

UTILIZAREA ZGURII DE FURNAL CA SURSĂ ALTERNATIVĂ ÎN AMESTECURILE DE BETOANE RUTIERE PENTRU UN MEDIU MAI DURABIL ȘI MAI CURAT USING THE BLAST FURNACE SLAG AS ALTERNATIVE-SOURCE IN MIXTURES FOR THE ROAD CONCRETES FOR A MORE SUSTAINABLE AND A CLEANER ENVIRONMENT

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This paper intends to analyse the characteristics of granulated and non-granulated blast furnace slag used in preparing the road concrete, respectively their influence on the most important characteristics of the concrete, such as consistency, apparent specific gravity, occluded air volume, mechanical resistance, wear resistance and freeze-thaw resistance. Three road concrete mixtures were prepared using conventional materials (Portland cement and natural aggregates) and with different ratios from artificial materials of local provenience, from granulated and ground blast furnace slag used as binder and non-granulated and crushed slag as substitute of the natural aggregate of 0/4 mm. The geometrical, physical and chemical characteristics of the analysed blast furnace slag confirm that it has the required properties for obtaining some sustainable road concrete mixtures. The content of the toxic elements tested for the blast furnace slag do not overpass the limit values admitted in the European regulation. The tensile resistances by binding obtained at 28 days registered values that allowed the ranging of the mixtures in road concrete class BcR 4.5 and BcR 5.0. The freeze-thaw and wear resistances of the road concretes with blast furnace slag were higher than the resistances of the reference road concrete.

Lucrarea curentă își propune să analizeze caracteristicile zgurii de furnal granulat și negranulat utilizată la prepararea betoanelor rutiere, respectiv influența acestora asupra celor mai importante caracteristici ale betonului cum ar fi consistența, densitatea aparentă, volumul de aer occlus, rezistențele mecanice, la uzură și la îngheț-dezgheț. S-au preparat trei amestecuri de betoane rutiere cu materiale convenționale (ciment Portland și agregate naturale) și cu diferite proporții de materiale artificiale de proveniență locală, din zgură de furnal granulat și măcinată utilizată ca liant și zgură negranulat și concasată utilizată ca substituție a agregatului natural sort 0/4 mm. Caracteristicile geometrice, fizice și chimice ale zgurii de furnal analizate confirmă că are proprietăți adecvate pentru realizarea unor amestecuri de betoane rutiere durabile. Conținutul elementelor toxice testate la zgura de furnal nu depășesc valorile limită admise în normele europene. Rezistențele la întindere prin încovoiere obținute la 28 de zile au înregistrat valori care au permis încadrarea amestecurilor în clase de beton rutier BcR 4.5 și BcR 5.0. Rezistențele la îngheț-dezgheț și la uzură a betoanelor rutiere cu zgură au fost mai mari decât rezistențele betoanelor rutiere de referință.

Keywords: blast furnace slag, substitution, mechanical resistances, freeze-thaw resis, road concrete

1. Introduction

Although nowadays the usage of the blast furnace slag as an aggregate in concrete is not frequently used, an increased interest is showed for the efficient recycling and re-using of products coming from the iron and steel industry. The most frequent usage in our country is under the form of granulated and ground blast furnace slag, in compliance with SR EN 197-1:2011 [1], in the field of hydro-technical constructions. The non-granulated slowly air-cooled blast furnace slag, crushed as aggregates has applications in civil constructions and as base layers for the road structures, in compliance with SR EN 13242+A1:2008 [2]. The

non-granulated blast furnace slag presents a crystalline molecular structure, with no use in the manufacturing of cements, [3]. At national level, the company Arcelor Mittal now Liberty, in Galați, has a capacity of 2.150.000 tons/year of cast iron production [4], resulting from approximately 430.000+645.000 tons/year of blast furnace slag. Taking into consideration the availability at national level of the blast furnace slag, in this experiment we recommend a new application for the road concretes. In this paper, a study is presented, regarding the influence of blast furnace slag as additional constituent cement and as artificial aggregate on several determined characteristics on fresh and hardened road concrete. Previously to this

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study, other researches were performed regarding the use of blast furnace slag in road concrete mixtures by totally replacing natural aggregates with artificial aggregates. The results registered a tensile resistance of 6,1 N/mm², in a ratio water/cement of 0,40 [5]. Dan P. Georgescu and Adelina Apostu investigated the cement with blast furnace slag (CEM I, CEM II/B-S) compared to the Portland cement (CEM I) in road concrete mixtures. The results showed that the flexural strength increased as the content of blast furnace slag increased and the as the cement grounding increased, [6]. Nippon Steel & Sumitomo Metal Corporation in Japan, the world's third largest steel producer, has a blast furnace slag production at a same level, collecting approximately 300 kilos of blast furnace slag per ton of iron. The company used the blast furnace slag as coarse aggregate for road pavement. The flexural strength obtained was of 5,9 N/mm² [7]. Wang Aiguo et al studied the influence of air-cooled blast furnace slag used as substitute of limestone natural aggregates on water absorption in concretes and mortars. The results of the research showed a reduced content of the capillary pores in the matrix of the blast furnace slag mortar, [8]. Mujedu K. A., et al investigated the replacement of limestone coarse aggregate with aggregate made of blast furnace slag. The results showed that in mixtures with blast furnace slag the workability, the density and the compressive strength decreased [9]. Neville A. M. and Brooks J. J. underlined the fact that the aggregates have a significant influence on concrete, representing in the skeleton of the concrete around 75%, and in the reaction with cement and with water the aggregates become active in the concrete mixture through their geometrical, physical and chemical properties [9,10].

2. Experimental program

In this paper are presented the results obtained for a second series of road concretes prepared with the same ratios of materials. Compared with the first series of mixtures analysed previously in the paper [11], we aimed to improve the workability, the increase of the volume of occluded air, classifying

the road concrete into classes and the analysis of some characteristics of sustainability. The projection of mixtures was made in compliance with the national regulation NE 014:2002 [12]. The characteristics of the road concrete required by this regulation have the values as in the table 12. The characteristic flexural strength at the age of 28 days minimum 4,9 MPa for class BcR 4,5, and maximum 5,5 MPa for class BcR 5,0. Some differences are to be noticed between the national regulation NE 014:2002 and other states, such as those regarding the content of occluded air between (3÷4) %. For example, the American Concrete Institute ACI 211.1 established the percentage for occluded air between (5÷6) % for the maximum dimension of the aggregate of 25 mm and exposure classes from moderate to severe, [13].

2.1 Materials

The cement used type CEM I 42,5R, was supplied by S.C. Lafarge-Holcim S.A. The declared performances presented in Table 1 were compared to the technical specifications in compliance with SR EN 197-1:2011.

The granulated blast furnace slag 0/12,5 mm obtained by fast-cooling in water, was supplied by the company Arcelor Mittal now Liberty, Galați. The specific surface determined in the laboratory of the Technical University of Cluj-Napoca was of 4385 cm²/g for the cement and of 3775 cm²/g for the blast furnace slag. The chemical analysis and main characteristics of the granulated blast furnace slag were determined by the manufacturer. The results in Table 2 were compared with the limits of the standard SR EN 15167-1:2007, [14]. The uncertainty of measuring the physical-mechanical properties of the materials offered a trust level of 95%.

The reproducibility of the medium samples for the oxidic composition of the granulated blast furnace slag during the period 2016÷2019 was expressed in percentage as mean square deviation (S), with values registered in Table 3. The deviation from the resulted annual mean was a lower one, in the range of (0.04÷0.71) %.

Table 1.

Cement characteristics CEM I 42.5R / Caracteristicile cimentului CEM I 42.5R.

Characteristics <i>Caracteristici</i>	Declared values <i>Valori declarate</i>	Characteristics <i>Caracteristici</i>	Declared values <i>Valori declarate</i>
Clincher-K (% of mass) <i>Clincher-K(% din masă)</i>	95÷100	Calcination loss, (%) <i>Pierdere la calcinare, (%)</i>	Max.5
Auxiliary components, % <i>Componente auxiliare, %</i>	0÷5	Insoluble residue, (%) <i>Reziduu insolubil, (%)</i>	Max.5
Initial intake time <i>Timp inițial de priză</i>	Min.60	Sulphate content (SO ₃), (%) <i>Conținutul de sulfați (SO₃), (%)</i>	Max.4
Stability (expansion), mm <i>Stabilitate (expansiune), mm</i>	Max.3	Chlorine content, (%), <i>Conținutul de cloruri, (%)</i>	Max.0.1
Initial compressive strength-- (MPa) <i>Rezistența la compresiune inițială, (MPa)</i>	Min.24	Standard compressive strength, (MPa) <i>Rezistența la compresiune standard, (MPa)</i>	Min.46

Table 2

Characteristics of the granulated blast furnace slag / Caracteristicile zgurii de furnal granulate			
Physical and chemical characteristics <i>Caracteristici fizice și chimice</i>	Obtained values <i>Valori obținute</i>	Limits SR EN 15167-1:2007 <i>Limite SR EN 15167-1:2007</i>	Analysis method in compliance with the standards <i>Metoda de analiză conform cu standardele</i>
Sum (CaO+MgO+SiO ₂) <i>Suma (CaO+MgO+SiO₂)</i>	84.05	≥ 2/3	-
Ratio (CaO+MgO)/SiO ₂ <i>Raportul (CaO+MgO)/SiO₂</i>	1.3	≥ 1.0	-
In compliance with the standard (CaO/SiO ₂) <i>Conform standarde(CaO/SiO₂)</i>	1.15	1.1...1.4	SR 648:2002
Magnesium oxide MgO, % <i>Oxidul de magneziu MgO, %</i>	5.80	≤ 18	SR EN 196/2-2013
Sulphides, % <i>Sulfuri, %</i>	0.58	≤ 2.0	SR EN 196/2-2013
Sulphate, % <i>Sulfat, %</i>	0.44	≤ 2.5	SR EN 196/2-2013
Calcination loss, % <i>Pierdere de calcinare, %</i>	0.00	≤ 3.0	SR EN 196/2-2013
Chlorine, % <i>Clorura, %</i>	0.004	≤ 0.10	SR EN 196/2-2013
Content of alkalis in cement (Na ₂ O equivalent) % <i>Conținutul de alcalii la ciment (Na₂O echivalent) %</i>	1.0 %	(0.5 +1.2)	SR EN 196/2-2013
Activity index at 7 days, % <i>Indice de activitate la 7 zile,%</i>	58.48	Min 45	SR EN 196/1-2016
Activity index at 28 days, % <i>Indice de activitate la 28 zile,%</i>	74.94	Min 70	SR EN 196/1-2016
Content of tricalcium aluminate in cement C ₃ A, % <i>Conținutul de aluminat tricalcic la ciment C₃A, %</i>	7.59	(6 +12)	-
Initial intake time. Min <i>Timp inițial de priză. min</i>	200	-	SR EN 196/3-2017
Stability (Le Chatelier), mm <i>Stabilitate (Le Chatelier), mm</i>	0.0	-	SR EN 196/3-2017
Vitreous mass content (X-ray diffraction), % <i>Conținutul de masă vitroasă (X-ray diffraction), %</i>	95±2.5	-	SR 648:2002
Waste insoluble in HCL, % <i>Rezidu insolubil în HCL, %</i>	0.29	-	SR EN 196/2-2013

Table 3

Oxidic composition of the granulated blast furnace slag, %. / *Compoziția oxidică a zgurii granulate, %.*

Oxides % <i>Oxizi %</i>	SiO ₂	Al ₂ O ₃	MnO	MgO	CaO	Fe ₂ O ₃	Na ₂ O	K ₂ O	TiO ₂	Mn ₂ O ₃
Individual values <i>Valori individuale</i>	36.44	11.60	0.55	5.8	41.81	0.78	0.345	0.428	0.30	0.62
Average values <i>Valori medii</i> 2016-2019	36.56	10.50	-	7.37	41.75	0.64	0.36	0.52	0.41	0.38
S % 2016+2019	0.71	0.50	-	0.68	0.11	0.09	0.06	0.04	0.06	0.1

Observation: the oxidic composition of the granulated blast furnace slag was determined using the testing method SR EN 196/2-2013 during the period 2016+2017, and for the following years 2018-2019 using the equivalent method, x-ray fluorescence (FRX).

Notă: Compoziția oxidică a zgurii granulate a fost determinată utilizând metoda de încercare SR EN 196/2-2013 în perioada 2016+2017, iar pentru anii 2018-2019 prin metoda echivalentă, fluorescența cu raze -X (FRX),

The artificial aggregates from non-granulated slowly air-cooled blast furnace slag (ABS) were crushed at a dimension of 0/4 mm. And they were supplied by the company Liberty, in Galați. The characteristics of the aggregates

registered values presented in Table 4 and 5, being assessed in compliance with the standard SR EN 12620:2003 and SR EN 12620:2003+A1:2008 [15] and SR 667:2001 [16].

Table 4

Characteristics of natural sand (NA) 0/4 mm and of aggregates from blast furnace slag (ABS) 0/4 mm.
Caracteristicile nisipului natural (NA) 0/4 mm și a agregatelor din zgură de furnal (ABS) 0/4 mm.

Technical characteristics <i>Caracteristici tehnice</i>	Obtained values ABS_0/4 mm <i>Valori obținute ABS_0/4 mm</i>	Obtained values <i>Valori obținute</i> NA_0/4 mm	Limits <i>Limite</i> SR EN 12620
Granularity / <i>Granulozitate</i>	G _F 85	G _F 85	G _F 85
Coefficient of water absorption <i>Coefficient de absorbție a apei</i>	WA ₂₄ 2	WA ₂₄ 2	-
Content of fine particles < 0.063 mm -f, % <i>Conținut de particule fine sub 0.063 mm -f,%</i>	f _{3,5}	f ₃	(3 ±22)
Sulphate soluble in acid, % <i>Sulfat solubil în acid,%</i>	AS _{0,52}	-	≤ 1.0
Total sulphate, % <i>Sulfat total, %</i>	0.96	-	≤ 2.0
Disintegration of iron from blast furnace slag <i>Dezintegrarea fierului din zgură</i>	Does not present cracks and disintegrate <i>Nu prezintă fisuri și nu se dezintegrază</i>		Visual aspect <i>Aspect vizual</i>
Disintegration of dicalcium silicate from blast furnace slag <i>Dezintegrarea silicatlui dicalcic din zgură</i>	Presents a uniform violet colour, with shining stains in small quantities uniformly distributed <i>Prezintă o culoare violet uniformă, cu pete strălucitoare în cantități mici distribuite uniform</i>	-	Visual aspect <i>Aspect vizual</i>

Table 5

Characteristics of coarse aggregates / *Caracteristicile agregatelor grosiere*

Characteristics <i>Caracteristici</i>	Obtained values <i>Valori obținute</i> CA_4/8	Obtained values <i>Valori obținute</i> CA_8/16	Limits <i>Limite</i> SR EN12620	Obtained values <i>Valori obținute</i> CA_16/25	Limits <i>Limite</i> SR 667
Granularity / <i>Granulozitate</i>	G _C 90/10	G _C 90/15	-	-	-
Coefficient of water absorption WA ₂₄ <i>Coefficient de absorbție a apei</i>	WA ₂₄ 2	WA ₂₄ 1.4	-	WA ₂₄ 1.2	-
Content of fine particles < 0.063 mm -f, % <i>Conținut de particule fine sub 0.063 mm -f,%</i>	-	f _{1,0}	(1.5 ±4)	-	-
Content of fractions < 0.1 mm, % <i>Conținut de fracțiuni sub 0.1 mm, %</i>	-	-	-	0,09	Max.0.5
Coefficient of form, % <i>Coefficient de formă ,%</i>	Sl ₂₀	Sl ₇	(15 ±50)	7	Max.25
Resistance to repeated action of Mg SO ₄ , % <i>Rezistența la acțiunea repetată a Mg SO₄,%</i>	-	0.38	(18 ±35)	0.38	Max.6
Freeze-thaw resistance, mass loss, % <i>Rezistența la îngheț-dezghet, pierdere de masă,%</i>	F ₁	0.20	(1 ±4)	0.20	Max.3
Wear resistance, micro-Deval coefficient <i>Rezistența la uzură,coeficientul micro-Deval</i>	-	M _{DE} 6	(10 ±35)	6	Max.20
Shatter resistance, Los Angeles coefficient <i>Rezistența la sfărâmare, coeficientul Los Angeles</i>	LA ₃₀	LA ₁₄	(15 ±50)	14	Max.18

The natural sand (0/4 mm) was supplied by the gravel pit from Beclean, the crushed gravel (4/8 mm) by the gravel pit from Sânicosara, and the crushed coarse aggregate (crushed rock 8/16 mm and 16/25 mm) by the rock quarry SC Grandemar SA Cluj.

The additives were purchases from Badische Anilin und Soda Fabrik (BASF). We used super-plasticizer additive MasterGlenium SKY 527 and air trainer additive Master Air 9060. The water from the concrete was taken from the water supply system of the city of Cluj-Napoca, in compliance with SR EN 1008:2003 [17].

2.2 Mixtures proportions

In this study, there were prepared a total number of five mixtures with the material quantities presented in Table 6. The first two control mixtures were made with Portland cement and natural aggregates, and, in the next three mixtures, we used granulated and grounded blast furnace slag under 63 μm (GGBS) and aggregates from air-cooled crushed blast furnace slag (ABS) at the dimension of 0/4 mm in different proportions:

S 360c, control mixture with 360 kg/m³ dosage Portland cement and natural aggregates;

Table 6

Quantities Cantități	Mixtures [Kg/m ³] / Amestecuri [Kg/m ³]				
	S 360 control	S 414 control	S 54/20	S 54/40	S 54/60
Mixture (Kg/m ³) Amestec (Kg/m ³)					
Cement (C) Ciment (C)	360	414	360	360	360
Blast furnace slag (GGBS) Zgură de furnal (GGBS)	-	-	54	54	54
Total binder (L) Liant total (L)	360	414	414	414	414
w/b (water/binder) w/b (apă /liant)	0.46	0.42	0.42	0.44	0.41
Ag /L, (aggregate/binder) Ag /L, (agregat/ liant)	5.27	4.48	4.51	4.46	4.53
Super-plasticizer additive Aditiv superplastifiant	3.60	4.14	4.39	4.55	4.97
Air trainer additive Aditiv antrenor de aer	1.80	2.07	2.07	2.07	2.07

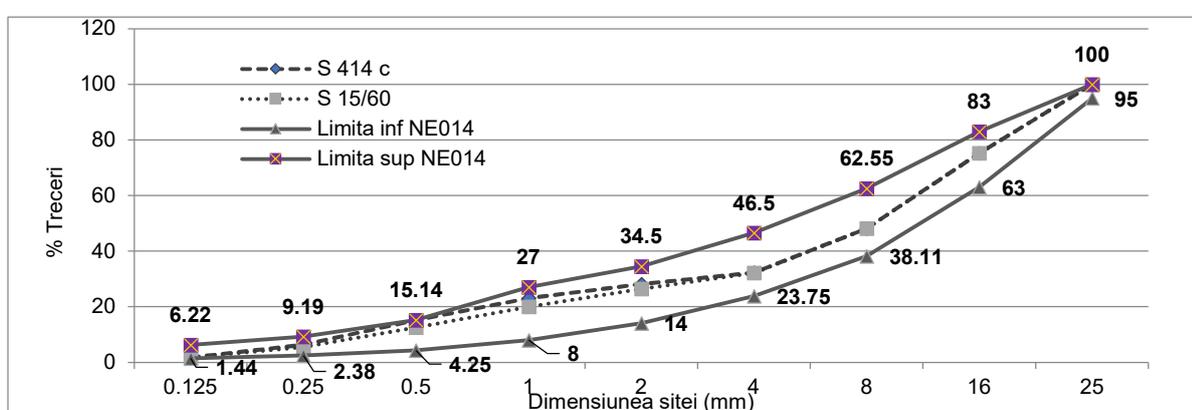


Fig. 1 - Granularity curves of aggregates for the total mixture / Curbele granulometrice ale agregatelor pentru amestecul total.

S 414c, control mixture with 414 kg/m³ dosage Portland cement and natural aggregates;

S 54/20, 360 kg/m³ (cement)+ 54 kg/m³ (GGBS) and 20% (ABS)_0/4 mm+80% natural sand;

S 54/40, 360 kg/m³ (cement)+ 54 kg/m³ (GGBS) and 40% (ABS)_0/4 mm+60% natural sand;

S 54/60, 360 kg/m³ (cement)+ 54 kg/m³ (GGBS) and 60% (ABS)_0/4 mm+40% natural sand;

The aggregate proportions were 32% in sand and 68% in coarse aggregate. The granularity curve of the total mixture ranged within the admitted granularity area, in compliance with NE 014-2002, [12] see Figure 1.

The percentage volume of passing of aggregates in the following mixtures S 360c, S 54/20, S 54/40 were situated within the granularity area indicated by the mixture S414c and S 15/60, in Figure 1, up to the mesh dimension of 4 mm. Over these dimensions the granularity curve was identified in all five mixtures.

2.3 Testing procedure

2.3.1 The characterization (GGBS) through the saturation degree in lime, mineralogical composition and content of toxic elements.

The ratio of free calcium oxide was calculated under molecular form in the chemical composition presented in Table 3. The saturation degree in lime (CaO) was calculated using the Kühl formula, also used in the experimental study [18].

$$S_k = \frac{CaO}{2.8\%SiO_2 + 1.1\%Al_2O_3 + 0.7\%Fe_2O_3} \quad (1).$$

The X-ray powder diffraction study allowed the determination of the mineralogical composition of the crystallized phase, after grinding the granulated slag to a size below 69 μm. The percentages were determined using the Eva program by Brucker. The measurements were

performed in the Mineralogy Laboratory of the Geological Institute of Romania. A Bruker D8 ADVANCE diffractometer was used. Ni-filtered Cu Ka radiation ($\lambda = 1.5406 \text{ \AA}$), a scan speed of $0.02^\circ 2\theta$ per second, a time per step of 2 s, an operating voltage of 40 kV for a current of 30 mA, and a slit system of 1/0.1/1 with a receiving slit of 0.6 mm, were used for measurements in a $\theta - 2\theta$ geometry. For the identification of the toxic elements within the granulated blast furnace slag the leachability tests were performed by the Wessling Environmental Protection Laboratory in Târgul Mureş. The working procedure was in compliance with: [19] SR EN 12457-2:2003, [20] SR EN 12457-4:2003, [21] SR EN 16192:2012, [22] SR EN ISO 10523:2012, [23] SR EN ISO 11885:2009. The obtained results were compared with the limits established in table 2.2 of the Order no. 95-2005 [24], transposing the Council Decision 2003/33/CE establishing criteria and procedures for the acceptance of waste at landfills in compliance with the Directive 1999/31/CE [25].

2.3.2 Characterisation of aggregates through geometric, physical and chemical properties, fineness modulus, volumetric mass, water absorption coefficient

The characteristics of the natural and artificial aggregates were tested in compliance with the normative references mentioned within the standards SR EN 12620:2003 and SR EN 12620:2003+A1:2008, [15] and the national standard SR 667:2001, [16]. The fineness modulus (M_f) was calculated for aggregates (0/4 mm), as sum of total percentage retained on mash series, in compliance with ACI-EB-E1-07, [26]. Depending on the obtained values, the aggregates were ranged in sand with big grains between (2.4÷4.0), sand with medium grains between (1.5÷2.8) and sand with fine grains between (0.6÷2.1) in compliance with SR EN 12620:2003 and SR EN 12620+A1:2008, [15]. The volumetric mass was calculated depending on the content of humidity of the permeable and impermeable pores, on the mass/volume ratio using the pycnometer method, and the water absorption coefficient was expressed in percentage from the dry mass after immersion for (24 ± 0,5) h, in compliance with SR EN 1097-6: 2002, [27].

2.3.3 Observations on fresh and hardened concrete: density, consistency, occluded air, mechanical resistances at 28 days old.

The samples cast in 150x150x600 moulds were kept for (24±2) hours, after which they were conserved in water at a temperature of (20±2)°C until the date of the testing, in compliance with SR EN 12390-2:2002, [28]. On the fresh concrete we determined the following: the density of the concrete in compliance with the standard SR EN 12350-6:2002, [29], the consistency of the concrete using the testing method in compliance with SR EN

12350-2 [30], the content of occluded air in compliance with SR EN 12350-7, [31]. On prisms, the tensile resistance by bending was determined in compliance with SR EN 12390-5:2002 [32], and on half of prisms, the compressive strength was determined at the age of 28 days, in compliance with SR EN 12390-3:2002, [33]. The average compressive strength f_{cm}^{28} , obtained on half of prisms with section of 150 mm from three samples, was corrected depending on the real resistance of the concrete.

2.3.4 Determining the freeze-thaw resistance

In order to compare the performances to 150 freeze-thaw cycles we cast 6 cubic samples (of which three witness samples) with an edge of 150 mm for each concrete mixture. The maintenance, the conservation and the testing of the samples was in compliance with the destructive method from SR-3518:2009 [34]. Until the age of 7 days, the samples were kept in water, and then they were kept cool air at a temperature of (20±2)°C and a humidity of (65±5) %. 4 days before starting the testing (at the age of 150 days) the samples were immersed in water bath at a temperature of (20±5) °C for saturation. The witness samples were kept under water, and those supposed for the freeze-thaw cycles were introduced in the thermostat chamber. The thermostat chamber was set at a temperature of (-17±2)°C for a freeze cycle of 4h and up to (20±2)°C for a thaw cycle of 4h.

2.3.5 Determining the wear resistance

The wear resistance was tested on the abrasive disk of the Böhme device, the brand Matest belonging to the Technical University of Cluj-Napoca, in compliance with the standard SR EN 1338:2004/AC:2006 [35], Annex H. For each mixture we prepared 3 cubic samples of (71 ± 1,5) mm, cast at the same time and conserved in the same conditions until the age of 200 days, as the witness samples used for the freeze-thaw testing. The dry samples to the constant mass were tested for 16 cycles of 22 rotations/cycle. For each cycle the abrasive material was replaced and the contact side was progressively rotated at 90°. The wear was calculated as average of the lost volume ΔV (mm³) resulted from the ratio between the mass loss Δm (g) and density ρ (g/mm³). Depending on the resulted value of the lost mass volume the class of resistance to abrasion was established, in compliance with the requirements set by the standard, [35].

3. Results and discussions

3.1 The characterization (GGBS) through the saturation degree in lime, mineralogical composition and content of toxic elements

Taking in consideration the fact that in the technological process of cast iron processing

Table 7

Saturation degree in limestone for the granulated and ground blast furnace slag, %.
 Gradul de saturare în calce a zgurii de furnal măcinată și granulate, %.

CaO	Skx100	Free CaO	Percentage of chemical combined CaO Ponderea CaO combinat chimic	Percentage of free CaO Ponderea CaO liber
41.81%	36.25%	5.56%	86.70%	13.30%

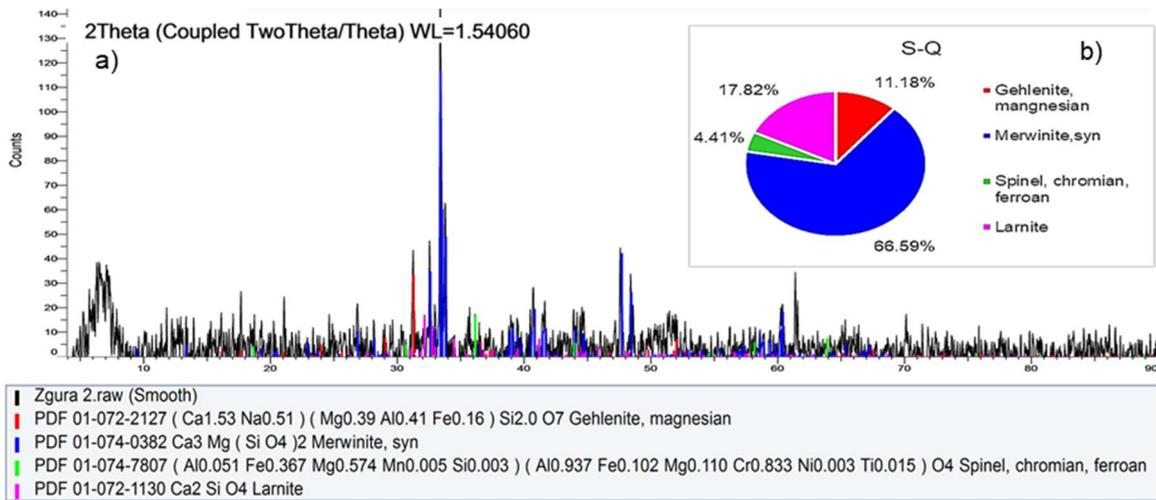


Fig. 2. a) X-ray powder diffraction pattern of a representative sample of (GGBS) and 2.b) Pie-chart showing the percentages of the mineral constituents from the crystallized phase / a) Difractograma de raze X în pulberi a unei probe reprezentative de zgură de (GGBS) și 2.b) Distribuția procentuală a constituenților mineralogici ai fazei cristalizate.

limestone is inserted in the blast furnace, through thermic dissociation are obtained free oxides of calcium and magnesium as a result of MgCO₂ presence in the limestone. Part of the resulted calcium oxide is necessary for the saturation of oxide acids (SiO₂, Al₂O₃ and Fe₂O₃), and the rest becomes free calcium oxide. The calcium oxide remaining un-combined through the hydration reaction increases the volume and can generate inconstancy within the volume (expansion). Applying Kühl's formula for the saturation degree in limestone resulted the following values, see Table 7.

The characteristics from Table 2 show that the granulated and ground blast furnace slag had good stability, 0 mm, measured with *Le Chatelier* rings. The expansion does not have significant effects if the free CaO is smaller than 2% from the mass of the cement clinker, [36]. On the other hand, from the substitution percentage (13%) of the cement with blast furnace slag in the mixture concrete the free CaO represents 0,72% which situates under the value of 2%. Another aspect related to free calcium and magnesium oxides refers to the degree of carbonatation and hydration due to the exposure in atmosphere of the blast furnace slag. This can be determined by the calcination loss, [37,38]. The blast furnace slag from Galați registered the value 0 for the calcination loss, which is under the maximum limit of 3%. The mineralogical composition determined through x-ray diffraction in granulated and grounded blast furnace slag, Figure 2 a) and b).

The X-ray powder diffraction (XRD) analysis on slag samples taken from Galați revealed the presence of the following mineral phases: merwinite [ideally Ca₃Mg(SiO₄)₂], gehlenite (ideally Ca₂Al₂SiO₇, in fact a member of the gehlenite – åkermanite series) and larnite (ideally Ca₂SiO₄), together with minerals in the spinel group. These are phases of high temperature and are characteristic of rocks such as the high-temperature skarns, formed at temperatures above 800°C. Their presence in the blast furnace slag can be explained by the use as flux for smelting of dolomite [CaMg(CO₃)₂], and fluorite (CaF₂), that mobilized and fixed the silica. The percentages of the crystallized phases in the slag, as determined by XRD, are given in Figure 2.b. The amorphous phase (glass) represents about 95 % of the total volume of the slag. Its chemical composition seems to parallel that of the crystallized phase.

The results obtained from the leachability test, as well as the limit values, are presented in Table 8.

The analysed chemical elements registered values below the limit values allowed in Order 95-2005, in Table 2.2 [24]. The leachability test was performed on powders but the concrete is a compact and dense construction material through which the water does not pass. In the study [39] the leachability test of the lead in the composite materials was performed on compact samples of cement mortar. The results showed that the glass coming from dismemberment of electrical waste can be used as construction material, in safe environment conditions.

Table 8

The toxic elements tested within the ground and granulated blast furnace slag
Elementele toxice testate din zgura de furnal măcinată și granulată

Description Denumire	Obtained values Valori obținute	Limit values Valori limită	Description Denumire	Obtained values Valori obținute	Limit values Valori limită
Eluate pH 10/1, pH units <i>pH-ul eluatului 10/1, Unități pH</i>	10.76	-	Mercury, mg/kg	< 0.005	0.01
Arsenic, mg/kg	<0.4	0.5	Nickel, mg/kg	< 0.2	0.4
Cadmium, mg/kg	< 0.02	0.04	Lead, mg/kg	< 0.2	0.5
Chromium, mg/kg	< 0.05	0.5	Zinc, mg/kg	< 1	4
Copper, mg/kg	< 0.2	2	Mercury, mg/kg	< 0.005	0.01

Table 9

The fineness modulus (M_f), of aggregates dimension 0/4 mm / *Modulul de finețe (M_f), al agregatelor de dimensiunea 0/4 mm*

Aggregate mixture <i>Amestec de agregate</i>	100% NA	80%NA+20%ABS	60%NA+40%ABS	40%NA+60%ABS	100%ABS
(M_f)	2.72	2.81	2.90	2.97	3.15

3.2 The characterisation of aggregates through geometrical, physical and chemical properties, the fineness modulus, volumetric mass, water absorption coefficient

The presence of sulphates within the blast furnace slag aggregates lead to concrete degradation, through swelling. The values resulted in Table 4 for the sulphate soluble in acid and for the total sulphate in air-cooled blast furnace slag are below the superior limit recommended in chapter 6.3 of the SR EN 12620, [15]. The blast furnace slag aggregates do not present disintegration of the dicalcium silicate, nor ferrous disintegrations, so the air-cooling of the blast furnace slag is not affected. In coarse aggregates (CA_8/16, CA_16/25) can be noticed in Table 5 that the freeze-thaw, wear and crushing resistances have superior performances compared with those established in the reference standards. [15,16]. The resulted value for the fineness modulus of the sands characterises the workability of concrete mixtures, [36]. Of the

obtained results in Table 9, in blast furnace slag mixtures can be noticed that the value of the fineness modulus increases linearly with the increase of the level of substitution of natural aggregates with blast furnace slag (ABS_0/4), which shows that the blast furnace slag influences through the decrease of the mixtures workability.

The values obtained for the volumetric mass and the water absorption coefficient are as in Table 10.

The volumetric masses of blast furnace slag are lower than those of natural sand and these are necessary for the calculus of the quantities within the mixture, [37]. The water absorption coefficient WA₂₄ in the two aggregates have the same value of 2%. But, the total content of humidity after 24 h of immersion is higher with 10% in aggregates with blast furnace slag than in those with natural sand, see Figure 3, because the free water quantity at the surface of the blast furnace slag aggregates is higher than that of sand.

Table 10

Volumetric mass and water absorption coefficient
Masa volumică și coeficientul de absorție a apei

Aggregate	ρ_a (Mg/m ³)	ρ_{rd} (Mg/m ³)	ρ_{ssd} (Mg/m ³)	WA ₂₄ (%)
NA_0/4	2.70	2.56	2.61	2.00
ABS_0/4	2.59	2.46	2.51	2.00
CA_4/8	2.68	2.59	2.62	1.40
CA_8/16	2.66	2.57	2.61	1.40
CA_16/25	2.67	2.58	2.62	1.20

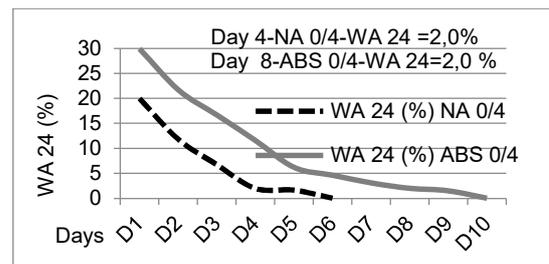


Fig. 3 - Water absorption in time for sand and slag / *Absorția apei în timp pentru nisip și zgură.*

Table 11

Apparent density of fresh concrete, consistency and occluded air content
Densitatea aparentă a betonului proaspăt, consistența și conținutul de aer oclus

Characteristics / <i>Caracteristici</i>	S 360 c	S 414 cl	S 54/20	S 54/40	S 54/60	Limits / <i>Limite</i> NE 014
Density, calculated (g/cm ³) <i>Densitatea, calculată (g/cm³)</i>	2.394	2.414	2.424	2.415	2.427	2400±40
Density, determined (g/cm ³) <i>Densitatea, determinată (g/cm³)</i>	2.399	2.434	2.442	2.435	2.446	2400±40
Consistency / <i>Consistența</i> S (mm)	39	25	29	26	30	30±10
Occluded air / <i>Aer oclus</i> (%)	3.80	3.00	3.20	3.05	3.25	3,5±0,5



Fig. 4 - Observations on fresh concrete. *Determinări pe betonul proaspăt.*

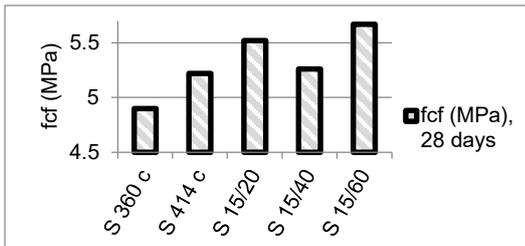


Fig. 6 - Average flexural tensile resistances / *Rezistențele medii la întindere prin încovoiere.*

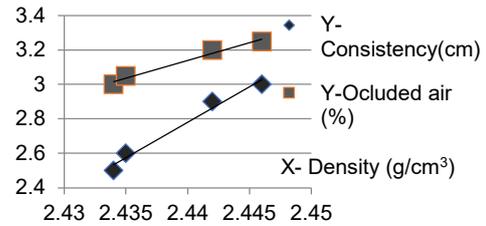


Fig. 5 - Relationship between apparent density – consistency and apparent density – occluded air / *Relația între densitatea aparentă - consistență și densitatea aparentă-aer oclus.*

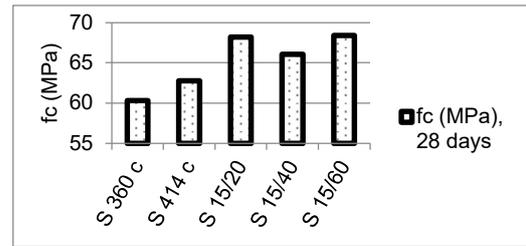


Fig. 7 - Average compression strength / *Rezistențele medii la compresiune.*

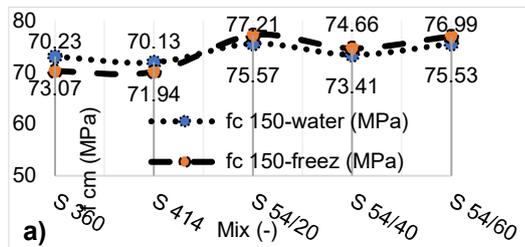


Fig. 8 a) Compressive strength fcm (MPa) / *Rezistențele la compresiune fcm (MPa).*

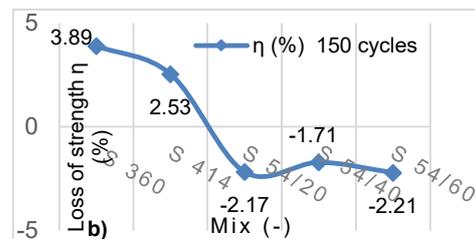


Fig. 8.b) Compressive strength losses η , (%) / *Pierderi de rezistență la compresiune η , (%).*

3.3 Observations on fresh and hardened concrete: density, consistency, occluded air, mechanical resistance at the age of 28 days

The values obtained in Table 11 for the density, consistency and the occluded air of the fresh concrete fit in the allowed limits range of NE 014:2002 [12], photo images from the laboratory in Figure 4.

Notice in Figure 5 that there is a linear relationship between the apparent density and the consistency of the mixtures and between the apparent density and the occluded air volume in mixtures. In the mixtures S 54/20 and S 54/60 the high values registered for consistency and occluded air led to higher density.

The mechanical resistances at the age of 28 days registered in Figure 6 and 7, in all mixtures with blast furnace slag have higher values than those in the control mixture S 414c. For the mixture S 360c we registered an accentuated decrease of the flexural tensile strength. The cause was the increase of the ratio water/binder to 0,46%, due to an insufficient control of humidity of the aggregates during the casting of the mixture. The water/binder ratio of 0,46% registered in the control mixture

S 360c overpasses the maximum limit of 0,45, allowed by NE 014-2002, [12]. As a result, the control value for the flexural tensile and compressive strength at the age of 28 days was considered the one from the control mixture S 414c.

3.4 Determining the freeze-thaw resistance

In Figure 8.a) are presented the average values obtained for the compressive strength after 150 freeze-thaw cycles. The compressive strength losses were calculated between the witness samples and the samples tested for freeze-thaw, see Figure 8.b). Notice values below 25 % than the maximum limit allowed by the national standard SR 3519-2009. The best results were obtained for the mixtures S 54/20 and S 54/60, that can be justified by the fact that these concretes are denser preventing the extension of water within the capillary pores.

3.5 Determining the wear resistance

The volume losses of the samples tested for abrasion have an inversely proportional tendency with the results of the compressive strength, see Figure 9.a). The higher the compressive strength, the lower the volume losses, as they are highlighted

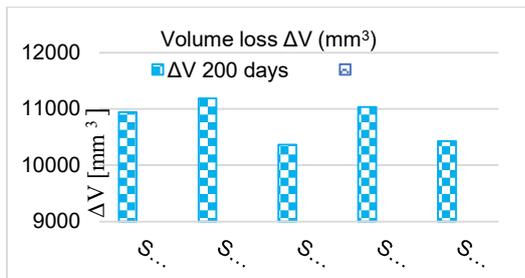


Fig. 9.- a) Volume loss through wear / Pierdere de volum din uzură (mm³).

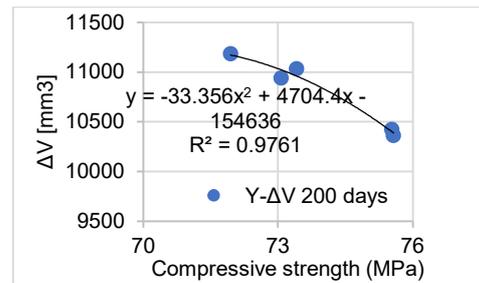


Fig. 9.- b) The relationship between fcm and ΔV at 200 days / Relația între fcm și ΔV la 200 de zile.

in the mixtures S 54/20 and S 54/60. All the concrete mixtures registered volume losses lower than 18000 mm³/5000 mm², values that allowed their classification in the class of resistance to abrasion 4, mark I, in compliance with the classification of the standard SR EN 1338:2004/AC:2006, [35].

Figure 9.b) shows the relationship between the compressive strength and the volume loss after the abrasion testing at the age of 200 days. Between the two characteristics was developed a second order polynomial equation derived through regression, with a very good correlation coefficient (value R). The obtained results confirm those offered by the Alaa M.R.2014, [40] who established a correlation coefficient close to 0,9298 through polynomial relationship between the compressive strength and the volume loss from wear.

4. Conclusions

The following conclusions were drawn from the experimental study conducted on mixtures from conventional materials and artificial material such as granulated and ground blast furnace slag (GGBS) and aggregates from crushed blast furnace slag (ABS):

I. The geometrical, physical and chemical characteristics of the granulated blast furnace slag (GGBS) and of the aggregates from crushed blast furnace slag (ABS) used in this experiment have the appropriate properties for their usage as materials with cement characteristics for road concrete, according to the technical specifications.

II. The leachability test performed on granulated blast furnace slag (GGBS) shows that the tested elements has a low content of toxic substances, below the limits allowed by the European legislation.

III. The results for the flexural tensile strength at the age of 28 days, allowed the classification of the following mixtures S 54/20 and S 54/60 in the road concrete class BcR 5,0 and in BcR 4,5 for the other mixtures.

IV. The compressive strengths registered after 150 freeze-thaw cycles registered high values in all the mixtures with blast furnace slag compared with mixtures made of conventional materials.

V. Up to 150 freeze-thaw cycles there were not registered any compressive strength losses for the

mixtures with blast furnace slag, which is why we recommend the continuing testing by supplementing the number of freeze-thaw cycles.

VI. The values resulted for the compressive strength were directly proportional with the wear resistance and implicitly, inversely proportional with the volume loss of the tested samples.

VII. Important factors influencing positively the compressive strength and the wear resistance were: aggregates resistant to crushing and wear, a low water/binder ratio and a hardening regime in humid environment of 7 days.

VIII. Subsequent investigations shall be focused on other aspects related to the sustainability of the concrete such as corrosion through penetration of the chlorine ion, corrosion from carbonation and the alkali-silica reaction.

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