

LOW-CEMENT DOSAGE REFRACTORY CONCRETE WITH LOW THERMAL CONDUCTIVITY

LUCIAN PAUNESCU^{1*}, ENIKO VOLCEANOV^{2,3}, BOGDAN-VALENTIN PAUNESCU⁴, IOANA MONICA SURUGIU⁵

¹*Cosfel Actual SRL, 95-97 Calea Grivitei, sector 1, Bucharest 010705, Romania*

²*Metallurgical Research Institute SA, 39 Mehadia street, sector 6, Bucharest 060543, Romania*

³*Faculty of Science and Materials Engineering, University "Politehnica" of Bucharest, 313 Independence Splai, sector 1, Bucharest 060032, Romania*

⁴*Consitrans SA, 56 Polona street, sector 1, Bucharest 010494, Romania*

⁵*Faculty of Computer Science, University "Politehnica" of Bucharest, 313 Independence Splai, sector 1, Bucharest 060032, Romania*

Abstract: Super-aluminous refractory concrete (over 94 % Al_2O_3) with low dosage of cement (9 %) was made, its physical, thermal, and mechanical characteristics being considered suitable for the intermediate layer of a steel casting ladle: porosity of 29.31 %, the apparent density of $2.32 \text{ g}\cdot\text{cm}^{-3}$ thermal conductivity of $1.45 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$, and compressive strength of 34.8 MPa (after heat treatment at 1500 °C). The aim of the research was achieving a super-aluminous concrete with low-cement dosage, which would have acceptable thermal insulation properties, so that the heat loss through this refractory lining layer would be significantly reduced compared to the reference situation.

Keywords: super-aluminous concrete, low-cement dosage, porosity, thermal conductivity, thermal insulation properties, compressive strength.

1. INTRODUCTION

The increase of the production of monolithic refractories at the expense of refractory bricks has exhibited in the last decades of the 20th century by the appearance of new types of high-performance concrete.

Concrete, considered as a composite material, can be defined as an artificial conglomerate obtained by hardening the mixture composed of hydraulic binder (cement), aggregate, and water. The alumina (Al_2O_3) content of both the cement and especially the aggregate is decisive for high temperature resistance and therefore, for its refractory character. The aggregate has the major role in structuring the concrete through the granules size and the granulometric distribution, while the cement has the role of strengthening the structure [1, 2]. The most frequently used aggregates for making refractory concrete with hydraulic binder are: chamotte, sillimanite, andalusite, kyanite, calcined bauxite, corundum, tabular alumina, chromite and zirconia (ZrO_2). Aggregates with

* Corresponding author, email: lucianpaunescu16@gmail.com
© 2022 Alma Mater Publishing House

very high content of Al_2O_3 (e.g. tabular alumina) and specific admixtures allowed making high refractoriness super-aluminous concretes with content of 90-96 % Al_2O_3 usable in the temperature range of 1500-1750 °C as the refractory lining of metallurgical furnaces [3]. Mechanical resistance as a decisive characteristic for the structural stability of concrete has a higher value when the intergranular cohesion is also higher. Therefore, in the case of refractory concrete, the hydraulic binder has a complementary role and its dosage in the starting mixture can be reduced. Reducing the cement dosage in refractory concrete leads to the following advantages: reducing the working water requirement (in direct relation to the final porosity of concrete), reducing the loss of concrete's mechanical strength in the critical temperature domain, and increasing its refractoriness [1].

The advanced reduction of the cement dosage favours the development of very dense structures with very high mechanical strength of the concrete mainly due to the very low water content. To compensate for this deficiency and to obtain adequate rheological properties, involving acceptable workability even at extremely low water/cement ratio, it is necessary to add specific additive substances (complex binding mixtures, dispersing and fluidizing admixtures, ultra-dispersing mineral powders, pH-modifying electrolytes, etc.), which ensure the conditions for the generation of gel binding forms. These can exist together with the forms of chemical and hydraulic binding, creating a complex binding system [2].

Ordinary refractory concrete has the dosage of cement within the limits 15-30 %. Until the appearance of concrete with low-cement dosage (below 10 %) on the market, the use of ordinary concrete did not allow to development of mechanical and structural characteristics similar to those of refractory bricks. Subsequently, the new type of refractory concrete had a rapid development, its properties being optimized. The consequence of the manufacturing technology and the bonding system applied to refractory concrete with low-cement dosage is obtaining a material type with low porosity and highly heat-resistant (at 1580-1770 °C or more). This super-aluminous material is used in industrial furnace lining and all other structures that require resistance to high prolonged heating.

Recently, numerous researches have been independently conducted worldwide with the objective of improving the performance of concrete, especially that with low and ultra-low dosage of cement.

According to Azmee and Shafiq [4], the achieve of ultra-high performance concrete with a low dosage of cement with a good consistency and the highest resistance can be obtained by combined addition of fly ash and ultrafine calcium carbonate substituting up to 50 % of the cement used as the hydraulic binder. The compressive strength of hardened concrete after 7 days increased by 12.5 %, after 28 days it increased by another 8 % and also by another 20 % after 90 days.

Having as its objective the manufacture of super-aluminous concrete (80-90 % Al_2O_3) with low-cement dosage, the paper of Ionita et al. [5] used aluminous cement (containing 72.6 % Al_2O_3 and 23.9 % CaO), bauxite, chamotte, and electrocorundum as aggregates, admixtures (refractory clay, amorphous silica, reactive alumina, metallic silicon, and sodium tripoly-phosphate), and working water were used. In the temperature range 110-1550 °C, apparent density had values between 2.39-2.42 g·cm⁻³, and porosity between 16-25 %. The loss of strength in the critical temperature range was not significant compared to concrete with normal cement dosage (20 %) as a consequence of the use of metallic silicon powder, reactive alumina, clay, and amorphous silica.

Researching the durability of concrete with low dosages of cement was the concern of Robalo et al. (2020) [6]. Two dosages of cement were used, one of 350 kg·m⁻³ with high plastic consistency and the other of 250 kg·m⁻³ with dry consistency, combined with the addition of fly ash and limestone filler. As conclusion, it was found that the mixtures with low-cement dosage and high compactness have low shrinkage despite the high water/cement ratio and those with higher strength have low creep. The resistance to carbonation, which influences the life span, was determined experimentally. Concrete with cement of 175 kg m⁻³ showed greater durability compared to ordinary concrete with cement of 250 kg·m⁻³.

The original combination of the structural core containing concrete with low-cement dosage and a concrete with recycled aggregates from the demolition of buildings and the peripheral layer of concrete with ultra-high durability to improve the overall durability was presented by Robalo et al., (2021) [7]. The objective of the paper was to identify the resistance to oblique shearing. The original constructive method had a major influence on the resistance at the interface, having differences of about 60 % compared to the predictions of the specific European

codes. The porosity and strength of the binder matrix, the interface profile, and the features of the aggregates had a great influence on the shearing strength at the interface.

Slag from ferroalloy manufacturing processes (especially, ferro-manganese and ferro-manganese-silicon) as a metallurgical by-product has been tested for use as a partial substitute for Portland cement [8]. Granulated slag with low manganese oxide (MnO) content is compatible when mixed with cement. The addition of slag reduces the compressive strength to the level of cement strength and a cement-slag mixture in the ratio 50/50 corresponds to the standard consistency, setting times and compressive strength (22 MPa after 7 days and 33 MPa after 28 days) of the hydraulic binder. The slag produced in the carbon steel making processes in the electric arc furnace (EAF) can be used for different purposes: as an aggregate in concrete or asphalt and mixed with cement for concrete [9]. It was experimentally found that EAF slag heated to 1000 °C acquires mechanical properties comparable to those of concrete with conventional refractory aggregate (e.g. bauxite).

Another technique for improving the performance of refractory concrete by applying nanotechnology was presented by Antonović et al. [10]. The use of materials of nano-particle composition (sodium silicate solution, amorphous silica) as binding materials for refractory concrete and also deflocculants can lead to the improvement of the compression resistance and the durability of concrete up to 2-3 times.

The application of nanotechnology to the manufacture of refractory concrete is also a concern of Zhang et al. [11]. The effects of using low dosage nano-silica on the mechanical strength of lightweight concrete were tested in this paper. It was observed that the interface between lightweight aggregates and cement paste can be strengthened by adding a low amount (0.1 wt. %) of nano-silica due to the new type of hydration products in form of fiber appearing at the interface contributing to the local toughening of concrete. The chemical composition of this fiber based-phase includes silicon, calcium and a large amount of aluminum [12].

The work of Stonys et al. [13] presents an original solution to substitute micro-silica, usually used as an additive from trade on making the refractory concrete, with cupola dust captured as waste from the industrial manufacture of mineral wool. The experimental results showed that this ultrafine waste can be successfully used in the production of refractory concrete, whose density, ultrasonic wave velocity, cold crushing strength, and thermal shock resistance were adequate. Also, the impact on the environment was favourable.

Three binding systems using successively colloidal silica, hydratable alumina, and a mixture of the two hydraulic binding agents were tested and presented by Ismael et al. [14]. The experiment concerned the processing of castable refractory materials. The castable matrix was composed of calcined alumina and was used as a fused alumina aggregate. Citric acid was also used as a dispersant in the binding system with colloidal silica and, respectively, in the system including the mixture of colloidal silica and hydratable alumina. The combined system showed a lower drying rate compared to that of the silica binding system, but the drying time was shorter compared to that of the alumina binding system. According to the authors' determinations, the hydration of alumina was much lower than the hydration of the silica-alumina mixture.

Previous tests for cement dosages between 6-9 % using tabular alumina (between 83.9-86.9 %) as aggregate, calcium lignosulfonate (0.11 %) as a fluidizing additive, aluminum monophosphate (2.5 %) as phosphate binder, hydrated alumina (3 %) and amorphous silica (1.5 %) as ultrafine mineral powder as well as working water (between 3.5-5.2 %) in a constant water/cement ratio of 0.58 led to the following values of the characteristics of concretes heat treated up to 1500 °C [15]. The apparent density had the highest values (3-3.1 g·cm⁻³) corresponding to concrete with 6 % cement and decreased to 2.6-2.8 g·cm⁻³ corresponding to concrete with 9 % cement. Porosity had the lowest values (19.6-20.2 %) in the case of concrete with 6 % cement and reached the highest values (21.7-23.5 %) in the case of concrete with 9 % cement.

The thermal conductivity of concrete in the temperature range 800-1500 °C had values within the limits of 2.7-2.9 W·m⁻¹·K⁻¹ for 6 % cement, decreasing up to 2.4-2.5 W·m⁻¹·K⁻¹ for 9 % cement, while the compressive strength reached the highest value (53.7-74 MPa) corresponding to concrete with 6 % cement and the lowest values (46.2-58.6 MPa) in case of concrete with 9 % cement. The increase of the structural compactness and the reduction of porosity of super-aluminous refractory concrete with low cement dosages (6-9 %) led to reaching high values of the compressive strength after firing at 1500 °C.

According to [15], the increase of compressive strength up to 1200 °C was slow being influenced to a small extent by the structural transformations of the matrix in the critical temperature range (600-1100 °C), but the continuation of firing up to 1500 °C accentuated the level of the compressive strength value. Increasing the degree of compactness of the matrix microstructure by reducing the cement dosage obviously influenced the compression strength, which reached very high values. Because the work is aimed at the intermediate layer of the refractory lining of steel casting ladles with compressive strength at a lower level compared to the values obtained in the previous test, the cement dosage of 9 % was adopted, the current experiment following the increase of concrete porosity to reducing its thermal conductivity.

The objective of the current work was to make a super-aluminous concrete with low-cement dosage (adopted by the authors at the value of 9 %) with high thermal conductivity obtained by partial substitution of the usual tabular alumina aggregate with globular alumina. The super-aluminous concrete was designed for the intermediate layer of thermal insulation of metallurgical casting ladles. The ladle insulation is composed of a permanent layer built on the inner wall of the ladle, made of high-aluminous refractory concrete or silico-aluminous bricks, a wear layer in direct contact with the molten steel, made of dolomite blocks or magnesium spinel bricks, and an intermediate layer made of granulated dolomite bound with tar (in the case of ArcelorMittal Galati) [15]. The research was focused on the intermediate layer whose thermal conductivity is too low allowing unjustified heat losses. Globular alumina representing alumina hollow spheres containing air inside was the density between 0.8-1 g·cm⁻³ and having very high alumina content (99 %) can contribute to the significant reduction of the thermal conductivity of refractory concrete. This technical solution has an innovative character as it has not been applied worldwide until now. The air spheres have the role of blocking the thermal flow propagated from the hot enclosure of the technological equipment to the outside, greatly reducing heat loss through thermal conductivity.

2. MATERIALS AND METHODS

2.1. Materials

The hydraulic binder used in the experiment was the super-aluminous cement CA-75 manufactured in China with Al₂O₃ (73-75 %), CaO (23-25 %), Fe₂O₃ (0.3 %), and SiO₂ (0.3 %). The cement grain is very fine (below 0.2 mm), the specific surface is 5500 cm² g⁻¹, and refractoriness reaches 1750 °C [16].

Tabular alumina commonly used for industrially making super-aluminous concrete with 99.5 % Al₂O₃ and globular alumina mentioned above adopted by the authors constituted the aggregate of the new concrete type. Four grain size fractions [17] were used: 6.35-2.38 mm, 2.38-1.19 mm, 1.19-0.149 mm, and below 0.149 mm.

Globular alumina in form of hollow spheres is produced by atomization with compressed air of high-purity aluminum in a molten state. The melting temperature of this material is 2100 °C. The hollow spheres are chemically inert, have low bulk density influenced by the sphere dimension, extremely low thermal conductivity, high hardness. Their thermal insulation properties are excellent. The standard dimensions of globular alumina are between 0-5 mm. The Al₂O₃ content is very high (99 %). Its chemical composition includes also very low proportions of SiO₂, MgO, Na₂O, Fe₂O₃, and CaO [18]. Three grain size fractions were used: 6.35-2.38 mm, 2.38-0.595 mm, and below 0.595 mm.

Improving the workability of concrete by its fluidizing allowing the reduction of the water/cement ratio was obtained with a fluidizing surfactant additive often used in industry (calcium lignosulfonate) in a proportion of 0.11 % related to the mass of dry concrete. The dry substance represents 92 % and the ash is 20 % [19].

The ultrafine mineral powders together with the fine fraction of the aggregate and the hydrated cement are the basic components required for the formation of the binding matrix in which the binding by coagulation develops (along with the other forms of binding). In this experiment, ultrafine powders of 3 % hydrated alumina (64.6 % Al₂O₃ and 34.8 % LOI) and 1.5 % amorphous silica (87.5 % SiO₂) were adopted due to their high reactivity (even at room temperature), large specific surface area, and high superficial activity. The mineral powders were introduced into the super-aluminous cement paste [20].

Under the conditions of low-cement dosage (9 %) the hydraulic binder (aluminum monophosphate) has a complementary role in facilitating the creation of gel bonding forms (coagulation-condensation), which can exist

together with the chemical and hydraulic ones forming the complex and strengthening system [21]. The adopted ratio of aluminum monophosphate was 2.5 % related to the dry concrete amount. Its chemical composition contains 32.2 % P_2O_5 and 7.8 % Al_2O_3 .

The grain size of raw materials and admixtures are centralized in Table 1.

Table 1. Grain size of raw materials and admixtures.

Material	Grain size analysis, [% remaining on sieve (mm)]										
	6	5	4	3	2	1	0.5	0.2	0.09	0.06	<0.06
Cement super-aluminous	-	-	-	-	-	-	-	-	7.5	9.7	82.8
Tabular alumina 6.35-2.38 mm	14	17	30	21	7	10	1	-	-	-	-
Tabular alumina 2.38-1.19 mm	-	-	-	-	33	52	5	10	-	-	-
Tabular alumina 1.19-0.149 mm	-	-	-	-	-	6	11	47	36	-	-
Tabular alumina below 0.149 mm	-	-	-	-	-	-	-	-	20	21	59
Globular alumina 6.35-2.38 mm	6	15	30	20	17	6	6	-	-	-	-
Globular alumina 2.38-0.595 mm	-	-	-	-	-	35	20	29	16	-	-
Globular alumina below 0.595 mm	-	-	-	-	-	-	-	10	17	53	20
Calcium lignosulfonate	-	-	-	-	-	-	-	-	-	-	100
Hydrated alumina	-	-	-	-	-	-	-	-	-	16.4	83.6
Amorphous silica	-	-	-	-	-	-	-	-	-	-	100

2.2. Methods

Taking into account the adopted proportions of cement (9 %), calcium lignosulfonate (0.11 %), aluminum monophosphate (2.5 %), hydrated alumina (3 %), amorphous silica (1.5 %), and the globular alumina/tabular alumina ratios in the three experimental variants (20/80, 30/70 and 40/60), the manufacturing composition of the new refractory concretes was established, being presented in Table 2.

Table 2. Manufacturing composition of the new refractory concretes.

Concrete composition	Experimental variant					
	Variant 1 20 % substitution with globular alumina		Variant 2 30 % substitution with globular alumina		Variant 3 40 % substitution with globular alumina	
	kg m ⁻³	%	kg m ⁻³	%	kg m ⁻³	%
Cement super-aluminous	218.70	9.00	201.60	9.00	184.50	9.00
Tabular alumina						
- 6.35-2.38 mm	535.82	22.05	448.00	19.29	374.74	18.28
- 2.38-1.19 mm	501.55	20.64	403.10	18.06	318.98	15.56
- 1.19-0.149 mm	294.27	12.11	221.16	10.60	151.91	7.41
- below 0.149 mm	299.13	12.31	243.14	10.77	186.14	9.08
Total tabular alumina	1630.78	67.11	1315.40	58.72	1031.77	50.03
Globular alumina						
- 6.35-2.38 mm	123.20	5.07	196.40	8.93	261.97	12.78
- 2.38-0.595 mm	162.32	6.68	187.12	8.21	199.88	9.75
- below 0.595 mm	122.23	5.03	180.22	8.03	226.12	11.03
Total globular alumina	407.75	16.78	563.74	25.17	687.97	33.56
Total aggregate	2038.53	83.89	1879.14	83.89	1719.74	83.89
Calcium lignosulfonate	2.67	0.11	2.46	0.11	2.26	0.11
Aluminum monophosphate	60.75	2.50	56.00	2.50	51.25	2.50
Hydrated alumina	72.90	3.00	67.20	3.00	61.50	3.00
Amorphous silica	36.45	1.50	33.60	1.50	30.75	1.50
Total dry concrete	2430	100	2240	100	2050	100
Working water	126.8	5.22	116.9	5.22	107.0	5.22
Water/cement ratio	-	0.58	-	0.58	-	0.58

Using the manufacturing recipes presented in Table 2, wet mixtures corresponding to the three experimental variants were prepared. Dosing the materials was performed separately for the components of the refractory aggregate and, respectively, for the fine-grained materials as binder matrix (super-aluminous cement, hydrated alumina, amorphous silica and calcium lignosulfonate). Their mixing was also performed separately. Then, a joint mixing in a vessel of the two components was carried out for 3 min, adding also the aluminum monophosphate. The working water was added gradually during the process of homogenizing the mixture. After drying, the specimens were fired in a Nabertherm muffle oven up to 1200 °C by heating with a constant warming rate of 50 °C/hour up to 1500 °C and then kept at this temperature for 5 hours. The specimens cooling took place slowly into the oven atmosphere. Super-aluminous concrete parallelepiped samples 230x54x64 mm for determining porosity (ultrasonic pulse velocity technique C830), apparent density (test method C914) and compressive strength as well as cylindrical samples with the diameter of 100 mm and thickness of 25 mm for measuring the thermal conductivity (on the apparatus existing in Metallurgical Research Institute Bucharest) were prepared.

3. RESULTS AND DISCUSSION

3.1. Results

The measurements were performed in Metallurgical Research Institute Bucharest. The cylindrical shape and the size of specimens used for determining the thermal conductivity were imposed by the dimensions of the space inside the apparatus. The temperature sensors were fixed on the surface of specimen and measurements of the material temperature were performed at different points on its surface. The compressive strength was determined on 120 tons-axial press with hydraulic drive. The method for determining the porosity of refractory concrete specimens is based on the displacement of air from the material pores using liquids according to the volumetric principle [19] and the apparent density of the samples was measured through the gravimetric method [22].

The oxide composition of the super-aluminous refractory concrete specimens was identified with the X-ray fluorescence spectrometer according to SR EN ISO 12677 and is shown in Table 3.

Table 3. Oxide composition of the experimental concretes.

Variant	Oxide composition (%)						
	Al ₂ O ₃	Fe ₂ O ₃	CaO	SiO ₂	MgO	Na ₂ O	K ₂ O
1	94.2	0.4	2.49	0.3	-	0.08	0.07
2	94.1	0.3	2.51	0.2	0.01	0.07	0.06
3	94.0	0.3	2.52	0.2	0.01	0.06	0.06

The partial substitution of tabular alumina with globular alumina at the same cement dosage of 9 % insignificantly influenced the refractoriness of the three concrete samples due to the almost identical content of Al₂O₃. The appearance of the three experimental variants of concrete are shown in Figure 1.

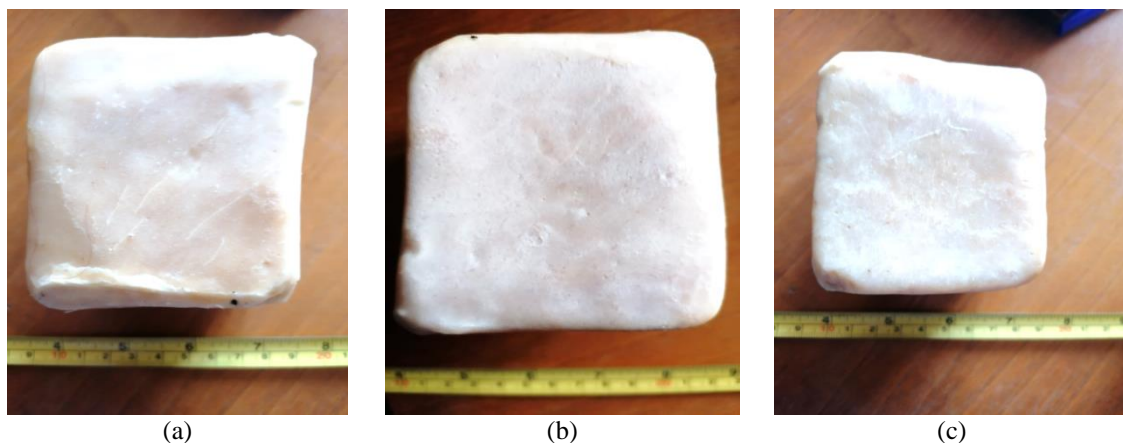


Fig. 1. Appearance of the super-aluminous concrete specimens prepared with globular alumina: (a) – 20 %; (b) – 30 %; (c) – 40 %.

The main physical, thermal, and mechanical characteristics of concrete specimens are shown in Table 4.

Table 4. Physical, thermal and mechanical characteristics of experimental concretes.

Variant	Porosity (%)	Apparent density ($\text{g}\cdot\text{cm}^{-3}$)	Thermal conductivity ($\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$)	Compressive strength (MPa)
1	27.14	2.41	1.60	37.7
2	29.31	2.32	1.45	34.8
3	34.08	2.15	1.32	28.5

According to the results in Table 4, the porosity of the super-aluminous concrete specimens with 9 % cement, in which the usual tabular alumina aggregate was replaced by 20, 30 and 40 % globular alumina, respectively, increased from 27.14 to 34.08 %, while the density of monolithic products was reduced from 2.41 to 2.15 $\text{g}\cdot\text{cm}^{-3}$. The main role of changing porosity and density values belongs to the inert hollow spheres of globular alumina introduced into the mass of concrete in the form of aggregate. As a consequence of the increase in porosity and, respectively, the decrease in the apparent density of the specimens due to the increase of the proportion of globular alumina up to 40 % of the mass of aggregate, the thermal conductivity of the heat-treated concrete at 1500 °C decreased from 1.60 to 1.32 $\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$. The presence of globular alumina spheres in the concrete macrostructure led to a significant reduction of the compressive strength value from 37.7 MPa in variant 1 to 28.5 MPa in variant 3. The decrease of the concrete mechanical strength is also the effect of that globular alumina as a stand-alone material does not excel by high values of compressive strength.

As a reference, it can consider a dense super-aluminous refractory concrete (90 % Al_2O_3 and 9 % SiO_2) with a low-cement dosage and bauxite-based aggregate used in the steel industry for the nozzle of lance for blowing metal powder in the molten metal bath having the following characteristics (after heat treatment at 1500 °C): density of 2.90 $\text{g}\cdot\text{cm}^{-3}$, porosity of 13.6 %, and compressive strength of 63 MPa [1]. Being a dense material, its thermal conductivity is very high and the thermal insulation properties are extremely low [15].

Figure 2 shows microstructure images of super-aluminous concrete matrix with 9 % cement dosage using globular alumina (between 20-40 wt. %) as aggregate in the three experimental variants.

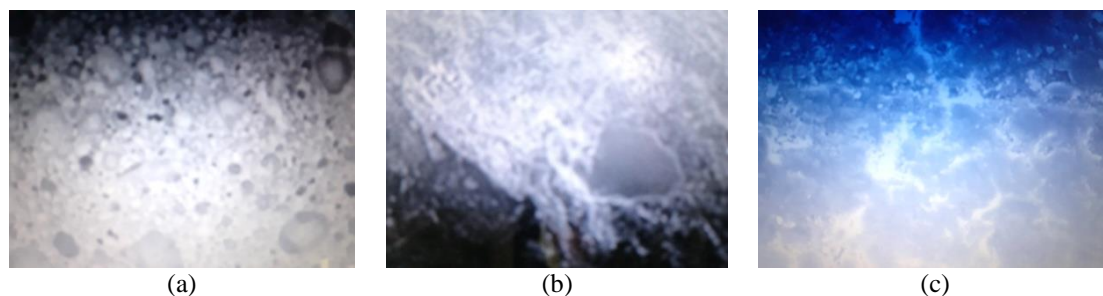


Fig. 2. Microstructure of super-aluminous concrete matrix with 9% cement dosage using globular alumina as aggregate (x1000): (a) – 20 %; (b) – 30 %; (c) – 40 %.

The change of the characteristics of concrete made with 20-40 % globular alumina introduced into the tabular alumina-based aggregate is mainly due to the hollow spheres represented by the coarse fraction of globular alumina and to a lesser extent to the increase of the binder matrix porosity, a fact also revealed by the microstructure images in Figure 2.

3.2. Discussion

The compressive strength of the specimen corresponding to variant 3 (28.5 MPa) was considered too low for the intermediate layer of ladle insulation, although the thermal conductivity (1.32 $\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$) and the apparent density (2.15 $\text{g}\cdot\text{cm}^{-3}$) are interesting in terms of the thermal insulation characteristics of the material. Under these conditions, variant 2 was adopted as the optimal one, having a compressive strength of 34.8 MPa (considered acceptable), a thermal conductivity of 1.45 $\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$, and an apparent density of 2.32 $\text{g}\cdot\text{cm}^{-3}$. Implicitly, the porosity has a lower value (29.31 %) compared to that corresponding to variant 3, but it is also acceptable. All these values of the characteristics of the super-aluminous concrete with a cement dosage of 9 % were

experimentally determined after the heat treatment at 1500 °C, i.e. the highest temperature of the insulating layer of the ladle filled with molten steel.

Generally, the super-aluminous refractory concrete with low-cement dosage having a dense aggregate has the ability to reach very high performances in terms of its mechanical strength. The solution adopted by the authors to reduce the dense nature of this type of concrete allowed the improvement of the thermal insulation properties of the material, maintaining a fairly high level of mechanical strength. Some techniques for making the masonry of the casting ladles in the steel industry include only two distinct layers (permanent and wear layers), in which the wear layer reaches higher values of the mechanical strength compared to the refractory concrete type made in this work for the intermediate layer.

The current work started from the analysis of the disadvantageous situation in terms of energy of the way of building the refractory lining of the 180 tons-steel casting ladle from ArcelorMittal Galati in the two constructive variants mentioned above, including the intermediate layer of granulated dolomite bound with tar. According to the measurements performed and presented in [15], the thermal conductivity of this layer had extremely high values (between $4.11\text{--}6.18\text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$) negatively influencing the heat loss value of the molten steel from the ladle through its entire thermal insulation, which reached $9.88\text{--}11.44\text{ MJ/ton steel}$. According to Kathait [23], worldwide the heat loss through the refractory lining of casting ladle in the steel industry made by performance materials is within the limits $6.8\text{--}7.6\text{ MJ/ton steel}$. The new refractory concrete achieved for the use in the refractory lining structure of ladle has a thermal conductivity of $1.45\text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ ensuring a significant reduction of heat loss outside the ladle.

4. CONCLUSIONS

The objective of the current work was to make a super-aluminous refractory concrete (over 94 % Al_2O_3) with low-cement dosage (9 %), in which the usual tabular alumina aggregate was experimentally replaced by 20-40 % globular alumina in form of inert hollow spheres. The purpose of this material substitution was obtaining thermal insulation properties for this concrete type in order to use it as an intermediate layer of refractory lining of steel casting ladle. The characteristics of the super-aluminous concrete with low-cement dosage (9 %) and the optimal substitution of 30 % of tabular alumina by globular alumina were: apparent density of $2.32\text{ g}\cdot\text{cm}^{-3}$, porosity of 29.31 %, thermal conductivity of $1.45\text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$, and compressive strength of 34.8 MPa (after firing at 1500 °C). This monolithic material could be adequate for the intermediate layer of the casting ladle, the solution being original. The huge difference between the thermal conductivity values of the two types of materials intended for the intermediate layer are a guarantee of the effectiveness of the new super-aluminous material.

REFERENCES

- [1] Angelescu, N., Materiale rezistente la coroziune-Betoane speciale, Macarie Publishing House, Targoviste, Romania, 2001.
- [2] Angelescu, N., Ionita, G., Special concrete with aluminous cement, Proceedings of Conference on Application and Marginal Materials in Construction ARMICON, Bagalore, India, August 6, 2006.
- [3] Mehta, P.K., Monteiro, P.J.M., Concrete: microstructure, properties and materials, 4th edition, McGraw Hill Publishing House, Lisbon, Portugal, 2013.
- [4] Azmee, N.M., Shafiq, N., Preparation of low cement ultra-high performance concrete, Proceedings of the 5th International Conference on Geotechnics, Civil Engineering Works and Structures, Innovation for Sustainable Infrastructure CIGOS, 2019, p. 331-336.
- [5] Ionita, C., Angelescu, N., Muntean, M., Consideration concerning research and testing methods for refractory concretes with low cement dosage, Proceedings of the 3th International Proficiency Testing Conference, Iasi, Romania, vol. 27, no. 28-30, 2011, p. 200-207.
- [6] Robalo, K., Soldado, E., Costa, H., Carvalho, L., do Carmo, R., Julio, E., Durability and time-dependent properties of low-cement concrete, Materials (Basel), vol. 13, no. 16, 2020, p. 3583.
- [7] Robalo, K., do Carmo, R., Costa, H., Julio, E., Experimental study on the interface between low cement recycled aggregates concrete and ultra-high durability concrete, Construction and Building Materials, vol. 304, 2021, p. 1-11.

- [8] Rai, A., Prabakar, J., Raju, C.B., Morchalle, R.K., Metallurgical slag as a component in blended cement, *Construction and Building Materials*, vol. 16, no. 8, 2002, p. 489-494.
- [9] Ducman, V., Mladenovic, A., The potential use of steel slag in refractory concrete, *Materials Characterization*, vol. 62, no. 7, 2011, p. 716-723.
- [10] Antonovic, V., Pundiene, I., Stonys, R., Cesniene, J., Keriene, J., A review of the possible applications of nanotechnology in refractory concrete, *Journal of Civil Engineering and Management*, vol. 16, no. 4, 2010, p. 595-602.
- [11] Zhang, P., Xie, N., Cheng, X., Feng, L., Hou, P., Wu, Y., Low dosage nano-silica modification on lightweight aggregate concrete, *Nanomaterials and Nanotechnology*, vol. 8, 2018, p. 1-8.
- [12] Kockeey-Lorentz, R., Buhr, A., Racher, R.P., Industrial application experiences with microporous calcium hexaluminate insulating material SLA-92, *Proceedings of the 48. Internationales Feuerfest-Kolloquium*, Altmatis GmbH, Ludwigshafen, Germany, 2005, p. 66-70.
- [13] Stonys, R., Kuznetsov, D., Krasnikovs, A., Skamat, J., Baltakys, K., Antonovic, V., Cernasejus, O., Reuse of ultrafine mineral wool production waste in the manufacture of refractory concrete, *Journal of Environmental Management*, vol. 176, 2016, p. 149-156.
- [14] Ismael, M., Salomao, R., Pandolfelli, V.C., Refractory castables based on colloidal silica and hydratable alumina, *American Ceramic Society Bulletin*, vol. 86, no. 9, 2007, p. 58-61.
- [15] Paunescu, L., Eficientizarea fluxurilor tehnologice functie de natura captuselor refractare ale oalelor de turnare din industria otelului, Teza de doctorat, Universitatea Valahia, Targoviste, Romania, 2011.
- [16] <https://www.rsrefractorygroup.com/high-alumina-cement-for-sale/> (23.01.2019).
- [17] <https://www.encosrl.it/ricerca/tecnologia-del-calcestruzzo/> (14.06.2011).
- [18] <https://www.samaterials.com> (20.03.2020).
- [19] Moldovan, V., *Aditivi in betoane*, Ed. Tehnica, Bucuresti, Romania, 1978.
- [20] Angelescu, N., Heating behaviour of monolithics bound by coagulation, *Cement and Concrete World*, vol. 8, no. 44, 2003, p. 52-59.
- [21] Angelescu, N., A new binding system for concrete, *Proceedings of the 6th International Conference of Concrete Technology*, Amman, Iordania, vol. 1, 2002, p. 213-223.
- [22] *Metrology in laboratory-Measurement of mass and derived values*, Radwag Balances and Scales, 2nd edition, Radom, Poland, 2015, p. 72-73.
- [23] Kathait, D.S., Heat loss in ladle furnace, *International Research Journal of Engineering and Technology*, vol. 3, no. 7, 2016, p. 1627-1631.