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CELLULAR GRAVEL PRODUCED FROM RESIDUAL ALUMINO-SILICATE MATERIALS (FLY ASH, METAKAOLIN, SLAG, AND ALKALINE EARTH ALUMINO-SILICATE GLASS) BY NONCONVENTIONAL TECHNIQUES

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ABSTRACT: New manufacturing recipe of glass waste-based foam glass gravel for special applications in construction was designed, tested, and presented in this paper. The work originality is the use of alumino-silicate materials in the form of waste (fly ash, blast furnace slag, alkaline earth alumino-silicate glass waste) as well as in the natural state (metakaolin) widely available in nature. Especially, in this work it was chosen the use of a waste of alumino-silicate glass recovered from halogen lamps, similar by chemical composition with the other materials adopted to constitute the material mixture. Three variants using a solid (SiC) and liquid (glycerin), respectively, blowing agent were tested, the mixtures being sintered and foamed at temperatures between 850-940 ºC. The heating was made by the economic and ecological technique of microwave irradiation. All tested versions led to obtaining cellular gravel types with characteristics suitable for special applications in construction, similar to industrially made foam glass gravel. Being more suitable for load-bearing properties, the variant made with alumino-silicate glass waste and glycerin associated with sodium silicate solution was chosen as the optimal alternative.
KEYWORDS: cellular gravel, alumina-silicate waste, metakaolin, glycerin, sodium silicate, load-bearing.

1. INTRODUCTION

Cellular gravel is a porous material with high compressive strength and low density being adequate for load-bearing heat insulation around the perimeter of building as well as under foundation or floor. The application field of this product in the form of pieces with dimensions between 15-80 mm is extended and also includes the underground insulation of heating tubes and storage tanks, the structure of railway and road construction as filling material, construction elements of bridges, drainage, sports fields, airport runways, etc. [1]. According to the literature, cellular gravel preparation is based in high proportions on recycled glass waste (container glass and flat glass) resulting from glass packaging after consumption or building demolition. Better known as "foam glass gravel", this excellent construction material has an important contribution to the recovery of residual glass, whose annual generation rate is alarmingly increasing. Glass is a silicate material with very high silica content (around 70 %), which, used in the manufacture of modern construction materials by sintering and foaming at high temperature, transmits to them part of its parental properties (mechanical strength, resistance to corrosion, fireproof, waterproof, and resistant to aggression of various external agents such as rodents, insects, bacteria, etc. [2].

The main industrial producers of foam glass gravel are Geocell (Austria), Misapor (Switzerland), Glapor (Germany) and other companies in general from countries with a harsher climate in Northern Europe.

Usually, the manufacturing process takes place in conveyor belt furnaces and cooling the foamed material is slightly forced to create internal stress in its mass and to facilitate the easy detachment of lumps at the end of the belt.

Foam glass gravel characteristics shows compressive strength values up to 6 MPa, bulk density within the limits of 0.12-0.17 $g \cdot cm^{-3}$, and thermal conductivity between 0.06-0.08 $W \cdot m^{-1} \cdot K^{-1}$ [3]. A research team including authors of the ongoing paper recently carried out research on the manufacture of this material type using as a novelty the microwave heating and obtaining results in terms of quality almost similar to those industrially produced. In addition, the specific consumption of energy was reduced to 0.86-0.88 kWh/kg, especially in the case of using glycerin in liquid state (as an blowing agent) together with the aqueous solution of sodium silicate [3].

The modern trend of the last two decades regarding the manufacture of especially construction materials is the use of residual alumino-silicate or natural products of the same type (fly ash, blast furnace slag, rice husk ash, red mud, volcanic rock powder, metakaolin, etc.) for manufacturing geopolymers [4]. This trend aims to reduce greenhouse gas emissions (CO_2) as well as the consumption of polluting fuels during the industrial manufacture of traditional materials.

The own analysis of the possibility of manufacturing cellular gravel through the technique of activating alumino-silicate materials in a highly alkaline aqueous medium, initiator of the geopolymerization reaction and the geopolymer formation, led to the conclusion that a geopolymer is not suitable for the foam glass gravel requirements (load-bearing properties).

Combining the geopolymer manufacturing technique by using glass waste powder activated in potassium hydroxide and sodium silicate solution with the material expansion technique by heating at 500-700 ºC for 1 hour was used in [5]. The expanding process generated open porosity, the pore size varying between 46-605 μm after heat treatment at 500 ºC, between 76-958 μm (at 600 ºC), and between 141-1335 μm (at 700 ºC). The work offered a new type of re-using the glass waste as thermal and acoustic insulation at a low price and with environmental protection.

The peculiarities of replacing the fine sand aggregate of geopolymer foam with fine glass powder were experimentally determined and analyzed in [6]. The results showed that the paste produced with glass aggregate was lighter by about 100 $kg \cdot m^{-3}$ compared to that made with sand aggregate. The heavier specimens with sand aggregate needed a more advanced foaming to reduce the density, but affecting their mechanical strength. The microstructural aspect of geopolymer foam with glass aggregate is more uniform and the number of interconnected pores is reduced, especially at lower densities. Therefore, the heat conductivity value of these geopolymer foams is lower, reaching 0.15 $W \cdot m^{-1} \cdot K^{-1}$ (for the specimen with the density of 600 $kg \cdot m^{-3}$). It was found that the compressive strength of the geopolymer with glass aggregate is higher than that of the same product with sand aggregate.

The present work is the result of the authors' research on the manufacture of construction materials with the features of industrial foam glass gravel under the conditions of using alumino-silicate materials (natural or waste) foamed by sintering at high temperature by economic nonconventional heating technique. Alkali alumino-silicate glass waste recovered from the glass bulb of halogen lamps, with high content of SiO_2 (60 %) and Al_2O_3 (25 %) as well as alkaline earth (15 %) [7, 8] was used replacing the usual Na_2O-CaO-SiO_2 glass waste tested in experiments presented above.

2. METHODS AND MATERIALS

2.1 Methods

The method chosen by authors is that of sintering and expanding at high-temperature level (almost 1000 ºC) of material mixture composed of different alumino-silicate wastes (fly ash, granulated blast furnace slag, alkali alumino-silicate glass) as well as metakaolin, natural material wide spread in nature, separately incorporating two types of blowing agent, one solid (silicon carbide) and one liquid (glycerin) associated with 38 % sodium silicate aqueous solution. The finely ground mixture was moistened with water as a binder in the case of options with solid expanding agent and was pressed into a metal die with the possibility removing from the die and depositing freely on a metal support placed on the thick layer of ceramic fiber mattress. The pressed mixture was protected with cylindrical tube provided with lid, both made of an 80/20 mixture of silicon carbide and nitride, highly susceptible materials to microwaves. The tube, purchased from China, had the exterior dimension of 125 mm, height of 100 mm and wall thickness of 2.5 mm. This wall size has the ability to allow both the predominant penetration of electromagnetic waves emitted through the waveguide of the magnetron (put on one side walls of microwave oven), as well as the absorption of waves into the die wall, its intense and quick heating being achieved. In this way, the pressed sample is subjected to both direct heating with microwaves (dielectric heating) and indirect heating through conventional thermal radiation. Direct microwave heating has the particularity of its initiation in the middle of material, followed by the volumetric expansion of the heating front from the inside to the outside [9, 10]. For this reason, the thermal protection of the exterior surface of cylindrical ceramic tube and the lid must be effectively done with thick ceramic fiber mattress. Main advantage of the nonconventional system of heating is the process selectivity [10], which allows only the heating of the target material, not other massive constructions inside the oven. The oven used in the experiment (Figure 1) was a microwave equipment type used for household-food preparation, but constructively modified to be used at high temperature. The control of the sintering/expanding temperature was performed with the Pyrovar type-pyrometer mounted above the oven at 400-450 mm, having the possibility to visualize the superior surface of the sintered product through 30 mm-holes made in the upper wall of the microwave oven and the lid.

Figure 1. Image of the microwave installation used in the experiment

2.2 Materials

As mentioned above, several alumino-silicate wastes (fly ash, blast furnace slag, alkaline earth alumino-silicate glass) as well as a natural material (metakaolin) of the same type were used separately in different experimental versions with the purpose of manufacturing cellular gravel with relatively similar properties to industrial foam glass gravel based on Na_2O-CaO-SiO_2 (soda-lime-silica) residual glass in very high proportions.

Metakaolin is commercially available as a very fine powder with the particle size of 1-2 µm. Its chemical composition contains 53 % SiO_2, 43 % Al_2O_3, 0.8 % TiO_2, 1.2 % Fe_2O_3, 0.5 % CaO, 0.4 % MgO, and 0.4 % Na_2O [11].

Fly ash resulted as a secondary product of coal burning process in the energy industry, being recovered after the electrostatic filtration of waste gases, was supplied to the companies Daily Sourcing & Research SRL and Cosfel Actual SRL by Paroseni-thermal power plant in 2016. The grain dimension of this waste was initially below 200 µm being reduced below 35 µm after grinding. The oxide composition of fly ash includes 54.4 % SiO_2, 26.5 % Al_2O_3, 1.5 % TiO_2, 4.8 % Fe_2O_3, 3.5 % CaO, 2.5 % MgO, 0.4 % Na_2O, 0.6 % K_2O, and 1.7 % SO_3.

Blast furnace slag is also a secondary product of metallurgical industry. In technological terms, the slag in a molten state is granulated by pouring into cold water-basins. As a result, the waste is granulated in the form of spheres with dimensions between 2-6 mm being used in road construction. By grinding in a ball mill, granulated slag can be transformed into a powder with grain dimension under 40 µm. The Romanian companies mentioned above received a batch of granulated slag from ArcelorMittal Galati (Romania) 6-7 years ago, the material being mechanically processed and used in experiments. The composition of blast furnace slag contains the following oxidic components: 37.4 % SiO_2, 6.4 % Al_2O_3, 6.9 % Fe_2O_3, 39.9 % CaO, 3.5 % MgO, 0.1 % Na_2O, 0.2 % K_2O, and 2.3 % MnO [12].

Alkaline earth alumino-silicate glass waste was recovered from the glass bulb of halogen lamps taken out of use. The chemical composition of this alumino-silicate glass contains 60 % SiO_2, 25 % Al_2O_3, and 15 % alkaline earth [7, 8].

Two versions of blowing agent were used. Silicon carbide (SiC) as a solid agent is considered one of the most effective foam formers [2]. The grain size used in this experiment was under 10 µm. Several reaction types for oxidizing the SiC in atmospheric medium have optimal conditions in thermodynamic terms to take place in the range of 900-1100 ºC, of which reaction (1) is the most suitable.

$$SiC + 2O_2 = SiO_2 + CO_2 \quad (1)$$

SiO_2 enters into the material mixture composition, while CO_2 is released forming bubbles as the base of porous structure.

Glycerin ($C_3H_8O_3$) as a carbon-based liquid blowing agent was also used in this experiment, because it has the capacity to dissipate easily through the fineness of solid mixture particles. Glycerin breaks up in the oxidizing medium of the oven releasing several compounds from CO_2 to pure carbon, including hydroxyl compounds [13, 14). The breaking up process reaches its maximum level at 750 ºC, at which it is almost complete [15]. Because an internal overpressure is created, the volume of gaseous pores grows, expanding the volume of the entire material. Due to the high oxidation capacity of carbon and to avoid its early-age burning, it is necessary to envelop the solid particles of the mixture with 38 % sodium silicate aqueous solution [14]. Therefore, glycerin was used in this experiment in association with sodium silicate solution.

2.3 Investigation methods to determine the specimen characteristics

Determining the physico-mechanical, thermal, and morphological features of cellular gravel samples was carried out by usual techniques. Bulk density was measured using Archimedes'principle based on water immersion method [16, 17]. The porosity was determined according to ASTM C642-97 by reporting the difference between wet and dry mass to the difference between wet and suspension mass of the sample [18]. The thermal conductivity was measured by the heat flow method (ASTM E1225-04). For determining the compressive strength, the TA.XTplus Texture analyzer was utilized. The traditional method of immersing under water of the porous sample was used to identify the water amount absorbed by the material (ASTM D570). The investigation of the microstructural features of specimens was done with ASONA 100X Zoom Smartphone Digital Microscope.

3. RESULTS AND DISCUSSION

3.1 Results

Three experimental versions for making cellular gravel were adopted. Their compositions are presented in Table 1.

Table 1. Composition of experimental versions

Composition (wt. %)	Version		
	1	2	3
Metakaolin	54	-	-
Fly ash	25	17	-
Alkaline earth alumino-silicate glass waste	18.7	16	83
Silicon carbide	2.3	2.0	-
Blast furnace slag	-	65	-
Sodium silicate	-	-	8
Glycerin	-	-	1.0
Water addition	13	13	8

According to the data in Table 1, version 1 had in the material mixture 54 % metakaolin, 25 % fly ash, 18.7 % alkaline earth alumino-silicate glass waste, the blowing agent being SiC (2.3 %). 13% water addition as a binder was added. Version 2 included 65 % granulated blast furnace slag, 16 % alkaline earth alumino-silicate glass waste, 2 % SiC as a blowing agent, and 13 % water addition. Version 3 used as raw material 83 % alkaline earth alumino-silicate glass waste, 1 % glycerin as a liquid foam former, 8 % sodium silicate solution, and 8 % water for dilution.

Main functional parameters of the sintering/expansion process corresponding to the three experimental alternatives are shown in Table 2.

Table 2. Functional parameters of the sintering and expansion process

Version	Wet raw material/cellular gravel amount (g)	Sintering/ expansion temperature (ºC)	Heating time (min)	Average rate (ºC/min)		Specific consumption of energy (kwh/kg)
				Heating	Cooling	
1	500/420	940	50	18.4	7.4	1.24
2	500/422	920	47.5	19.4	7.4	1.17
3	500/415	850	43	19.3	7.5	1.08

Examining functional parameters of process in the three options exposed in Table 2, the superiority of version 3 using the liquid blowing agent can be seen. The final temperature of the process is lower (850 ºC) compared to that of versions 1 and 2. The heating rate had high values (18.4-19.4 ºC/min) due to the special efficiency of microwave heating. The peculiarity of the cellular gravel manufacturing was the higher rate (7.4-7.5 ºC/min) of cooling the foamed material compared to cooling the glass foam (5.0-5.5 ºC/min).

The main features of cellular gravel specimens are presented in Table 3.

Table 3. Features of cellular gravel specimens

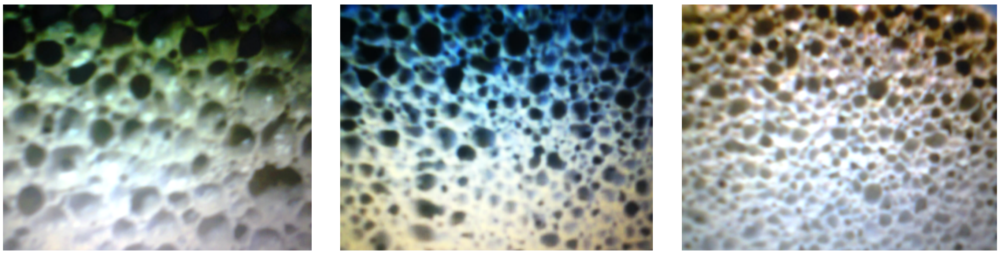
Feature	Version		
	1	2	3
Bulk density ($g \cdot cm^{-3}$)	0.21	0.26	0.24
Porosity (%)	90.0	87.6	88.6
Thermal conductivity ($W \cdot m^{-1} \cdot K^{-1}$)	0.060	0.068	0.063
Compressive strength (MPa)	5.0	8.5	5.9
Water absorption (vol. %)	6.0	6.4	7.3
Pore size (mm)	0.80-2.50	0.35-0.80	0.30-0.60

The data in Table 3 shows that performances of all samples are generally adequate for the cellular gravel type required in specific applications in construction mentioned above. A slight difference is obvious in the case of version 2 having the highest bulk density (0.26 $g \cdot cm^{-3}$) and the highest compressive strength (8.5 MPa). Thermal conductivity had slightly different values in the three alternatives, but all values fall perfectly within the accepted range for industrial foam glass gravel (0.060-0.080 $W \cdot m^{-1} \cdot K^{-1}$). Version 3 has the advantage of higher water absorption (7.3 vol. %) compared to the other versions.

Appearance images of cellular gravel specimens produced in the three experimental versions are shown in Figure 2 and the microstructural aspect of them is presented in Figure 3.

a b c

Figure 2. Appearance pictures of cellular gravel samples
a – version 1; b – version 2; c – version 3.



a b c ____ **2 mm**

Figure 3. Microstructural aspect of cellular gravel samples
a – version 1; b – version 2; c – version 3.

3.2 Discussion

The replacement of soda-lime-silica glass waste in the composition of the material mixture for the manufacture of foam glass gravel was the main element of the work originality. The use of residual glass recovered from the glass bulb of halogen lamps instead of the glass waste mentioned above contributed to the exclusive use of alumino-silicate materials in this making process.

Other wastes of alumino-silicate materials (rich in SiO_2 and Al_2O_3) already usable in the world (such as fly ash or blast furnace slag) were also tested in this experiment. The results allowed the conclusion that the designed manufacturing recipes are adequate for the production of cellular gravel with features similar to those of foam glass gravel manufactured on an industrial scale.

Although all the tested versions led to obtaining materials suitable for the proposed purpose in terms of quality, the optimal version was chosen that used alumino-silicate glass waste (83 %), glycerin (1 %), sodium silicate solution (8 %), and water addition (8 %). This option exhibited higher load-bearing properties.

4. CONCLUSION

The work aimed at testing several options of the manufacturing recipe of cellular gravel, using only alumino-silicate materials (fly ash, blast furnace slag, alkaline earth alumino-silicate glass waste) recyclable as waste as well as a similar natural material (metakaolin). The blowing agent was both in solid state (SiC) and in liquid state (glycerin) associated with aqueous solution of sodium silicate. The results showed that all the tested versions led to products adequate in terms of quality for special applications in construction (insulations around the perimeter of building as well as under foundation or floor, underground insulation of energy equipment, drainage, road construction as filling material, etc.). The optimal version was chosen the version made with glycerin, sodium silicate, and alkaline earth alumino-silicate glass waste.

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