Methods for Assessing the Freeze-Thaw Resistance of Road Concrete Used in our Country and at European Level

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Abstract. The paper addresses three methods of assessing the freeze-thaw resistance of road concretes prepared with conventional and artificial materials. The blast furnace slag was used, as an artificial material, in granulated and milled form and in the form of crushed aggregates from the steel industry. The most common method used in our country to determine the freeze-thaw resistance is the destructive method by measuring the variation of the compressive strength of the samples subjected to repeated freeze-thaw cycles. The most severe method of testing the freeze resistance considered at the European level, is based on the calculation of the amount of exfoliated material in the presence of defrosting agents. Another method used is to determine the values of the dynamic modulus of elasticity after repeated cycles of freeze-thaw. The results obtained were interpreted according to different evaluation criteria and compared with limit values proposed by the standardized methods.

1. Introduction

For the beginning it is presented an general analysis of the requirements and recommendations related to the freeze-thaw exposure of the concrete structures at international level, but the purpose of the present paper is to select the testing methods for freeze-thaw used in our country, used at European level, with applicability for the on-going experimental study. This study is related to the usage in the road concrete mixtures of blast furnace slag as mineral addition from the ground-granulated blast furnace slag (GGBS) and as partial substitution of natural aggregates with crushed, non-granulated air-cooled furnace blast slag (ABS). The concept of equivalent durability defined in the paper “Advanced solutions for durable concrete”, 2019 [1] in compliance with CEN/TR16563 [2], has as objective the correlation of the ground experience with the results obtained in the laboratory by developing a data base with different concrete mixtures as reference and with exposures to different exploitation environments. In the European countries the concept of concrete equivalent performance can be found in the Directive EN 206 [1, 3], but it’s application in most of the countries is not implemented because in requires a national system renowned with clear information about the reference concrete. By definition, the concrete freeze durability represents the capacity of resisting in repeated freeze-thaw cycles during over the life span without deteriorating caused by material loss of the concrete surface or by internal cracks, [1]. The general parameters established by projection of the freeze-thaw resistant concrete are: the
water/cement (w/c) ratio or the water/binder (w/l) ratio, the compressive strength and the content of occluded air, but besides these, there would be other requirement that are researched with a lot of interest: the factor of pore spacing, the proportion of supplementary constituents with cement characteristics (CSCC) defined as in the paper with reference [4], the limiting of the permeability and the freeze-thaw resistance of aggregates and concrete. Most of these parameters are tested according to the European standards, exception is the factor of pore spacing that can be found in the durability requirements of Norway, Denmark, Canada and USA, [1,4]. The standard PN-EN 480-11 [5] describes the structure of the air entrained in the concrete using the following parameters: the total air content A [%], the specific surface α [mm²], the spacing factor L [mm] and the content of micropores A₃₀₀ [%]. The spacing factor L of the air pores can be determined after the simplified model of Powers, which supposes that all the air bubbles have the same diameter and are distributed in the corners of a cube. Another approach for determining the spacing factor (L) of the air pores is based on the Pileo concept, which takes into consideration both the air gap system and the characteristics of the aggregate particles. The principles of the calculus methods of the spacing factor was described by J. Wawrzeńczyka in the paper [6]. As example, the Canadian standard CSA A23.1-09 A23.2-09 [7] establishes the requirements for the occluded air spacing factor of 230 μm. [1]. In Russia, the standard GOST 26633-2015 [1,8] limits the (w/c) ratio at 0.45 and the content of occluded air at 5±7% for road structures. In our country, by applying the standard SR EN 206+A1:2017 [9] and the normative NE 014:2002 [10] is previewed for freeze resistant concrete, the usage of air-entraining agents with minimum values established depending on the maximum dimension of the aggregate, then the limiting of the (w/c) ratio and minimum values for the compressive strength. For the road concrete are stipulated supplementary requirements regarding the minimum values for the flexural strength and the freeze-thaw resistance.

As for the use of supplementary constituents with cement characteristics (CSCC) in concrete mixtures exposed to freeze-thaw, the German standard DIN 1045-2 [11] indicate limit values for the concrete with slow hardening, such as those with fly ash, the Canadian standard [7] suggests the use of (CSCC) for the sulphur and chlorine combined attacks, and the requirements for the materials for concrete resistant to freeze, the Russian standard GOST R 55224-2012, clause 5.11.2 [12] accepts the blast furnace slag as main mineral supplement in the cement manufacturing for road concrete, reinforced elements and bridge structures [1]. In our country, in compliance with SR EN 206 [9] it is accepted the use of type II supplements (the pozzolanic or the latent hydraulic supplements) thus, fly ash maximum 33% of the cement mass, depending on the usage domain, and the ultrafine silica in percentage of maximum 11% of the cement mass. Hooton mentions that for obtaining a durable concrete for the most aggressive exposure conditions is conditioned by the materials, the projection of the mixtures and the compliance with some appropriate construction technologies [1,13]. The testing methods of the freeze resistance and the acceptance criteria differ from one area to another, depending on the experimented type, the sample conservation plan, the duration and the temperature interval in the thermostat chamber and the acceptance criteria. All these parameters are conditioned by the exposure environment of the road concrete structure. Several main observations can be noticed regarding the testing methods, such as for the structures placed in a dry environment, but made of high-performance concrete, the resistance to freeze is evaluated only by the internal cracks, through method ASTM C666, procedure A [14]. But the road authorities require first the performance of the exfoliation testing with thawing agents, [1,15]. The Russian standards require for a freeze-thaw class F a minimum compressive strength that needs to be reached before the freeze-thaw exposure. There are other methods to assess the freeze resistance, such as the method of assessing the factor of protecting the pores known as (PF), representing a criteria for the assessment of the concrete freeze-thaw resistance, in compliance with the Finish standard SFS 4475:1998, [1, 16-18], and another one by assessing the concrete permeability [1, 19]. In Europe, the assessing of the internal cracks of the structure exposed to freeze is done in compliance with CEN/TR 15177:2006 [20], by which, depending on the chosen procedure, it is measured the dynamic elasticity module, the length variation and the water uptake after 56 freeze-thaw cycles, and the material loss testing of the concrete surface is done in compliance with the Swedish standard SS 137244 [21] and CEN/TS 12390-9:2009 [22], by which it is measured the material mass loss of the concrete surface after...
56 or 112 freeze-thaw cycles, [1]. In North America, the assessment of the internal cracks is done in compliance with ASTM 666/C666-15 [14], after 300 freeze-thaw cycles, and the material mass loss testing of the concrete surface is done in compliance with ASTM C672 [1,23] at 50 freeze-thaw cycles [1]. The methods adopted in China for the internal crack assessments are in compliance with the standard GB/T 50082-2009 [24] by which it is measured the mass loss and the compressive strength after minimum 25 freeze-thaw cycles [1]. This method is close to the one used in our country, in compliance with the national standard SR 3518-2009 [25], regarding the preparation of specimens, the length and the temperature of the freeze-thaw cycles and the acceptance criteria. From this paper it can be observed that the testing methods are structured in two deterioration types: first the scaling of the concrete surface and the second the internal cracks of the concrete structures. The term of scaling is currently used in international studies, but in our country the usual term is exfoliation of the concrete surface. The definition of the term scaling can be found in CEN/TS 12390-9:2009 and represented the material loss of the concrete surface caused by the freeze-thaw cycles. Regarding the acceptance criteria, the results obtained by different testing methods there are reservations regarding the preparation, preserving modes, the age of the samples compared to the real exposure of structures. Due to these disagreements it is concluded that some methods do not present explicitly the acceptance criteria, such as method CEN/TR 15177:2006 used in Europe for the internal cracks testing, and the obtained results are seldom compared with those of the reference concrete. The described testing methods are frequently used for the assessment of the freeze-thaw resistance and they are still presented in several experimental studies that approach this issue.

Peter B. tested the freeze resistance in compliance with CEN/TS 12390-9:2007 of concrete made with three types of cement CEM I, CEM II, CEM III supplied by four European factories. The surface exfoliation was increased in mixtures containing CEM II and CEM III compared to mixtures containing CEM I. By changing the preserving conditions previously to the freeze-thaw testing of the concrete containing CEM II/III the material loss of the concrete surface was within the CEM I range [26]. The technical bulletin Frostprüfung von Beton from the Federal Waterways Engineering and Research, [27] recommends a 14-day preservation instead of 7-day under water for slow hardening concrete and the freeze-thaw testing to be done after 56 or 90 days. D Kocab et al [28], from Czech Republic, determined the freeze-thaw resistance of concrete made with aggregates coming from different crushing quarries. The chosen testing methods were GB/T50082-2009, a destructive method used for assessing the internal cracks of the structure, and ASTM 666-03, a non-destructive method used for the measuring of the relative dynamic modulus (RDM) of elasticity. Daria J.N.[29], carried out a study, in Poland, related to the influence of the light aggregate on the deterioration of the concrete surface, in the present of defrost agents due to the freeze-thaw phenomena. She used the Borås method, in compliance with the Swedish standard SS137244. Syamak Tavasoli, Mahmoud Nili and Behrad Sepou, [30] used the ASTM666 method for determining the relative module of elasticity, the length variation and the mass loss in the study regarding the influence of GGBS on the freeze resistance in self-compacting concrete (SCC). Marta K.K.[31], studied the freeze-thaw resistance by testing the surface scaling in compliance with the method CEN/TS 12390-9:2007 of concrete (slab test) with fly ash, undergoing 112 freeze-thaw cycles in presence of the NaCl solution with 3% concentration. Marta K.K. showed that the test results analysed statistically, in compliance with the accepted criteria from SS 137244:1995, allow the usage of up to 25% fly ash, taking into consideration the air-trainer supplement and appropriate hardening conditions, lead to obtaining a durable concrete. Jun Phil Hwang, Hyun Bo Shim, Sooyoung Lim and Ki Young Ann, [32] studied the durable properties of concrete containing recycled aggregates and pozzolanic materials such as fly ash and grounded blast furnace slag. The freeze resistance was determined using the ASTM666 method through a fast test. Huai-Shuau and Ting-Hua Yi, 2013 [33] studied the freeze-thaw durability of air-entrained concrete. They measured the relative dynamic modulus of elasticity and the mass loss up to 400 freeze-thaw cycles using the GB/T50082-2009 method. The results were compliant up to 300 freeze-thaw cycles. In our country, there were experimental researches for the assessment of the freeze-thaw resistance of concrete using the method CEN/TS 12390-9 (cube test) for
the exfoliation of the surface, using the national standard SR 3518:2009 and the method CEN/TR 15177:2006 for assessing the internal cracks of the structure. [34].

In this paper there are presented three testing methods for the freeze-thaw resistance by material loss of the concrete surface (scaling) using the method CEN/TS 12390-9:2007 [22] (slab test), by assessing the internal cracks of the structure using the method CEN/TR15177:2006 [20] and using thedestructive method in compliance with the national standard SR 3518:2009 [25]. The first two methods are freeze-thaw testing methods used in the European countries, and the third one is the most frequent method used in our country.

2. Materials and Methods

2.1. Prime conventional materials

The cement used in road concrete mixtures is type CEM I 42.5R, and it was supplied from the factory of Aleșd, by the company S.C. HOLCIM Romania S.A. The natural sand, 0/4 mm dimension, comes from the gravel pit from Beclănuc, Bistrița County, the coarse cover aggregate (gravel), 4/8 mm dimension, comes from the gravel pit from Sanicorea, Cluj County, and the coarse cover aggregate (crushed), 8/16 mm and 16/25 mm dimension, comes from the company SC Grandemar Cluj. The used aggregate proportions were 32% sand (fine aggregate) and 68% coarse aggregate. The granularity curve of the total aggregate mixture was within the granularity range in compliance with NE 014-2002 [10]. The testing procedure on aggregates was done in compliance with the normative references SR EN 12620:2003 and SR EN 12620:2003+A1:2008 [35] and SR 667:2001 [36]. The used additives were supplied by the company BASF Romania, the super-plasticizer additive MasterGlenium SKY 527 and the air-trainer additive Master Air 9060. The water from the concrete was taken from the water supply system of the city Cluj-Napoca, in compliance with SR EN 1008:2003 [37].

2.2. Prime non-conventional materials

The blast furnace slag represents a secondary product of the metallurgic industry after the melting of cast iron. This secondary product can be reused as prime material for constructions. Depending on the chosen cooling process, two types of blast furnace slag can be obtained granulated and non-granulated distributed by the company ArcelorMittal from Galați, (Romania). The granulated blast furnace slag was grounded at the cement factory from Aleșd, and the specific surface with the value of 5770 cm²/g was determined by the university’s laboratory. The ground granulated blast furnace slag called (GGBS) is part of type II supplements category due to the fact that it has hydraulic properties, in compliance with SR EN 15167-1:2007 [38], with usage in concrete mixtures for improving certain properties and to grant special properties in compliance with the provisions from SR EN 206 [9]. According to the chemical composition, the blast furnace slag from the company ArcelorMittal fits within the category of basic slags because of the basicity index, Nicula et al [39], because the basic oxides prevail (CaO, MgO, FeO, MnO) in proportion of 49.01%, see the Table 1.

| Table 1. Chemical composition of the granulated blast furnace slag (GGBS), %.
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| SiO₂          | Al₂O₃          | MnO          | MgO            | CaO            | Fe₂O₃          | Na₂O          | K₂O          | TiO₂          | Mn₂O₃          |
| 36.44         | 11.60         | 0.55         | 5.8            | 41.81         | 0.78           | 0.345         | 0.428        | 0.30         | 0.62           |

The non-granulated blast furnace slag is not used in cement manufacturing, it presents with a crystallin molecular structure [40], which after crushing can be used as air-cooled blast furnace slag (ABS) crushed aggregate in different field. The crushing of the non-granulated blast furnace slag was ensured by the supplier at a dimension of 0/4 mm. The characteristics of artificial blast furnace slag were tested by the supplier in the reports [41, 42] for the blast furnace slag dimension 0/4 mm.
2.3. Methods

It is known that the granulated blast furnace slag has hydraulic properties when it is activated suitable in compliance with SR EN 197-1:2011 [43] and with SR EN 15167-1:2007 [38], it was introduced in the road concrete mixture grounded at a dimension of 63 µm, as a binding agent. The non-granulated, crushed blast furnace slag with the dimension of 0/4 mm was used as substitute for the related sand that was part of the total mixture of aggregates defined within SR EN 12620:2003+A1:2008 [35]. Three mixtures made with blast furnace slag were compared with two road concrete mixtures made with conventional materials with different cement dosages. The samples were named symbolically to make the connection with the quantities of the used material, see Table 2. The quantity of 54 kg of (GGBS) was used as addition 15% to the mass of the cement, compared with the S 360c mixture, and compared with the S 414c mixture, the quantity of 54 kg of (GGBS) substituted 13% from the mass of the cement. The mixtures were projected to be used in exposure conditions class XF4 (exposure to freeze F with strong water saturation with defrost agents, with humidity level 4). In compliance with the durability requirements for the road concrete established within [9, 10, 44], the minimum conditions for the projecting were: a cement dosage of minimum 340 kg/m$^3$, the W/L ratio maximum 0.45, minimum resistance class C35/45 and air-entraining agent within the mixtures. All the tests were performed in the labs of Cluj-Napoca Technical University, Faculty of Constructions.

| Quantities                     | Mixtures [Kg/m$^3$] |
|-------------------------------|---------------------|
| Mixture (Kg/m$^3$)            | S 360 c  | S 414 c  | S 54/20 | S 54/40 | S 54/60 |
| Cement (C)                    | 360      | 414      | 360     | 360     | 360     |
| Ground-granulated blast       | -        | -        | 54      | 54      | 54      |
| furnace slag powder (GGBS)    |          |          |         |         |         |
| Total binding agent (L)       | 360      | 414      | 414     | 414     | 414     |
| W/L, (water/binder)           | 0.44     | 0.41     | 0.41    | 0.43    | 0.43    |
| Aggregate                     | 1864     | 1831     | 1863    | 1810    | 1810    |
| Fresh state density           | 2380     | 2415     | 2444    | 2402    | 2402    |
| Super-plasticizer additive    | 3.60     | 4.14     | 4.14    | 4.97    | 4.97    |
| Air-trainer additive          | 1.08     | 2.07     | 2.07    | 2.07    | 2.07    |

2.3.1. Casting specimens, hardening, maintaining and preparing samples for testing. The mixtures analysed in this study are part of the first casting series. For each mixture we casted 4 cubic samples with side of 200 mm and 12 cubic samples with side of 150 mm, kept in air for 24 h, afterwards they were removed from forms and sunk in water at a temperature of (20±2)°C. At the age of 7 days, the samples were removed from water and kept in air, in a climatic chamber, at a temperature of (20±2) °C and a humidity of (65±5) % for the freeze-thaw testing, in compliance with SR-3518:2009 [25]. At the age of 50 days started the freeze-thaw testing using the destructive method. From the 200 mm-side cubes we cut concrete stripes of 150x150x50 mm, and at 150 days we started the freeze-thaw testing with defrost agents in compliance with CEN/TS 12390-9:2009 [22] and using the method of measuring the propagation time of ultrasonic impulse (UPTT) in compliance with CEN/TR 15177:2006 [20].

2.3.2. Determining the freeze-thaw resistance using the destructive method. The freeze-thaw resistances of the concrete mixtures were determined on 12 samples with a side of 150 mm (6 control samples and 6 samples that underwent 150 and 300 repeated freeze-thaw cycles), in compliance with the national standard SR-3518:2009 [21]. The testing period of our study extended compared to the provisions from NE014-2002 [7] from 100 to 300 freeze-thaw cycles, similarly to the number of freeze-thaw cycles requested by the standard ASTM C666/C666M-03 [18], but the testing procedure for the two standards is different. The method ASTM C666 has the average temperature range between (+5 and -18) °C, the
length of a cycle between \((2 \pm 5)\) h, the freeze-thaw cycle in water (in compliance with procedure A), respectively the freeze cycle in the air/thaw cycle in the water (in compliance with procedure B, also called the fast test). According to the testing procedure mentioned in SR-3518:2009, the thermostat chamber maintains the temperature for the freeze cycle at \((-17\pm2)\)°C for 4h, and for the thaw cycle up to \((20\pm2)\)°C for 4h. 4 days before starting the sample testing, they were taken from the climatic chamber and inserted in the water at a temperature of \((20\pm5)\)°C for saturation. The water was added gradually on \(\frac{1}{4}\) of the height of the samples for 3 days, after 3 days the water was added up to 20 mm over the height of the specimens. The samples completely covered with water were kept like that for 24 h, and afterwards the control samples continued to be kept in water, while those prepared for the freeze-thaw cycles were introduced in the thermostat chamber. The admissibility condition in compliance with SR-3518:2009 is that the compressive strength losses of the samples undergoing successive freeze-thaw cycles should not decrease with more than 25% compared to those of the control samples kept in water. The value of the resistance loss after \(n\) freeze-thaw cycles is calculated using the equation 1.

\[
\eta_n = \frac{f_{cm,water} - f_{cm,freeze}}{f_{cm,water}} \times 100\% \tag{1}
\]

\(\eta_n\) – the compressive strength loss after “n” freeze-thaw cycles,
\(f_{cm,water}\) – the average compressive strength of the samples maintained in water during “n” freeze-thaw cycles,
\(f_{cm,freeze}\) – the average compressive resistance of the samples maintained in the thermostat chamber during “n” freeze-thaw cycles.

2.3.3. Determining the freeze-thaw resistance by measuring the exfoliant mass of the concrete surface. The material loss at the hardened concrete surface after the 56 repeated freeze-thaw cycles, defined shortly as scaling of the concrete surface, in the presence of defrost agents, is determined using the alternative “slab test”: method mentioned within SR CEN/TS 12390-9:2009 [22]. The reference method requires the testing to start at the age of 31 days, and the alternative method allows the beginning of the testing at a concrete age different than 31 days. The exfoliated mass measuring method on the sample surface is appreciated as the most severe method of testing the freeze resistance and it is based on the Swedish standard SS 13 72 44 using the Borås method [21]. For each mixture, we cut 4 concrete stripes of 150x150x50 mm from the 200 mm cubes that were preserved in a climatic chamber at a humidity of \((65\pm5)\) % and a temperature of \((20\pm2)\) °C until the testing. A 3 mm rubber sheet was first glued an all the sample surfaces, except for the testing surface, then a silicon glue cord was applied between the rubber and the concrete surface. A test was performed to check the tightness of the rubber sheet by pouring on the testing surface 67 ml of deionized water, maintained for 72 h. The water evaporation rate was measured in a container filled with water with a surface of 225 cm², for which it resulted, after 7 days, an evaporation of 44.59 g. After the tightness testing all the sample surfaces, except the testing surface, were isolated thermic with polystyrene of \((20\pm1)\) mm. 15 minutes before introducing it in the thermostat chamber, on the testing surface it was poured 67 ml solution for testing with thaw agent with a thickness of 3 mm, consisting of 97% drinkable water and 3% sodium chloride NaCl of the total mass. Then the samples were introduced in the thermostat chamber, from the brand Controls, they were covered with a polyethylene sheet and they were tested in repeated freeze-thaw cycles. The length of a freeze-thaw cycle was 24 h, of which the thaw cycle range was between \((7\pm9)\) h, and the freeze cycle range was between \((15\pm17)\) and the temperature range minimum/maximum between \((-22\) and +22) °C. The temperature variation registered during the testing at the testing surface is represented in Figure 1.a), and in Figure 1.b) there is the image with the samples deposited in the thermostat chamber. The freeze-thaw resistance was assessed by measuring the exfoliated mass on the sample surface after 7, 14, 28 and 56 freeze-thaw cycles. At 7, 14, 28, 42 and 56 cycles, at the end of the thaw phase it was collected in a filter paper the exfoliated material from the testing surface and a new testing medium was added on
the surface exposed to the freeze-thaw in the climatized chamber. The exfoliated material and the used filter were dried until the constant mass of \((110\pm10){}^\circ\text{C}\) and then weighted (images just like in Figure 2).

\[ m_{s,n} = m_{s,\text{initial}} + (m_{s+f} - m_{v+f}) \]  

The cumulated value \(S_n\) of exfoliated material, after \((n)\) freeze-thaw cycles in kg/m\(^2\) is expressed using the equation 3.

\[ S_n = \frac{m_{s,n}}{A} \times 10^3 \]  

\(m_{s,n}\) – total mass of the exfoliated and dried material after \((n)\) freeze-thaw cycles, rounded value to the closest 0.1 g;
The accepted criteria used for the freeze-thaw testing with defrost agents in this experiment are compliant with the Swedish standard SS 13 72 44 (the Borás method), method included in the study [1] from 2019 performed by Andrei Shapak, and criteria adopted as well by Daria J.N. 2002 in the study [29]. The Swedish standard SS 13 72 44 (the Borás method) is based on the average exfoliated mass at 28 days ($m_{28}$), at 56 days ($m_{56}$) and, optionally, at 112 days ($m_{112}$), see Table 3.

Table 3. Acceptance criteria for the freeze resistance, the exfoliation testing.

| Scaling resistance | Requirements |
|--------------------|--------------|
| Very good          | $m_{56} < 0.10$ kg/m² |
|                     | $m_{56} < 0.20$ kg/m² |
| Good               | $m_{56} < 0.50$ kg/m² and $m_{56}/m_{28} < 2$ |
|                     | $m_{112} < 0.50$ kg/m² |
| Acceptable         | $m_{56} < 1.00$ kg/m² and $m_{56}/m_{28} < 2$ |
|                     | $m_{112} < 1.00$ kg/m² |
| Unacceptable       | $m_{56} \geq 1.00$ kg/m² and $m_{56}/m_{28} \geq 2$ |
|                     | $m_{112} \geq 1.00$ kg/m² |

2.3.4. Determining the freeze-thaw resistance by percentage decrease the dynamic module of elasticity.

In compliance with the Technical Report CEN/TR 15177:2006 [20], the freeze-thaw resistance was determined through the alternative method "the slab test", as relative dynamic modulus of elasticity. The measurements were made on prismatic sample of 150x150x50 mm before test, after 28 freeze-thaw cycles and after 56 freeze-thaw cycles, on prisms of 150x150x50 mm. The method is based on measuring the propagation time of ultrasonic impulses (UPTT) between 2 transducers in compliance with SR EN 12504-4, [45]. The measuring equipment, the brand Controls, having its own frequency in the range of 40-100 KHz, was graduated before usage. The transducers were pressed on the coupling environment of the concrete surface in order to reach a minimal constant value. The transmission time was read with an approximation of 0.2 µs. The percentage decrease of the dynamic module of elasticity was determined using equation 4 for each mixture. The method CEN/TR 15177:2006 does not present a value threshold for the acceptance criteria of the relative dynamic modulus of elasticity. The GB/T 50082-2009 method used in China limits the RDM loss up to 60% [1, 24], and with the method used in Russia GOST 10060-2012 [1, 46], the module RDM variation must be smaller than 25%. Because the testing procedure is different from one method to another, for this study the acceptance criteria was based on the equivalent performance concept of mixtures with blast furnace slag compared with reference mixtures made with conventional materials.

$$RDM_n = \left( \frac{t_0}{t_n} \right)^2 \times 100 \text{ (\%)}$$

Where $t_0$ and $t_n$ is the initial propagation time of ultrasounds, respectively after n cycles (µs), RDM the relative dynamic modulus of elasticity after n freeze-thaw cycles, $E_{d0}$ and $E_{dn}$ in (MPa) the dynamic module of elasticity at the beginning and after n freeze-thaw cycles, (MPa).
3. Results and discussions

3.1. Freeze-thaw results using the destructive method

The results obtained using the method from SR 3518:2009 are presented in Table 4, and graphically represented in Figure 3 a) and b). The obtained values represent the compressive strengths for the control samples and for the samples undergoing repeated freeze-thaw cycles. The compressive strength losses were calculated between the control samples kept in water and the samples undergoing repeated freeze-thaw cycles.

| Mixture     | fcm,150 water (MPa) | fcm,150 freeze (MPa) | η150 (%) | fcm,300 water (MPa) | fcm,300 freeze (MPa) | η300 (%) |
|-------------|--------------------|----------------------|----------|---------------------|----------------------|----------|
| S 360 control | 85.83              | 88.32                | -2.91    | 87.78               | 83.06                | 5.38     |
| S 414 control | 81.46              | 75.64                | 7.14     | 80.96               | 71.15                | 12.10    |
| S 54/20       | 87.06              | 85.75                | 1.51     | 84.80               | 77.82                | 8.32     |
| S 54/40       | 80.85              | 76.29                | 5.63     | 79.38               | 73.06                | 7.96     |
| S 54/60       | 76.79              | 67.92                | 11.55    | 74.77               | 60.95                | 18.47    |

In Figure 3 (a) can be noticed that the highest compressive strengths were obtained in the S 360c mixture, and the closest to these were the values of the S 54/20 mixture. By comparison with the resistances of the control mixture S 414c, the obtained values were superior in the S 54/20 mixture, closer in the S 54/40 mixture, but inferior in the S 54/60 mixture. Also, the resistance losses in the S 54/20 and S 54/40 mixtures are smaller than those in the control mixture S 414c. The control mixture S 360c registered the lowest resistance losses, but the S 54/60 mixture registered the highest compressive strengths losses. In all mixtures, the resistance losses are lower than the admitted limit of 25%.

3.2. Results of freeze-thaw resistance by measuring the exfoliated mass of the sample surface

Individual values were calculated for each specimen, and then the cumulated value of exfoliated material for each mixture at 7, 14, 28, 42, 56 freeze-thaw cycles, see Table 5, represented graphically as in Figure 4 a) and b).
Table 5. The cumulated quantity of exfoliated concrete $S_{56}$ after 56 freeze-thaw cycles, in stripes of 150x150x50 mm reported to the measured surfaced of 0.02103 m$^2$.

| Mixtures     | $m_{s,7}$ [g] | $m_{s,14}$ [g] | $m_{s,28}$ [g] | $m_{s,42}$ [g] | $m_{s,56}$ [g] | $S_{56}$, cumulated [g] | $S_{56}$, cumulated [kg/m$^2$] |
|--------------|---------------|---------------|---------------|---------------|---------------|---------------------|-----------------------------|
| $S_{360c}$   | 0.200         | 0.225         | 0.300         | 0.400         | 0.550         | 1.675               | 0.080                      |
| $S_{414c}$   | 0.225         | 0.250         | 0.350         | 0.425         | 0.550         | 1.800               | 0.086                      |
| S 15/20      | 0.225         | 0.250         | 0.275         | 0.350         | 0.450         | 1.550               | 0.074                      |
| S 15/40      | 0.250         | 0.275         | 0.325         | 0.400         | 0.475         | 1.725               | 0.082                      |
| S 15/60      | 0.225         | 0.250         | 0.350         | 0.450         | 0.575         | 1.850               | 0.088                      |

The exfoliation resistance was evaluated qualitatively considering the criteria (SS 13 72 44- the Borås method) presented in Table 3. The scaled mass value $S_{56}$ was lower than 0.1 kg/m$^2$ in all mixtures, criterium that has placed the concretes with very good exfoliation resistance. The usage of the blast furnace slag had a positive influence on the scaling resistance in mixtures $S_{54/20}$ and $S_{54/40}$, in which the rate of exfoliated material cumulation was lower than that in the two control mixtures.

Figure 4. (a) Cumulated exfoliated concrete quantity $S_{56}$; (b) Exfoliated mass at 7, 14, 28, 42 and 56 cycles.

The results are similar with those obtained in the study carried out by [31], in which the exfoliation resistance after 56 freeze-thaw cycles was very good, for concretes in which fly ash was used up to 15%.

3.3 Results of the freeze-thaw resistance by percentage decrease of the relative dynamic modulus RDM of elasticity

The values registered for the propagation time of ultrasonic impulses (UPTT) and the values calculated for RDM are presented in Table 6 and images in Figure 6.

As observed in Figure 5, the relative dynamic modulus of elasticity registers a reduction of up to 2% in the following mixtures $S_{360c}$, $S_{54/20}$, $S_{54/40}$ and up to 3% in the following mixtures $S_{414c}$ and $S_{54/60}$. The percentage decrease in the mixtures $S_{54/20}$ and $S_{54/40}$ is lower than that in the control mixture $S_{414c}$, but higher for the $S_{54/60}$ mixture. Compared with the $S_{360c}$ mixture the percentage decrease is lower for the $S_{54/20}$ mixture, but higher for the following mixtures $S_{54/40}$ and $S_{54/60}$.
Table 6. Measuring the propagation time of ultrasounds (UPTT) before and after 56 freeze-thaw cycles and the RDM calculus.

| Mixtures | Characteristics | S 360c | S 414c | S 54/20 | S 54/40 | S54/60 |
|----------|----------------|--------|--------|---------|---------|--------|
|          | T₀ (µs)        | 31.97  | 32.35  | 31.98   | 32.21   | 32.44  |
|          | T₂₈ (µs)       | 32.19  | 32.63  | 32.15   | 32.47   | 32.79  |
|          | T₅₆ (µs)       | 32.24  | 32.75  | 32.23   | 32.53   | 32.89  |
|          | RDM₂₈ (%)      | 98.68  | 98.30  | 98.93   | 98.43   | 98.20  |
|          | RDM₅₆ (%)      | 98.37  | 97.59  | 98.49   | 98.09   | 97.65  |
|          | (100-RDM₅₆) (%)| 1.63   | 2.41   | 1.51    | 1.91    | 2.35   |

Figure 5. RDM at 28 and 56 freeze-thaw cycles.

Figure 6. (a) and (b) Images for measuring (UPTT).

The ultrasonic impulse method allows the localisation of structural degrading, such as cracks caused by the freeze-thaw phenomenon through values registered during the measuring of the propagation time of the ultrasonic impulses (UPTT). If the cracks create a right angle with the propagation velocity of the impulse, the wave suffers a diffraction around the crack and leads to the increase of the duration of the wave. If the direction of the crack coincides with the direction of propagation of the impulse the wave passes through the concrete on both sides of the crack and the duration of the wave is not affected [47,48]. The lowest the travel time (UPTT), indicate the highest the relative dynamic modulus (RDM) of elasticity and the compressive strength of the concrete. If the wave travel time is low, it means that the concrete sample that was tested has fewer voids and internal cracks, which leads to the conclusion that the density of the concrete is higher [49-51]. From the analysis of the results obtained in Table 6 it can be noticed that the lowest propagation duration (UPTT) was obtained for the following mixtures S 360c and S 54/20, in which the best results were obtained in all the performed testing, because these
mixtures have lower porosity. The propagation duration (UPTT) increased, while the freeze-thaw resistance results decreased, in the order enumerated in the following mixtures S 54/40 and S 414c. The longest propagation duration (UPTT) was registered for the S 54/60 mixture, which obtained the weakest freeze-thaw resistance, because it is a mixture with porosity higher than the reference mixture S 414c.

4. Conclusions
In this paper are presented three testing methods for the freeze-thaw resistance, two for the assessment of the internal degrading and one for the material loss at the road concrete surface. Selecting a working method depends on many factors: the research target, the concrete usage field, the severity of the climatic conditions of exposure, etc. The testing represents the measuring of different concrete parameters, comparing results between methods being extremely difficult. But the testing of a mixture using several methods offers supplementary results for each tested parameter that afterwards leads to a more precise interpretation regarding the freeze-thaw behaviour of the concrete. The obtained results by using the methods in this study for testing the road concrete with blast furnace slag in repeated freeze-thaw cycles leads to the following conclusions:

The freeze-thaw resistances in the two control mixtures were higher in the S 360c mixture, compared with S 414c. These results are due to the fact that by increasing the cement dosage from 360 to 414 kg/m³ it led to the increase of the water quantity necessary and it decreased the quantity of aggregate in the S 414c mixture;

The compressive strength losses determined in compliance with SR-3518:2009 (the destructive method for testing the internal cracks) after 150 freeze-thaw cycles, were the lowest in the S 54/20 mixture, and after 300 freeze-thaw cycles in the S 54/40 mixture. The two mixtures with blast furnace slag have the compressive strength losses lower than the control mixture S 414c, but higher than S 360c.

Applying the method SR CEN/TS 12390-9:2009 of assessing the material loss of the concrete surface (the exfoliated mass) proved that the concrete with blast furnace slag S 54/20 obtained better results than the two control mixtures S 360c and S 414c, and the S 54/40 mixture situated at a superior level only compared to the S 414c mixture. Because the road concretes are exposed to the freeze-thaw phenomenon with defrost agents, we consider this method very important and compulsory for the freeze-thaw testing.

The results of the experiments show that the percentage decrease of the relative dynamic modulus RDM of elasticity determined using the method CEN/TR 15177:2006 (non-destructive method for testing the internal cracks) is situated in the 2±3% range, in all mixtures. It can be noticed that the evolution of the percentage decrease of the RDM is similar to that of the compressive strength losses after 150 and 300 freeze-thaw cycle, but the size order is different.

An important advantage for the non-destructive method is the possibility of observing the progress of the internal damages caused by the freeze-thaw during the testing, using the same set of specimens, while for the destructive method it is a disadvantage because we need a higher number of specimens. Using the destructive method, with each age the measuring is performed on different sets of specimens, which can affect the interpretation of the results. The destructive method (resistance loss) is more severe compared to the non-destructive method (percentage decrease of RDM) as it can be noticed from this study. After 300 freeze-thaw cycles, for the same mixture S 54/60, the compressive strength losses reached the value of 18.47%, and the percentage decrease of the RDM 300 was only 2.35%, which shows that the destructive method is more precise. But the two methods prove to be complementary because the propagation time of ultrasonic impulses (UPTT) through concrete is the direct liaison with the compressive resistance having the common factor of concrete density.

The results of the study show that by replacing the cement with 13% (GGBS) and up to 40% natural aggregate with artificial aggregate from crushed blast furnace slag (ABS) with a dimensions of 0/4 mm in the following mixtures S 54/20 and S 54/40, the durability factors are above those of the control mixture S 414c, hence the material proportions combined in these mixtures led to equivalent performances with the reference mixture S 414c made with conventional materials.
For the mixture with blast furnace slag S 54/60, the results obtained were below those of the two control mixtures, both in assessing the internal damages, and the assessment of the structure surface damages, caused by the increase of porosity in the structure of this mixture.

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