commences with a sample of 28 days and lasts for 25 cycles (1 cycle=24 hours). At each 5th cycle, a possible damage is measured and concrete is assessed after 25th cycle (Table 4) [4].

HRN U.M1.056:1987 – Testing of the air entrained concrete's resistance to frost action and the concrete surface resistance to the frost and deicing salts impact by a linear microscopic analysis. Samples are obtained from a cube or a cylinder. Testing is performed on plates of 10 × 10 cm area or 10 × 15 cm. Three parameters are determined: air voids content, spacing factor and specific surface. The linear microscopic analysis is conducted according to conceived lines (for D_{max}=16 mm and 32 mm is 240 cm) [5].

1.4.2 Used testing metods
Korištene ispitne metode

Determination of concrete resistance to freezing and salt at fresh concrete (AVA method). A syringe is used to extract a 20 cm^3 mortar sample from the cage (Figure 4).

Figure 4 / Slika 4.

Figure 5 / Slika 5.

Mortar is injected into the viscous, blue liquid at the bottom of the AVA cylinder. The sample is gently stirred for 30 seconds. Air bubbles are released from mortar and rise through the viscous liquid and then through water in the cylinder. The rate the bubbles rise at is a function of their

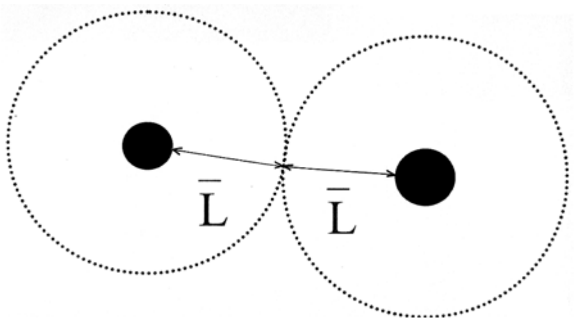

Figure 6 / Slika 6.

size; larger bubbles rise faster than smaller ones, according to the Stoke's Law. The bubbles collect at the top of the cylinder under a buoyancy recorder bowl attached to a balance. The buoyancy of the bowl changes over time as air bubbles accumulate. The weight change over time is recorded for 25 minutes or until no weight change is recorded for 2 consecutive minutes. The arrival rate of air bubbles indicates their size. Their volume is calculated from the weight change. The AVA is used in conjunction with a laptop computer. Computer software uses an algorithm to determine the specific surface, spacing factor, and entrained air content (Figure 5).

Air void – a space entrapped by cement paste and filled with air. Spacing factor – a parameter related to the maximum distance in the cement paste from the periphery of an air void. Specific surface – the surface area of air voids divided by their volume (Figure 6).

The air voids analyzer determines the quantity and distribution of air bubbles <3 mm. It is very important that the liquid temperature during measurement remains in the range the system is calibrated for (21 - 25 °C). The instrument is applicable only at fresh concrete with a minimal slump of 1 cm and the entrained air quantity between 3,5 and 10 %.

Determination of concrete resistance to the impact of frost and salt at hardened concrete (microscopic analysis) (HRN EN 480-11:2005). Determination of air void characteristics in hardened concrete is performed in accordance with HRN EN 480-11:2005 - Admixtures for concrete, mortar and grout – Test methods – Part 11: Determination of air void characteristics in hardened concrete [6]. Samples of hardened concrete are cut out from concrete cubes with dimensions of 150×150×150 mm. When a sample is cut out from a concrete cube it is necessary to prepare the sample for the air void determination. The analyzed surface needs to be prepared in the manner that a void present at surface becomes as sharp as possible without any interstice at their edges and as much as possible similar to ideal circle. The software in RapidAir 457 (Figure 7) presumes all voids as ideal circle during traversing the sample surface and that is the reason why it is important to prepare the samples' surface in such manner. The sample cut out from the concrete cube needs to be prepared by means of polishing equipment. At the beginning of the procedure, the surface has to be grinded with coarse silicon powder to level the uneven surface resulting from the sample cutting from the concrete cube.

After this first step, the sample preparation proceeds with the silicon small-grain powder polishing. At the end of the polishing procedure the concrete sample needs to be very smooth with sharp air voids edges. Now, on the well polished sample surface it is important to produce contrast enhancement between air voids and the rest of concrete sample, cement paste and aggregates. Polished surface can be colored black with black marker pen. Black color covers only cement paste and aggregate, while air voids are filled with white $BaSO_4$ powder. This is the way how to make contrast enhancement between air voids in hardened concrete and the remaining part of concrete sample. The quality of contrast enhancement is checked by means of stereomicroscope.

This method for determination of concrete durability to freezing according to HRN EN 480-11:2005 can be performed with the 7 days old concrete sample. The sample preparation according to HRN EN 480-11:2005 requires about 15 min for cutting from the concrete cube, 120 min for good surface polishing, 60 min for surface contrasting and drying on 60 °C and, at the end, 15 min for the sample analysis of the final air void characterization in hardened concrete by means of the RapidAir 457 instrument. Total required time for concrete durability testing to freezing according to this method, from the time of the concrete placing into the mould to the time of air void characterization, is about 10 days.

Total air content is calculated according to the following formula:

$$A = \frac{T_{\mathrm{a}}}{T_{\mathrm{tot}}} \cdot 100$$

required as % through a volume, where:

T_{tot} - total traverse length $T_{\mathrm{tot}} = T_{\mathrm{s}} + T_{\mathrm{a}}$ in mm

T_{s} - length at a hard stage in mm

T_{a} - length over air voids in mm.

The air voids' specific surface is calculated according to the formula

$$\alpha = \frac{4 \cdot N}{T_{\mathrm{a}}} \text{ in mm}^{-1}$$

The spacing factor is calculated according to the formula

$$L' = \frac{3 \cdot \left[1{,}4 \cdot (1+R)^{\frac{1}{3}} - 1 \right]}{\alpha} \text{ in mm}$$

if R>4,342 (R is a ratio of the paste P and total air content A), or according to the formula

$$L' = \frac{P \cdot T_{\mathrm{tot}}}{400 \cdot N} \text{ in mm}$$

if $R \leq 4{,}342$.

Concrete is resistant if it is proved that the spacing factor of entrained air micropores is lesser than 0,20 and the specific surface greater than 25 mm^{-1} [6].

Determination of concrete resistance to the impact of frost and salt at hardened concrete (freezing and thawing cycles) (HRN CEN/TS 12390-9:2006). This determination has been conducted according to the standard HRN CEN/TS 12390-9:2006. This standard specifies three different methods for the concrete resistance determination. In this paper, a slab method is used. This method is used for

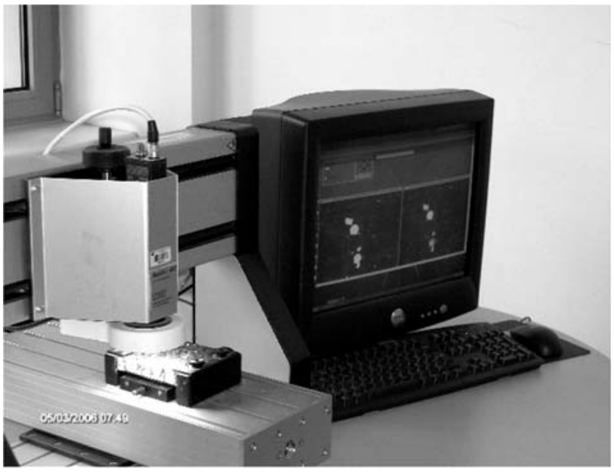

Figure 7 / Slika 7.

the determination of concrete resistance to freezing thawing cycles in contact with water or 3 % NaCl solution. Four test samples are in procedure, sawed from four different samples of concrete cubes. A test surface is the sawed surface and the only surface exposed to test conditions. All other surfaces of the test sample are covered with isolation materials. Samples have to be exposed to freezing and thawing. One cycle requires 24 hours. In each cycle temperature is above 0 °C at least 7 hours but no longer than 9 hours. After each 7^{th}, 14^{th}, 28^{th} and 42^{nd} cycles test samples should be drawn out from the freezer and scaled material should be collected from each surface. This material should be dried to constant mass and weight to the nearest 0,1 g. After that, new quantity of 3% NaCl solution should be placed to the sample surface and samples returned to the freezer. Scaled material is cumulatively added until 56^{th} cycles. The largest admissible mass deficit after 28 and 56 cycles is 1,0 kg/m^2 [7].

Concrete exposed to the aggressive impact of environment, with the exposure class XF2 is resistant to freezing thawing cycles and deicing salts if it fulfills the requirements of standard

HRN CEN/TS 12390-9:2006 for at least 28 cycles, and with the exposure class XF4 for at least 56 cycles.

2 Experimetal section
Eksperimentalni dio

A testing plan has determined mixing of the air entrained and reference concrete mixes where the cement type, w/c factor, type and quantity of the air entrained agent vary to determine what has the direct impact on the resistance of concrete to freezing and thawing. In the first testing stage, the possibility of formation of optimal micropores structure, which is one of conditions for the concrete resistance to freezing, is tested. (Testing process is shown in Table 5, 6 and 7). By a so called AVA-method, the air entrained agent with the best composition of entrained air, regarding the spacing factor and specific surface (Cementol ETA S), is selected. Testings have been performed with four air entrained agents from different manufacturers and one superplasticizer.

First, mixes of composition **I** have been mixed where the air entrained agent and superplasticizer are used as admixtures (Table 5). Five mixes have been mixed with different quantity of the air entrained agent. But, since the desired voids percentage is not obtained in these mixes, it is concluded that the interaction of this combination of the air

Table 5 / Tablica 5.

Group of mixes I		
Aggregate	Tounj (0-4, 8-16) mm	
Cement	CEM II/A-S 42,5R (360 kg/m^3)	
Air entrained agent	Meta-air	
Superplasticizer	Glenium 51 (0,5 %)	
Mark of mix	w/c	Quantity of air entrainment agent, %
1	0,45	0,050
2	0,45	0,055
3	0,45	0,045
4	0,48	0,050
5	0,50	0,050

Table 6 / Tablica 6.

Group of mixes II			
Aggregate	Tounj (0-4, 8-16) mm		
Cement quantity	360 kg/m^3		
Air entrained agent	Meta-air		
Superplastifizer	-		
Mark of mix	w/c	Cement type	Quantity of air entrainment agent, %
6	0,52	CEM II/A-S 42,5R	0,060
7	0,50	CEM II/A-S 42,5R	0,060
8	0,50	CEM II/A-S 42,5R	0,045
9	0,50	CEM II/A-S 42,5R	0,080
10	0,50	CEM III/B 32,5N-SR/LH	0,100
11	0,50	CEM III/B 32,5N-SR/LH	0,060
12	0,50	CEM III/B 32,5N-SR/LH	0,200
13	0,50	CEM III/B 32,5N-SR/LH	0,08

entrained agent and superplasticizer reduces the voids quantity and, consequently, testings on hardened concrete have not been performed.

At mixes **II**, the type of cement, w/c factor and air entrained agent's quantity have been varied (Table 6). Eight mixes have been mixed. The air entrained agent's portion was from 0,045 to 0,2 but the desired voids quantity has not been obtained also in these mixes and the usage of the air entrained agent Meta-air is given up and further tests on hardened concrete are not performed.

At mixes **III**, four types of air entrained agents are used in quantities recommended by manufacturers (Table 7). The air entrained agent Cementol ETA S has demonstrated the formation of the most favourable voids structure and thus, it is selected for further testings.

Table 7 / Tablica 7.

Group of mixes III		
Aggregate	Tounj (0-4, 8-16, 16-32) mm	
Cement	CEM III/B 32,5N-SR/LH (250 kg/m^3)	
w/c	0,54	
Superplasticizer	-	
Mark of mix	Air entrainment agent	Quantity of air entrainment agent, %
14	Meta-air	0,1
15	Monolit LP	0,2
16	Sika	0,2
17	Cementol ETA S	0,2

Table 8 / Tablica 8.

Group of mixes IV		
Aggregate	Tounj (0 -4, 8 -16, 16 -32) mm	
Cement quantity	300 kg/m^3	
Air entrainment agent	-	
Superplasticizer	-	
Mark of mix	w/c	Cement type
18	0,52	CEM III/B 32,5N -SR/LH
21	0,50	CEM III/B 32,5N -SR/LH
22	0,54	CE M III/B 32,5N -SR/LH
19	0,52	CEM II/A -S 42,5R
20	0,50	CEM II/A -S 42,5R
23	0,54	CEM II/A -S 42,5R

In Table 8, compositions of the reference mixes are presented. Table 9 presents compositions of the mixes V. Six mixes have been mixed and the water cement ratio has been varied as well as the air entrainment agent. Table 10 presents compositions of the mixes VI. Ten mixes have been mixed and water cement ratio has been varied, as well as quantities of the air entrainment agent and cement.

The laboratory concrete mixes are prepared with two cement types: CEM II/A-S 42,5R (mixed portland cement, 80-94 % portland cement clinker and 6-20 % slag from a furnace, strength class 42,5, high initial strength) and CEM III/B 32,5N-SR-LH (metallurgical cement containing 20-34 % portland cement clinker and 66-80 % of granulated furnace slag, strength class 32,5, ordinary initial strength, sulphate resistant, low hydration heat).

Table 9 / Tablica 9.

Group of mixes V		
Aggregate	Tounj (0-4, 8-16, 16-32) mm	
Cement	CEM II/A-S 42,5R (300 kg/m^3)	
Air entrainment agent	Cementol ETA S	
Superplasticizer	-	
Mark of mix	w/c	Quantity of air entrainment agent, %
24	0,52	0,20
25	0,52	0,15
26	0,50	0,20
27	0,50	0,15
28	0,52	0,30
29	0,54	0,15

Table 10 / Tablica 10.

Group of mixes VI			
Aggregate	Tounj (0-4, 8-16, 16-32)mm		
Cement	CEM III/B 32,5N-SR/LH		
Air entrainment agent	Cementol ETA S		
Superplasticizer	-		
Mark of mix	w/c	Cement quantity, kg/m^3	Quantity of air entrainment agent, %
30	0,52	300	0,20
31	0,52	300	0,15
32	0,50	300	0,15
33	0,50	300	0,20
34	0,54	300	0,15
35	0,52	300	0,30
36	0,50	320	0,20
37	0,52	250	0,20
38	0,52	250	0,20
39	0,50	320	0,20

Air voids characteristics (the spacing factor, entrained air content and specific surface) have been tested in fresh concrete (by the analyzer) and in hardened concrete (by the microscope). All the samples' pairs have been prepared from the same concrete mixes. Later, the results have been checked out by the direct testing of the concrete resistance to freezing with presence of deicing salts according to the HRN CEN/TS 12390-9:2006 standard.

3 Results
Rezultati

Comparing the results of mixes with same composition but mixed with different types of cement, it is obvious (Table 11-16) that the slump results obtained by the CEM II/A-S 42,5R cement are higher than those obtained by the CEM III/B 32,5N-SR/LH cement.

It is logical that the volume mass of fresh and hardened concrete was higher at reference than at aerated concretes (Table 11-16).

Quantity of the air voids in mixes prepared with the air entrained agent and superplasticizer was lower than in mixes prepared only with the air entrained agent. This has made it clear that the superplasticizer decreases the impact of the air entrained agent. The share of voids quantity has increased with the increase of the air entrained agent's share (Table 11-16).

The compressive strength decreases with the increasing share of the air entrained agent. Thus, the compressive strength is significantly higher at referent than at aerated concretes (Table 11-16). It can also be seen that the compressive strength of concrete mixes with cement class 42,5R (CEM II/A-S 42,5R) is higher than in concrete mixes with cement class 32,5N (CEM III/B 32,5N-SR/LH). At the group of mixes V, the compressive strength is over 32,0 MPa and at the group of mixes VI it is lower than 32,0 MPa.

In Table 14-16, the testing results of the concrete resistance to freezing and thawing effects according to HRN CEN/TS 12390-9:2006 standard are presented. It is evident that all referent concretes showed the concrete non-resistance to the freezing and thawing cycles which was actually expected because such concretes do not have the necessary quantity of voids and, consequently, no favourable concrete microstructure. All the mixes (24-29) prepared with cement CEM II/A-S 42,5R had the quantity of scaled material less than 1 kg/m^2 which is the condition for concrete resistance to the freezing and thawing. The quantity of scaled material at mixes 30-35 was greater than 1 kg/m^2 and those concretes are non-resistant.

The air voids analyzer showed significantly lower quantity of voids at referent concretes than at aerated concretes which confirmed the results already obtained by the porometer method (Figure 8).

***Table 11** Testing results - group of mixes I*
***Tablica 11.** Ispitni rezultati - grupa mješavina I*

Mix		1	2	3	4	5
T_c, °C		22,5	22,5	21,5	21,3	21,1
S, mm		7	10	25	40	115
D, kg/m^3		2408	2520	2395	2370	2370
f_c, MPa		58,5	50,3	49,4	47,0	45,6
Characteristics of air voids						
Air content, %	TM	2,9	3,4	2,9	2,9	2,5
	AVA	1,9	1,1	1,6	1,4	0,6
	MA	3,95	3,50	-	-	-
$\bar{L}$, mm	AVA	0,333	0,785	2,007	0,993	0,996
	MA	8,31	0,702	-	-	-
α, mm^{-1}	AVA	23,1	12,4	5,8	8,9	12,3
	MA	13,59	8,31	-	-	-
Scaling, kg/m^2		-	-	-	-	-

Results of the specific surface are presented in Figure 9. The specific surface of referent concretes is lesser than the specific surface of aerated concretes which is still one more of indicators of the non-resistance of referent concretes to the freezing and thawing cycles.

The spacing factor tested by the AVA method is presented in Figure 10. Referent concretes had the spacing factor greater than 0,20 mm which is a limit for the concrete resistance to freezing and thawing, thus proving as non-resistant. On the other hand, aerated concretes with cement CEM II/A-S 42,5R proved resistant (except mixes 28 and 29), and concretes with cement CEM III/B 32,5N-SR/LH proved non-resistant (except the mix 30).

The comparison of the spacing factor testing results by the AVA method and microscopic analysis is presented at Figure 10. Both methods have proved concretes of the mix composition IV (referent concretes) non-resistant. The AVA method showed higher spacing factors due to the fact that the testing area of air voids tested by means of the analyzer is within the limits if voids are from 3,5 % to 10 %.

The comparison of the spacing factor's results of compositions of the mixes V (mixes with cement CEM II/A-S 42,5R) presented in Figure 10 has indicated the resistance of concrete to freezing and thawing at four mixes, while the results at two mixes have been different.

***Table 12** Testing results – group of mixes II*
***Tablica 12.** Ispitni rezultati – grupa mješavina II*

Mix		6	7	8	9	10	11	12	13
T_c, °C		20	21,1	21,9	20,3	20,0	19,3	21,3	21,1
S, mm		115	70	25	75	25	23	30	70
D, kg/m^3		2239	2283	2320	2295	2302	2289	2283	2283
f_c, MPa		32,2	41,3	44,2	40,8	34,3	37,2	-	-
Characteristics of air voids									
Air content, %	TM	6,0	5,5	4,4	6,0	4,5	4,5	4,8	4,9
	AVA	3,3	3,6	2,9	2,6	2,6	2,5	2,6	2,9
	MA	-	-	-	-	-	-	-	-
$\bar{L}$, mm	AVA	0,570	0,401	0,324	0,515	0,390	0,546	0,334	0,391
	MA	-	-	-	-	-	-	-	-
α, mm^{-1}	AVA	10,7	14,5	19,8	13,1	17,4	12,6	20,2	16,6
	MA	-	-	-	-	-	-	-	-
Scaling, kg/m^2		-	-	-	-	-	-	-	-

The comparison of the spacing factor's testing results of compositions of the mixes VI with cement CEM III/B 32,5N-SR/LH has indicated the discrepancy of results about the concrete resistance to freezing and thawing. Results obtained by the AVA method have indicated the concrete non-resistance (except mixes 17 and 30), and results obtained by the microcsopic analysis have indicated the concrete resistance to freezing and thawing.

Table 13 *Testing results - group of mixes III*
Tablica 13. *Ispitni rezultati - grupa mješavina III*

Mix		14	15	16	17
T_c, °C		17,8	17,8	17,8	18
S, mm		30	25	30	35
D, kg/m^3		2289	2308	2333	2264
f_c, MPa		28,8	33,5	34,1	29,2
Characteristics of air voids					
Air content, %	TM	5,2	4,6	3,8	5,8
	AVA	6,2	4,4	3,1	6,1
	MA	-	-	-	5,82
$\overline{L}$, mm	AVA	0,286	0,237	0,391	0,192
	MA	-	-	-	0,105
α, mm^{-1}	AVA	15,9	22,7	16,0	23,9
	MA	-	-	-	35,96
Scaling, kg/m^2		-	-	-	-

Tablica 14 *Testing results - group of mixes IV*
Tablica 14. *Ispitni rezultati - grupa mješavina IV*

Mix		18	19	20	21	22	23
T_c, °C		20,7	20,6	22,9	22,6	22,5	21,8
S, mm		95	115	70	35	150	160
D, kg/m^3		2370	2264	2389	2370	2377	2408
f_c, MPa		36,5	45,8	45,1	35,4	36,7	47,8
Characteristics of air voids							
Air content, %	TM	1,9	1,5	1,7	1,7	1,4	1,2
	AVA	6,1	4,1	0,6	0,5	0,3	0,7
	MA	2,51	1,76	2,83	1,74	2,19	0,94
$\overline{L}$, mm	AVA	0,192	0,316	1,370	2,595	2,476	1,668
	MA	0,496	0,340	0,405	0,416	0,269	0,291
α, mm^{-1}	AVA	23,9	17,4	9,3	5,4	7,0	7,1
	MA	13,31	22,02	15,0	18,06	24,92	33,54
Scaling, kg/m^2		2,26	2,99	1,06	1,83	1,74	1,59

Table 15 *Testing results - group of mixes V*
Tablica 15. *Ispitni rezultati - grupa mješavina V*

Mix		24	25	26	27	28	29
T_c, °C		21,9	21,8	20,6	20,9	20,6	22,0
S, mm		150	125	140	120	150	160
D, kg/m^3		2245	2258	2252	2270	2220	2277
f_c, MPa		32,5	33,9	36,6	38,5	30,8	35,0
Characteristics of air voids							
Air content, %	TM	6,0	5,7	6,0	5,6	6,5	5,1
	AVA	7,9	8,5	9,0	8,0	4,5	3,5
	MA	6,3	5,43	6,72	6,53	8,46	6,48
$\overline{L}$, mm	AVA	0,185	0,198	0,172	0,192	0,426	0,55
	MA	0,172	0,170	0,123	0,143	0,135	0,164
α, mm^{-1}	AVA	20,5	22,5	25,0	21,0	12,4	6,0
	MA	24,46	26,72	29,82	33,81	22,80	24,78
Scaling, kg/m^2		0,13	0,04	0,04	0,05	0,12	0,04

***Table 16** Testing results – group of mixes VI*
***Tablica 16.** Ispitni rezultati – grupa mješavina VI*

Mix		30	31	32	33	34	35	36	37	38	39
T_c, °C		20,6	22,4	21,9	20,6	21,9	21,8	20,8	21,2	20,9	21,4
S, mm		130	100	50	85	160	130	50	10	10	50
D, kg/m^3		2258	2270	2308	2258	2258	2214	2290	2245	2320	2295
f_c, MPa		31,1	32,0	31,4	29,1	33,0	27,1	28,4	29,0	31,2	29,2
Characteristics of air voids											
Air content, %	TM	5,3	4,8	4,5	5,4	5,0	6,5	3,9	5,2	4,2	4,7
	AVA	5,1	5,5	3,6	4,5	5,7	5,6	8,7	6,8	4,9	4,7
	MA	5,21	4,98	4,88	5,69	6,25	7,44	4,53	5,12	4,14	2,63
$\bar{L}$, mm	AVA	0,185	0,276	0,451	0,494	0,628	0,675	0,136	0,227	0,204	0,199
	MA	0,153	0,138	0,140	0,128	0,114	0,081	0,112	0,118	0,137	0,186
α, mm^{-1}	AVA	27,1	17,5	13,0	10,7	7,5	7,1	25,5	19,2	24,8	26,0
	MA	29,91	34,39	33,33	34,08	36,32	42,33	44,43	40,09	33,62	30,39
Scaling, kg/m^2		1,7	1,95	1,48	1,65	1,42	1,63	-	-	-	-

4
Analysis of results
Analiza rezultata

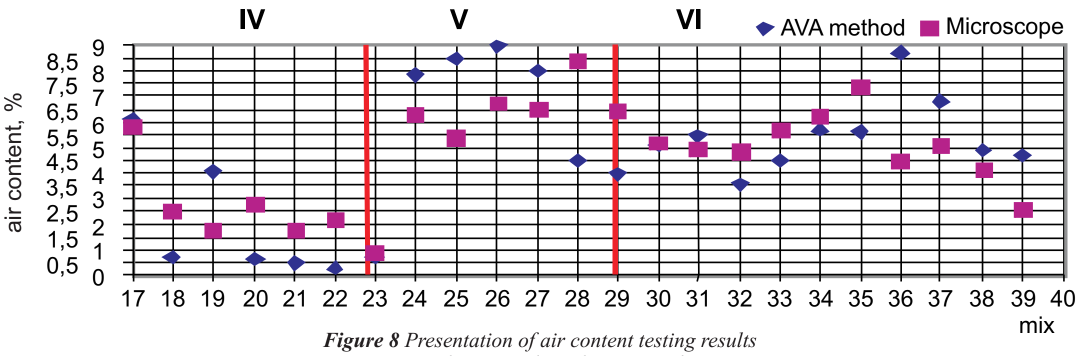

***Figure 8** Presentation of air content testing results*
***Slika 8.** Prikaz ispitnihrezultata zračnih pora*

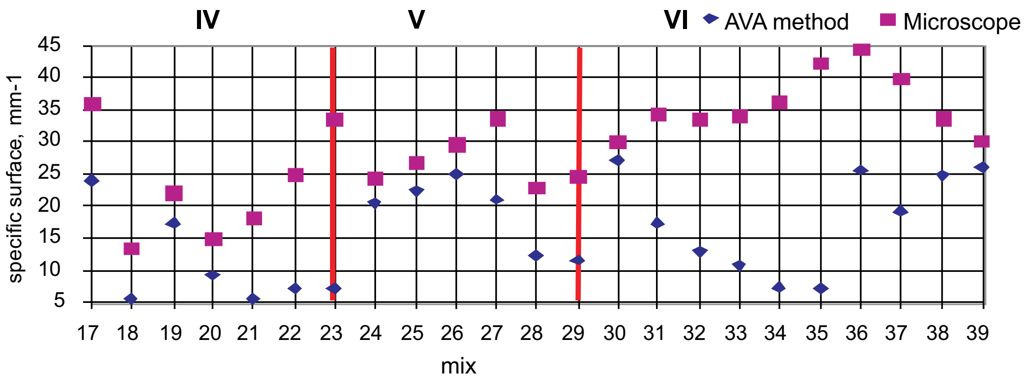

***Figure 9** Presentation of the specific surface testing results*
***Slika 9.** Prikaz ispitnih rezultata specifične površine*

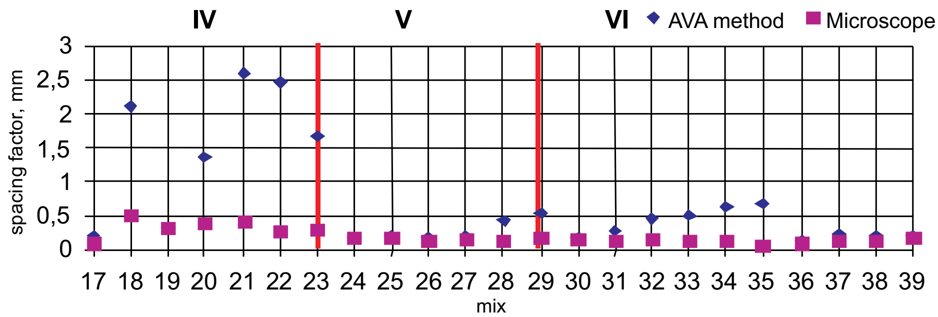

***Figure 10** Presentation of the spacing factor's testing results*
***Slika 10.** Prikaz ispitnih rezultata faktora razmaka*

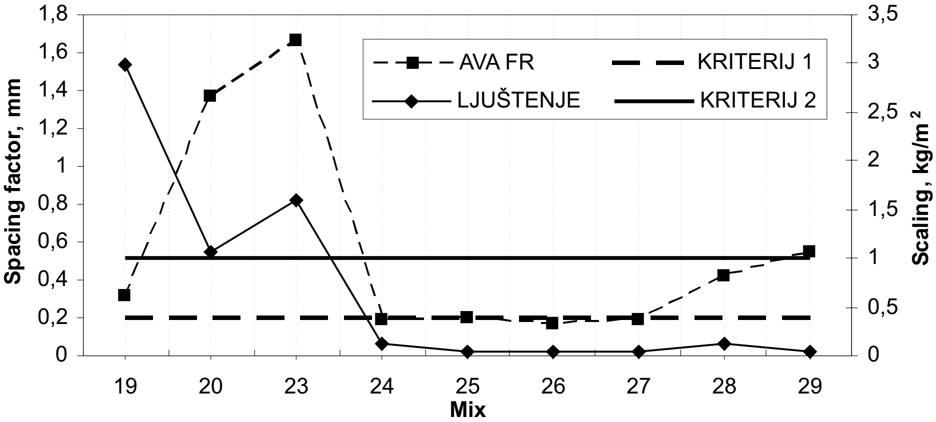

Figure 11 *Comparison of concrete resistance by testing of the spacing factor by means of the analyzer of air voids and surface scaling of concrete with cement CEM II/A-S 42,5R*
Slika 11. *Usporedba otpornosti betona ispitivanjem faktora razmaka izmjerenih analizatorom zračnih pora i ljuštenjem površine betona s cementom CEM II/A-S 42,5R*

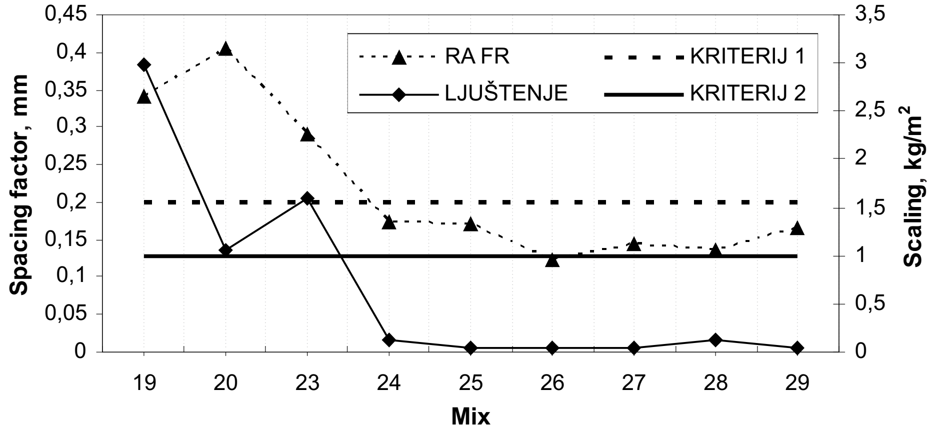

Figure 12 *Comparison of concrete resistance by testing of the spacing factor by means of the microscopic analysis and surface scaling of concrete with cement CEM II/A-S 42,5R*
Slika 12. *Usporedba otpornosti betona ispitivanjem faktora razmaka izmjerenih analizatorom zračnih pora i ljuštenjem površine betona s cementom CEM II/A-S 42,5R*

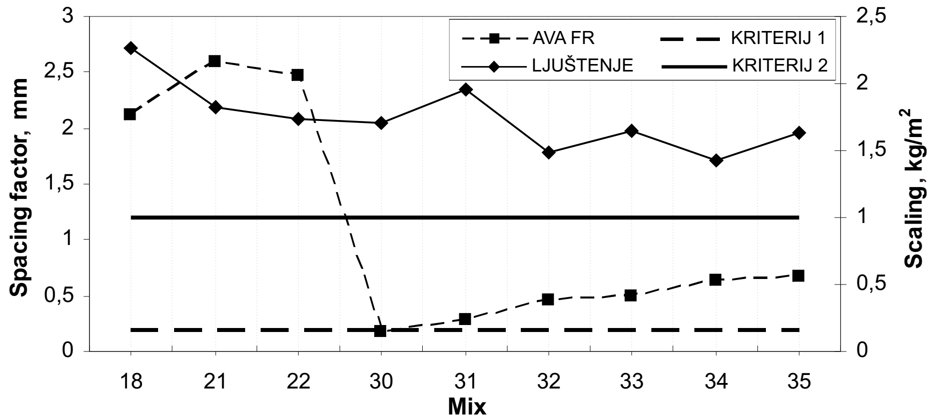

Figure 13 *Comparison of concrete resistance by testing the spacing factor by means of the analyzer of air voids and surface scaling of concrete with cement CEM III/B 32,5N-SR/LH*
Slika 13. *Usporedba otpornosti betona ispitivanjem faktora razmaka izmjerenih analizatorom zračnih pora i ljuštenjem površine betona s cementom CEM III/B 32,5N-SR/LH*

5 Conclusion
Zaključak

Depending on requirements for the concrete durability, class of exposure of samples exposed to the freezing and thawing cycles, testings may last 28 or 56 cycles (cycles being a simulation of the "actual" stuation in local conditions). However, in any case, the method of defining the concrete durability to freezing according to HRN EN 480-11:2005 standard is multiply faster than the direct method of testing by cycles of freezing and thawing (HRN CEN\TS 12390-9:2006).

Still, the analysis of air voids according to HRN EN 480-11:2005 cannot give timely information during the concrete production process. Timely information is very important since the experience has indicated that the structure of voids obtained by the air entrained agents may be easily changed during the process of concrete

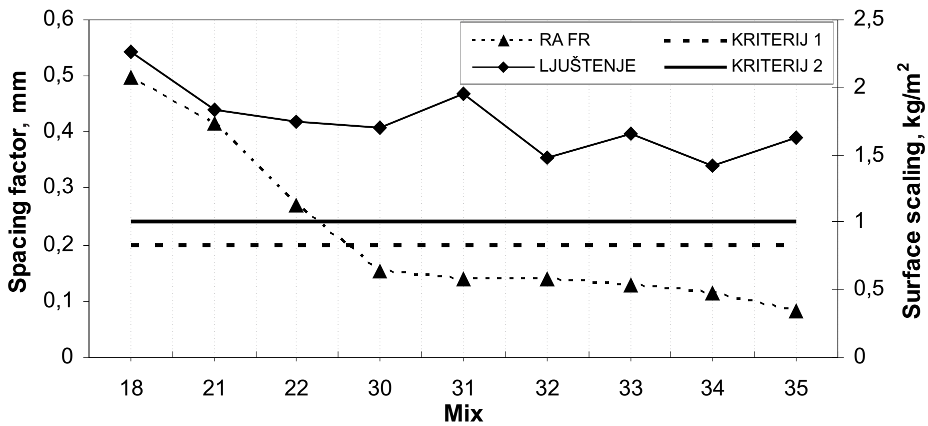

Figure 14 *Comparison of concrete resistance by testing of the spacing factor by microscopic analysis and surface scaling of concrete with cement CEM III/B 32,5N-SR/LH*
Slika 14. *Usporedba otpornosti betona ispitivanjem faktora razmaka izmjerenih analizatorom zračnih pora i ljuštenjem površine betona s cementom CEM III/B 32,5N-SR/LH*

production. It has been determined that the efficiency of the system of the entrained air voids is not defined by the volume of voids but by a number of very small air voids placed close to each other. So far, usually during the testing by the porometer method **(**HRN EN 12350-7:2000) the total quantity of air in fresh concrete has been determined, which is not a sufficient parameter but one of conditions in the system of air voids which needs to meet both requirements, the specific surface and spacing factor.

The advantage of the AVA method is its ability to define the structure of air voids in fresh concrete in less than 30 minutes. Having this in mind, any adjustments in the concrete production process may be performed and consequently, avoid placing of non-resistant concrete. Changes made during the production process which affect the characteristics of air voids in fresh concrete include the mixing time variation, replacement of additives type, its dosage share or the sequence of dosage and modification of the aggregate humidity.

The aim of this paper has been the analysis of the parameters of air voids in fresh concrete and proving of the concrete resistance to the freezing and thawing effects with deicing salts already at fresh concrete. The results of the concrete resistance obtained at fresh concrete are compared with the results obtained at hardened concrete.

It is clear from the paper that non-aerated concretes (referent concretes – Figure 14) did not meet the conditions of resistance to freezing with salts in 28 cycles according to HRN EN 480-11:2005, HRN CEN/TS 12390-9:2006 standards and by the AVA method. Optimally aerated concretes (with the spacing factor of <0,2 mm) prepared with cement type CEM II/A-S 42,5R proved resistant which was confirmed by all three ways of the resistance determination. Concretes prepared with cement CEM III/B 32,5N-SR/LH, with or without aeration, were not resistant to the freezing and thawing effects with salts presence. Cement type CEM III/B 32,5N-SR/LH and similar, with a high share of slag from the blast furnaces (66–80 %), should not be used for the preparation of concrete for structures exposed to the aggressive influence of the environment, class XF 2 and 4.

Differences in the testing results of individual parameters (quantity of voids, specific surface, spacing factor) come out of different testing methods at fresh and hardened concrete, and some higher values of the spacing factor, determined by the AVA method, refer to the safety. The reliable perception about the resistance to freezing and thawing at fresh concrete already in preparation stage is obtained successfully by the right preliminary choice of concrete components by means of the AVA method. Checking by the microscopic analysis (HRN EN 480-11:2005) at hardened concrete is possible after seven days. This significantly reduces time necessary for execution of preliminary testings.

Other mentioned methods are based on the samples of already hardened concrete and require long waiting for maturing.

The possibility to continue research concerning the concrete resistance to freezing and thawing already at fresh mix has been opened and it would significantly reduce the number of possible errors in the choice of concrete components.

6
References
Literatura

[1] Tehnički propis za betonske konstrukcije, Narodne novine 101/2005
[2] HRN EN 206-1:2002 Beton-1.dio: Specifikacija, svojstva, proizvodnja i sukladnost
[3] Đureković, A. Cement, cementni kompozit i dodaci za beton, IGH, Školska knjiga, Zagreb, 1996.
[4] HRN U.M1.055:1984: Ispitivanje otpornosti površine betona na djelovanje mraza i soli za odmrzavanje
[5] HRN U.M1.056:1987: Ispitivanje otpornosti prema djelovanju mraza i otpornosti površine betona na djelovanje mraza i soli za odmrzavanje aeriranih betona linijskom mikroskopskom analizom
[6] HRN EN 480-11:2005: Dodaci betonu, mortu i mortu za injektiranje - Ispitne metode -11. dio: Određivanje značajka zračnih pora u očvrslom betonu (EN 480-11:1998)
[7] HRN CEN/TS 12390-9:2006: Ispitivanje očvrsloga betona - 9. dio: Otpornost na smrzavanje i odmrzavanje - Ljuštenje (CEN/TS 12390-9:2006)
[8] Hranilović Trubić, A. Otpornost betona na djelovanje mraza i soli, Građevinski fakultet, Sveučilište u Zagrebu, magistarski rad, Zagreb, 2006.
[9] Sanitsky, M.; Sobol, H.; Marushchak, U. Structure formation of hardening cement pastes at freezing, Proceedings of the 2nd International RILEM Workshop, Essen, Germany, 18-19 April 2002, Edited by M. J. Setzer, R. Auberg and H.-J. Keck, (RILEM Publications), 1 Vol., 400 pp., ISBN: 2-912143-30-6
[10] Setzer M. J.; Fagerlund, G.; Janssen D. J. CDF TEST-Test method for the freeze-thaw resistance of concrete-tests with sodium chloride solution (CDF): TC 117-FDC: Freeze-thaw

and deicing resistance of concrete
[11] Setzer, M. J.; Heine, P.; Kasparek, S.; Palecki, S.; Auberg, R.; Feldrappe, V.; Siebel, E. Test methods of frost resistance of concrete: CIF-Test: Capillary suction, internal damage and freeze thaw test-Reference method and alternative methods A and B, RILEM TC 176-IDC: Internal damage of concrete due to frost action, Final Recommendation; Materials and Structures, Vol 37, December 2004, str. 743-753.
[12] Stark, J.; Möser, B. Nano and microstructure of portland cement paste, Proceedings of the 2nd International RILEM Workshop, Essen, Germany, 18-19 April 2002, Edited by M. J. Setzer, R. Auberg and H.-J. Keck, (RILEM Publications), 1 Vol., 400 pp., ISBN: 2-912143-30-6

Acknowledgment. We wish to thank the Ministry of Science, Education and Sports of Republic of Croatia for their support in the scientific project "From nano to macro structure of concrete", No. 082-0822161-2990, as part of which this research was done.

Authors' addresses
Adrese autora

mr. sc. Ana Hranilović Trubić, dipl. ing. građ.
Institut IGH d.d.
J. Rakuše 1, 10000 Zagreb
tel.: 047 601-688, mob.: 098 9844-217
e-mail: ana.hranilovic@igh.hr

prof. dr. sc. Dunja Mikulić, dipl. ing .fiz.
Građevinski fakultet Zagreb
Kačićeva 26, 10000 Zagreb

Srđan Uzelac, dipl. ing. građ.
Institut IGH d.d.
J. Rakuše 1, 10000 Zagreb