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ORIGINAL ARTICLE

Amorphous silica wastes for reusing in highly porous ceramics

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Abstract

The paper analyzes a solution in green manufacturing of foamed or cellular ceramics. The objective of this study was to determine the technical solution for rice husk ash and "tales" of mixed glass cullet reusing based on the specific properties of these materials for creation of spherical holes inside ceramic using the process of coalescence of cellular glass. The paper reports on experimental results obtained from the production of lightweight cellular glass granules produced using glass cullet and rice husk ash. Lightweight cellular glass granules were mixed with clay, pressed and fired in air at 920°C. Clay sintering and the formation of ceramic were followed with the coalescence of cellular structure of glass granules and with the formation of spherical hollows inside the matrix. Density and strength of the fired ceramic bodies were determined. It is observed that the lightweight ceramics with density 900 ÷ 920 kg/m^3 possess a compressive strength of about 5 MPa that is acceptable for bricks or tiles manufacture. The utilization of amorphous silica waste for lightweight ceramics manufacture helps in reducing waste disposal concerns and costs associated, and also transforms the waste into an alternative raw material with added value, moreover making the final product cheap.

KEYWORDS

glass, granules, microstructure, waste disposal

1 | INTRODUCTION

Porous ceramic is one of the most usable functional ceramic materials. The sizes of pores rarely exceed 100 ÷ 200 mkm. Usually increasing of porous quota and porous sizes leads to the strength drop. Foaming of melted silica compositions by various chemicals is the mail method of foamed ceramics obtaining.[1] In our work we propose the untraditional method for the obtainment of foamed ceramic by using non-foaming but adding of lightweight foamed glass granules made from amorphous silica wastes. Therefore the process of foamed ceramic achievement leads not only to manufacture of new sustainable material but also to the resolution of ecological issues and to the use of renewable resources. Silica in the form of various compounds is the most significant part of all the earth's minerals. Therefore, silica waste cannot be valuable; it is easier and cheaper to produce a new silica material usually than to extract a material resource from silica waste. Ones of the most common silica wastes can be considered rice husk ash and glass cullet. Utilization of solid wastes to prepare ceramic products with high added value is an effective way that could relieve environmental pollution and create huge economic benefits.[2]

Approximately 134 million tons of rice husk are produced annually in the world, of which over 90% are burned in open air or discharged into rivers and oceans in order to dispose of them.[3] Rice husk is included in the natural assimilation process, but in the conditions of anthropogenic huge increasing production of rice husk, natural processes cannot cope with so much material. The problem is complicated by the low rate

of natural assimilation associated with the high content of silica in rice husk. Nevertheless, one effective method used nowadays to limit rice husk disposal is to use it as fuel for kilns to produce bricks or in the rice mills to generate steam for the parboiling process with the production of heat and electrical energy. Burning rice husk, approximately 25% of it is converted into ash (the so-called rice husk ash, RHA) with a content of around 90%–95% of amorphous silica formed during combustion in 550–800°C temperature range, developing crystalline phase only at higher temperatures.[4] The transformations reported in some papers[5,6] are: (a) below 700–800°C, amorphous silica with disordered SiO_2 structure that is the product of decomposition and sintering of opaline or hydrate silica, without fusion; (b) above 700–800°C, crystallization of silicon dioxide in cristobalite. Besides, increasing temperature (1000°C), or as a result of further combustion of ash for a long time and at high temperatures (e.g. to remove residual carbon), an increase in crystalline silica is noted and the tridymite development is observed, underlining that the final crystalline structure of silica is conditioned by combustion parameters (time, temperature, heating rate, etc). The use of RHA as silica precursor in ceramic field is not new and has also been addressed by the authors in the past in the obtainment of ceramic glazes,[7] glass ceramics,[8,9] ceramic pigments,[10] bricks,[11] and sodium silicate solutions.[12]

Another example of amorphous silica waste is the multi-tonnage glass cullet waste. Unlike rice husk, glass contains, in addition to amorphous silicon oxide, inorganic compounds, namely sodium and calcium oxides. From an environmental point of view, the principal difference between glass and rice husk is the absence of natural assimilation for glass. In addition, rainwater leaches glass waste stored at the landfill, resulting in leachate from glass cullet stocks should not be released to surface water.[13] Therefore, the recycling of glass waste became developing in the end of the 20th century. It is interesting to trace approaches to glass waste management over the past two or three decades. Glass waste was mostly landfilled due to the low cost of glass as a material and its low danger to the environment in the beginning. The first solutions that allowed to break this tradition were the allocation of subsidies for glass as a secondary resource. So in the early 2000s, Professor C. Meyer writes[14] about the compensation of "bottle bills" as a deposit of typically 5 cents per container in New York and some other States. Streets and parks were cleared of secondary glass bottles and cans as a result. The methods of collecting and sorting secondary glass that existed at the beginning of the century allowed for a significant proportion of non-standard glass waste, while glass factories accepted only color-separated glass as raw materials. However, the addition of cullet to the raw charge when firing new glass significantly reduces energy consumption. Therefore, the growth in energy prices during this time period contributed to the search for organizational and technical methods of glass sorting. As a result of these objective processes, at the end of the first decade of the 21st century, almost all developed countries adopted separate wastes collection and rapidly developed methods of optical sorting of glass. As a result, secondary glass has became a popular product at the market and its cost had increased to about 40 ÷ 60 US$ per ton. However, the certain amount of waste glass waste still is not recycled and is landfilled recently.

Glass that remains is mainly the result of glass sorting and glass that is chemically different from soda-lime-silica glass.

According to the authors[15] the amount of glass cullet that cannot be sorted and is allocated in the form of fraction of the selective urban glass collection is at least 10 masses. % of the total glass waste stream. The composition of impurities includes crystal items (containing at least 25 wt% of lead oxide), ceramics (including porcelain), Pyrex (borosilicate glass), light bulbs, neon tubes, mirrors, television and computer monitors (like cathode ray tubes and liquid crystal displays) and other inert materials. Because of high heterogeneity these fractions presently have no alternatives to landfilling. Therefore, the task of recycling glass waste in recent years has transformed into a problem of reusing of "tails" of glass sorting, that is, glass waste, usually of small fractions containing up to 10 ÷ 15 mass% of impurities. Both organic and inorganic substances can act as impurities, including various types of glass, such as borosilicate glass or lead glass, and ceramic or oxide crystal particles.

The low environmental hazard of such glass waste and the low cost of the glass itself as a material allows for extensive use of landfilling in the case of soft environmental legislation. So according to[16] in the United States in 2013, only 27% of the generated waste glass was recycled, and the rest, amounting to 7.59 million tons, was landfilled.

It can be argued that in spite of the introduction of separate waste collection and the development of technologies for sorting glass cullet, there is a significant part of waste glass that is not reused. This is mainly the glass cullet, contaminated with alien impurities, usually consisting of small fractions of chemically heterogeneous glass. Therefore, its reuse is based usually on physical and mechanical properties, when the cullet acts as an alternative to natural resources. For example, it is used as a substitute of sand in Portland mortars.[17,18] In the case of high dispersion of glass, surface properties such as binding and pozzolanic properties begin to appear for the material. Waste glass powder is a material that offers an excellent alternative also to replace cement due to its well-known pozzolanic properties.[19] However, the technology needs in deep grinding of glass and obtaining glass powder with a maximum size of 38 μm. Therefore, the process requires high energy consumption for dispersion of the material.

In the case of using glass waste as partial replacement of coarse aggregate in concrete[20] glass does not acquire

additional physical and chemical properties but is used simply as an inert aggregate in concrete, replacing more traditional aggregates. When glass is used as aggregate in concrete or mortar, expansions and internal stresses occur due to an alkali–silica reaction.[21] In addition, expansion increases with an increase in amount of glass. The effect of alkali–silica reaction and concrete expansion can lead to the formation of cracks and in the limit to the destruction of structures, which increases the risks of using glass as a filler on a mass scale.

Using of glass waste as a large aggregate in concrete has much in common with using of glass as an aggregate in road construction. In these cases, glass is considered an inert material and replaces traditional aggregates, such as construction sand or crushed stone. This is how glass waste is disposed for replacing aggregate in asphalt mixes for road construction.[22,23]

Glass waste is used in road work applications as alternative of natural crushed stones. Laboratory testing results indicated that medium and fine sized recycled glass sources exhibit geotechnical behavior similar to natural aggregates. Coarse recycled glass was. however, found to be unsuitable for geotechnical engineering applications. Shear strength tests indicate that the fine and medium glass encompass shear strength parameters similar to that of natural sand and gravel mixtures comprising of angular particles. Environmental assessment tests indicated that the material meets the requirements of environmental protection authorities for filler material. The results were used to discuss potential usages of recycled glass as a construction material in geotechnical engineering applications particularly road works.[24]

In the above described cases glass waste competes in the market with traditional materials, the primary production of which from natural resources is quite cheap. However, collecting and transporting of dispersed glass waste requires costs, so often the cost of collected culling is higher than market prices for primary natural resources. A possible way for mixed cullet reusing may be a technical solution that uses the properties of glass that are not found for natural materials, namely, thermoplasticity.

In contrast to hydrated methods of glass and silica reusing thermal methods completely exclude the risk of alkali–silica reaction and allow the formation of sintered products with high consumer properties. In this case the main problem is the high contamination and heterogeneity of glass waste. A possible solution is the use of waste glass for the production of ceramic materials. The temperature range of transition to the plastic state of the most widespread soda-lime-silica glass is 650 ÷ 800°C that is significantly lower than the temperature range of sintering of most types of ceramics. Therefore, glass additives to ceramic raw materials contribute to the sintering process of ceramics.

Oil shale fly ash and slag with a high concentration of silica were transformed into a value-added various products such as sintered bricks and ceramics via melting and sintering method. The maximum mechanical properties, good chemical resistances, and low heavy metals leaching concentrations showed that it could be used as a substitute material for construction applications.[25] The authors[26] note that glass additives play the role of flux, lowering the firing temperature. Glass binds high-melting minerals and this method can produce unusual ceramic-like composite materials. For example,[27] the glass binds basalt rock mining waste into tiles with high application properties at firing temperatures of only about 1000°C.

The addition of glass reduces the porosity of ceramics and thus improves properties such as water absorption and strength. Replacing of traditional fluxes for the ceramic industry, such as feldspar, with waste glass allows to produce traditional ceramic products, such as tiles, without losing the quality of the product.[28,29]

The above-mentioned cases involve the exploitation of thermoplastic properties of glass and therefore their logical development leads to obtain foamed materials with adding gas-forming agents to the raw material composition. The composition of the glass has little effect on the foaming process of the composition, if the dispersed glass is used as a filler in the composite raw material, in which the matrix contains a flux and a gas-forming agent. So glass ceramic foams were prepared by direct foaming method, using coal fly ash and waste glass as the main materials, borax and calcium carbonate as fluxing agent and foaming agent, respectively.[30] Sodium polysilicate can be used as a matrix, which simultaneously serves as a binder for dispersed glass and a gas-forming agent during forming of a composite preform.[31] The authors note that in the described case, the raw glass was a waste container glasses of mixed colors.

A similar technical solution was described[32] and it is based on using of dispersed glass waste in a matrix of hydrated sodium polysilicate for the production of cellular silicate materials. In this case, sodium hydrosilicate obtained from amorphous silica is a matrix filled with glass particles. Heat treatment leads to the release of steam from the hydrosilicate that foams the material, and the chemical composition of the glass particles plays an insignificant role in the formation of the cellular structure. The only one requirement for a dispersed aggregate is its thermoplasticity. Any amorphous silica can be used as a raw material for the synthesis of hydrated polysilicate. In this context, rice husk ash can be a good raw for the synthesis of hydrated polysilicate, when the task is to minimize the cost of raw materials and waste recycling.

In the proposed scheme for the joint secondary recycling of rice husk ash and glass waste for the production of silicate cellular material, the only controversial point is the presence of impurities in the hard-to-recycle glass that do not possess thermoplasticity. Alien impurities can lead to weak foaming

and poor quality foam glass with high density.[33] However, weak foaming or even foam destruction can be applied to the directed removal of cellular glass inside the composite material. Indeed, foam glass at high temperatures or a long time of synthesis is prone to the process of coalescence,[34] leading to fusion, cell enlargement and, in the final form, to the subsidence and destruction of the foam. Based on the above, the possibility of joint utilization of rice husk ash and contaminated glass waste by creating a granular cellular material and further coalescence of the obtained granules inside the ceramic matrix and obtaining light ceramics was suggested. For the proposed technical solution of reusing waste silica materials for the obtainment of the lightweight products, the impurities content in the glass or in rice hulls ash are not so important as, on the contrary, they are in the case of the production of pure foamed glass. The possibility of joint recycling of contaminated glass waste and rice husk ash to produce light ceramics in the form of bricks, stoneware or tiles is considered and the economic reasons of this technology are discussed.

2 | MATERIALS AND METHODS

The rice husk ash was obtained by the procedure described earlier.[35] The ash was an X-ray amorphous silicon oxide with a content of 6.5 wt% residual carbon after burning in air.

Glass waste with a mass ratio of 1:1:1 of white, green, and amber glass was used for experiments. Figure 1 shows the morphology of used glass cullet.

Glass was milled in a ball mill and a fraction less than 0.1 mm was selected by sieving. Raw preforms were obtained from glass waste using the method described earlier,[36] but replacing silica gel with an equivalent amount of rice husk ash. Water solution of liquid glass was also changed for mixture of rice husk ash and aqua solution of sodium hydroxide. The glass was dispersed in a bead mill until the passage through a 0.1 mm mesh sieve. The rice husk ash was added to the glass powder in the ratio of 1/5 mass. The working solution was prepared by dissolving in water of 1/5 mass of sodium hydroxide from the mass of rice hulls ash. The powder and the working solution were mixed up until a homogeneous paste composition was obtained. The paste was filled into forms and the forms were placed in a thermostat and held at a temperature of 80°C and 100% relative humidity for 24 hours. As a result, the paste gained strength and green specimens were obtained. Natural silicate sand fraction of <0.1 mm was used to simulate crystalline inorganic impurities. The calculated amount of sand was added to the mixture during the preparation of paste for raw preforms.

FIGURE 1 Morphology of used glass cullet [Color figure can be viewed at wileyonlinelibrary.com]

The electron microscopic investigations were carried out on a Hitachi S-3400N microscope. Compression strength was determined with the PGM-MG4 press (Priborkomplekt).

The clay used for preparing the samples was a commercial product CG/G-002 produced by Gzhel (Russia). The manufacturer defines the material as red clay with a firing temperature of 920 ÷ 1020°C. The raw clay was dried at 90°C for 24 hours, and then prepared to a suitable particle size through grinding in a ball mill up to a powder passing through a sieve with a cell size of 200 microns for obtaining of raw clay powder.

The ceramic cellular structure was prepared as the following. Water was added to the granules of cellular glass in a rotary mixer. The calculated amount of raw clay powder was added to the wet granules. The resulting composition was placed into a metal mold and pressed at a pressure of 3.0 MPa for formation of composite billets. Composite billets were fired in a muffle furnace at 920°C for 3 hours.

Following, the procedure for sample preparation was reported, it consists of four main steps.

The first step is the preparation of green specimens from amorphous silica wastes namely waste glass cullet and rice husk ash. For this purpose the paste is prepared from mixture of glass powder and rice husk ash in the presence of alkali solution. The paste becomes solid green specimens after heat treatment at 80°C.

The second step is the obtainment of cellular granules from green specimens. The green specimens are crushed and the necessary fraction of green granules is separated by sieving. The cellular granules are produced by heat treatment of green granules at 760 ÷ 850°C.

The third step is the preparation of raw ceramic bricks by mixing of raw clay powder and wet cellular glass granules. The resulted mixture is pressed for obtaining of raw ceramic bricks.

The fourth step is heat treatment of raw ceramic bricks for obtaining of porous ceramic bricks. The temperature of ceramic sintering is higher for 150-200°C than the temperature of glass melting. So cellular glass filler melts inside ceramic

matrix and only spherical holes (pores) stay inside ceramic on the place of filler.

As a result of these procedures the role played by the amorphous silica wastes is not as a real filler but as poring agent inside ceramic matrix.

3 | RESULTS AND DISCUSSION

3.1 | General characteristics of the method

The solution of the recycling problem of inhomogeneous glass cullet contaminated with inorganic impurities was assumed by creating a cellular granular silicate material using a method that is not sensitive to the composition of the raw material. The behavior of the obtained granules during heat treatment as a part of a composite material in a ceramic matrix, which has a sintering temperature obviously higher than the softening temperature of the cellular granule material was studied.

3.2 | Preparation of the granulated porous filler (step 2)

Rice husk ash, as amorphous silica, in the presence of an alkaline agent, such as a solution of sodium hydroxide or liquid glass, forms a hydrogel that is a hydrated sodium polysilicate. During heat treatment of the raw composition, hydrated sodium polysilicate releases steam, forming an anhydrous glassy silicate of a cellular structure. The films between the cells and the lintels have an abnormally low thickness, which is impossible for traditional foamed glass. An example of the structure of such a silicate foam is shown in Figure 2. The thickness of the films between the cells is less than one micron in some cases, which causes an extremely low bulk density of the obtained granules and their low strength. The bulk density of granules is 70–110 kg/m^3, but the low strength makes it difficult the directly use of the obtained granules in various applications. However, high gas formation during heat treatment of raw hydrated sodium polysilicate and high thermoplasticity allow using such a material as component together with clay for creation of cellular materials with thermoplastic fillers. As a result of mixing dispersed glass and rice husk ash in the presence of an aqueous solution of an alkaline agent, a paste that cures at temperatures of 60–95°C due to the formation of hydrated sodium polysilicate between the glass grains is obtained (Figure 3).

The only one requirement for aggregate in the synthesis of cellular material in this case is thermoplasticity. Exactly this property is distinguished by waste glass, therefore, during the heat treatment of the composition of the filler in the form of waste glass grains and a binder of sodium polysilicate, a

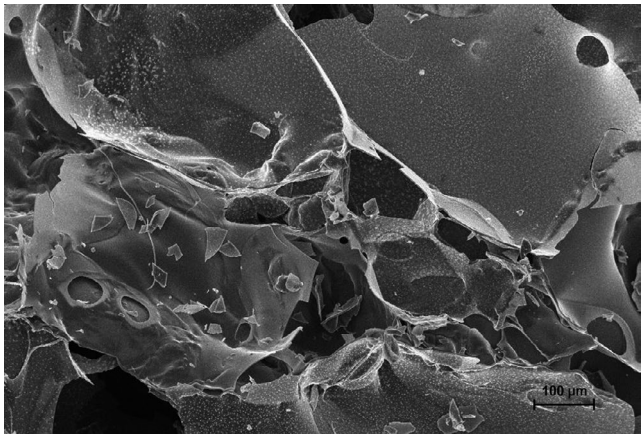

FIGURE 2 SEM photograph of cellular granule obtained from polysilicate cellular granule

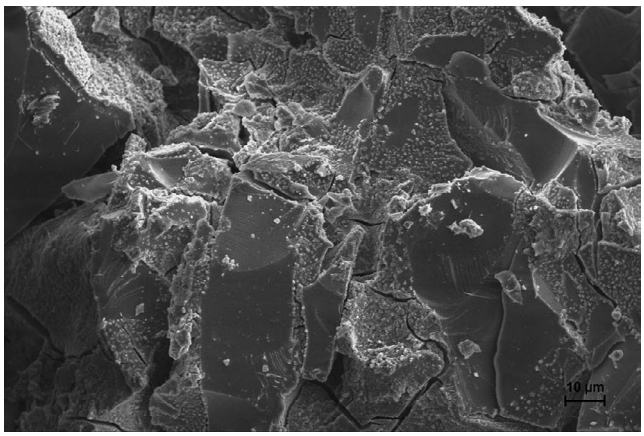

FIGURE 3 SEM photograph of raw composite produced from waste glass and rice husk ash in the presence of an aqueous solution of an alkaline agent

cellular silicate material is formed. In this case, in the hydrated sodium polysilicate under the action of the evolving gases the composition in a thermoplastic state is foamed. The waste glass grains dissolves forming a single silicate with polysilicate of matrix and a cellular structure is formed. An example of a chip of a cellular granule is shown in Figure 4.

The resulting cellular structure has a film thickness between the cells of 5–20 microns, which is significantly higher than in the case of polysilicate foam without a filler. The bulk density of the obtained granules is also higher than for granules obtained from pure polysilicate and it is 180 ÷ 350 kg/m^3. It depends on the size of the granule fraction, on the quality of the added dispersed waste glass filler and on the amount of possible impurities. The technological solution allows you to process even contaminated waste glass into a cellular structure granulated material. However, the direct use of the resulting granular material can be difficult in various applications due to the variability of density and strength. However, the inherent properties of these silicate granules are

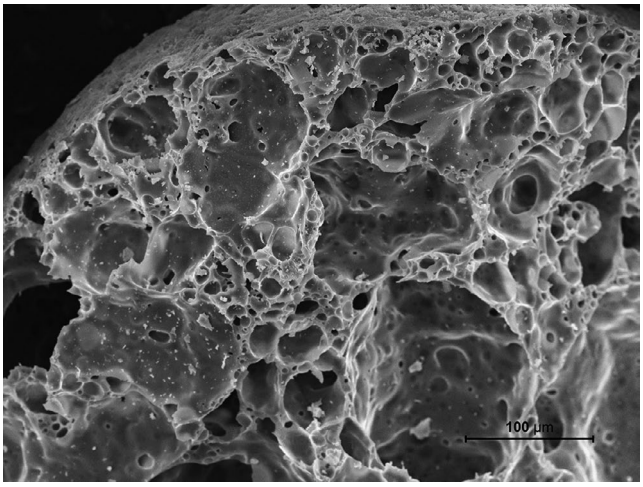

FIGURE 4 SEM photograph of a chip of a cellular granule

their low density and the thermoplasticity. It makes it possible to use these granules for creating lightweight ceramics.

The presence of dispersed glass as a more fusible aggregate in clay raw materials for the production of ceramics does not significantly affect the quality of the produced ceramics so glass waste may be suitable for industrial production of ceramic tiles.[37] In the presence of refractory materials, glass acts as a binder in high-temperature treatment of the composition, for example, in the manufacture of compositions of metallurgical slag and cullet.[38]

Therefore, it is assumed that the addition of foamed glass within a clayey matrix should also not reduce the quality of the resulting ceramic material. Moreover, the researchers observed a positive effect,[39] when the introduction of low-melting additives of cullet into the raw red clay significantly reduced the sintering time of porous bricks and varied their strength properties. The addition of foamed glass to the initial matrix as a filler can lead not only to chemical but also structural changes. In contrast to the glass granules the foamed glass granules are able to change the volume especially at high temperatures. The low viscosity of silica melt at high temperatures leads to coalescence of foam and its following collapse.[40] Therefore the behavior of initial silica composition was investigated not only at the process of foaming but also at the high temperature of foam collapse. The results are shown in Figure 5. Two types of hydrated polysilicates were investigated. The first one was prepared from pure silica and the solution of sodium hydroxide and the second one was prepared from rice hulls ash the solution of sodium hydroxide. The thermogravimetric curve TG is similar for the both so only one curve is shown in Figure 5. A gradual decrease in mass associates with the smooth removal of water from the sample over the entire temperature range. The differential scanning calorimetric curve for the first sample DSC_1 is also typical for thermal behavior of hydrated polysilicates.

The unexpectable effect was found at the differential scanning calorimetric curve prepared from rice hulls ash DSC_2. The initial sample of hydrogel contains a small amount of carbon. The exothermal effect at 600 ÷ 660°C is corresponding to the oxidation of carbon and typical for carbon oxidation in ceramic composition. But at the temperatures higher than 800°C there is a series of exothermic effects that exceed the equipment error. Moreover the additional experiments show the constant existing of this effect but the position and intensity of peaks are changes from one to another experiment. The combination of DSC curve with the curve of ion current m/z = 44 (carbon dioxide) shows the relation of each exothermal effect with formation of carbon dioxide. The correspondence of the five biggest peaks at the DSC and Ion Current curves are demonstrated by the grey arrows.

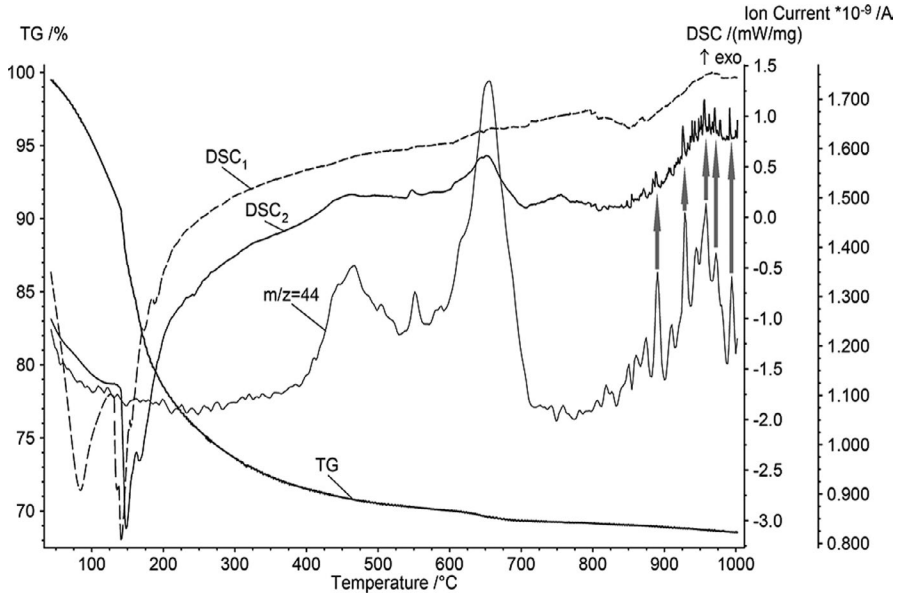

FIGURE 5 The results thermogravimetric analysis synchronic with mass-spectrum analysis of hydrated polysilicates (made from pure silica gel and from rice hulls ash)

The totality of the data obtained suggests that we observe the effect of carbon monoxide oxidation when destruction individual foam bubbles. The carbon monoxide appears as a result of oxidation of carbon by steam of hydrogel at the temperatures higher than 500°C, the carbon monoxide foams the thermoplastic matrix and stays inside bubbles of foam. The increasing of the temperature higher than 800°C leads to the drop of obtained glass viscosity and destruction of bubbles one by one. The collapse of each bubble gives the emission of carbon monoxide to the air gas flow of the equipment and oxidation of carbon monoxide up to carbon dioxide. So the exo-effect at DCS curve and emission of carbon dioxide accompany each bubble destruction of silica glass foam.

One can monitor the process of glass foam coalescence by the observation of "coalescence saw" synchronic at the curves of DCC and MS ion current of carbon dioxide m/z = 44. The effect is not controlled by TG because of too low mass of the removed carbon monoxide from the sample. The peaks obligatorily present at the DSC and MS curves of all samples used carbon as a foaming agent but the position and intensively of the peaks are varies from one sample to another because depends not on the chemical process but on the collapse of individual bubbles of foam.

A similar effect of "coalescence saw" is observed for composite cellular granules (Figure 6).

It can be argued that the structure of foamed glass at temperatures above 800°C is destroyed. The mechanism of this destruction consists in the successive collapse of individual bubbles one after another until all the foam turns into a monolithic material without gas inclusions. The volume of the glass itself in the volume of foamed glass is usually lower than 5–7 vol. percents, so the collapse of the foamed glass granules inside the solid ceramic matrix at temperatures higher 800°C leads to the formation of caverns in places of the foamed glass granules. This effect can be used for formation of porous foamed ceramics.

3.3 | Preparation of cellular ceramic material (steps 3 and 4)

Two series of composite bricks with two types of fillers were prepared: first filler was composite cellular granules (made from rice husk ash and waste glass) and the second filler was polysilicate cellular granules (made from rice husk ash).

Composite billets to be subjected to firing were obtained by pressing the mixture of cellular granules with clay. Selection of clay with a sintering temperature higher for 150–200°C than the synthesis temperature of cellular glass is due to the assumption that at the temperature of clay sintering the glass has a low viscosity. The foamed glass coalesces due to the low viscosity of the glass at the temperature of the clay sintering. The usual foam coalescence process is accompanied by its subsidence and a decrease in the volume of the gas-filled composition at the normal conditions. However, in the described case, the surface of granules of cellular material has a high adhesion to the material of alumosilicate clay matrix. Therefore, the glass from the cellular granule during the process of coalescence forms a layer on the inner surface of the ceramic cells and it is partially absorbed into the aluminosilicate frame. As a result, a cellular structure is formed in the ceramic matrix with voids in places of disposition of cellular glass granules. Figure 7 shows a photo of fresh fracture of the resulted cellular ceramic material.

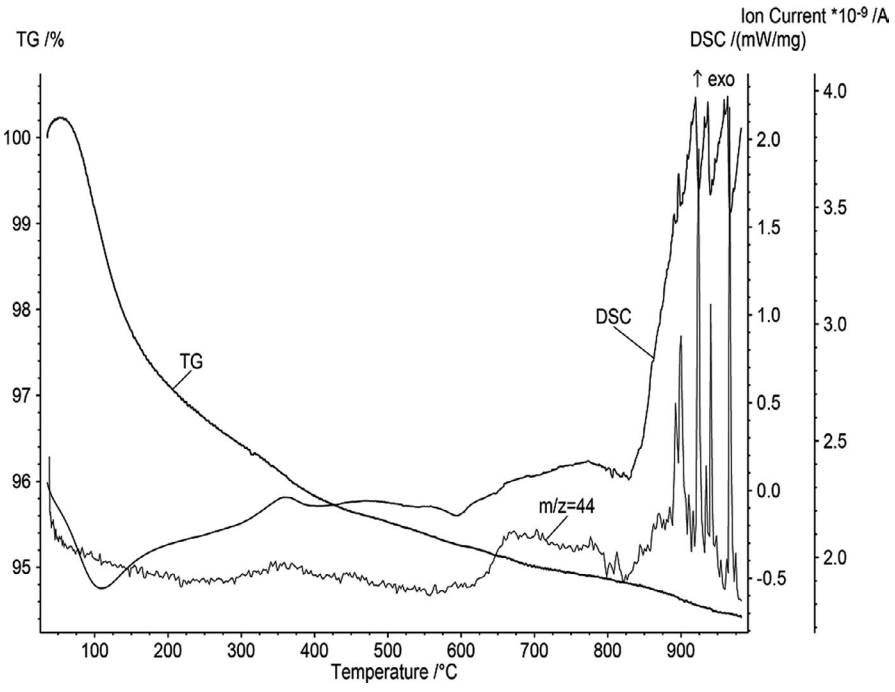

FIGURE 6 The results thermogravimetric analysis synchronic with mass-spectrum analysis of raw composition for composite cellular granules

In the resulting cellular material, the cells sizes are determined by the fractional composition of cellular glass granules used for the synthesis of ceramics. The presence of residual carbon in the ash of rice husks contributes to an increase in gas formation during the synthesis of granular cellular material but gives the granules a gray color. The residual carbon of foamed glass is oxidized during the composite material heat treatment and the resulting lightweight ceramic material has a natural color.

It can be assumed that the presence of inorganic impurities in the initial waste glass would have influence for the foaming process of the composition and for the properties of the resulting cellular foamed glass granules.

3.4 | Influence of impurities for the bulk density of granulated cellular glass material

The resulting cellular granules prepared according to the above-mentioned procedures have a bulk density that differs for different fractions (Table 1).

The observed effect of reducing bulk density with increasing granule sizes is explained by more intensive diffusion of foaming gases during synthesis through the outer surface of the granule for small granules with a larger specific surface area.

Various amounts of natural sand to the original composition in order to study the effect of impurities on the process of foaming granules were added. The results are presented in Figure 8.

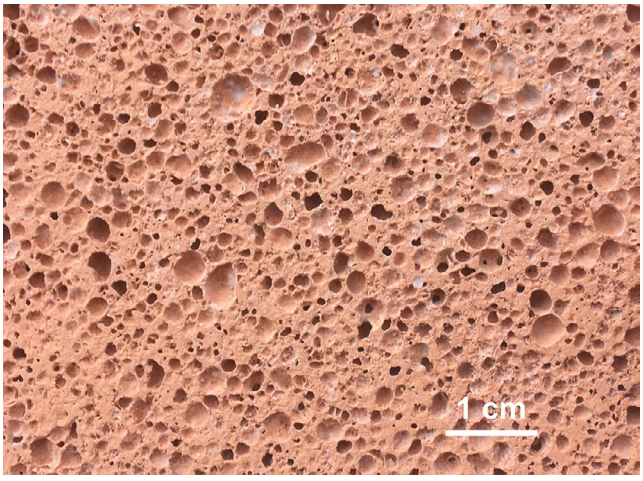

FIGURE 7 Photograph of a cut of the resulted cellular ceramic material [Color figure can be viewed at wileyonlinelibrary.com]

The obtained results allow to conclude that at low concentrations of impurity bulk density increases slightly and only at a concentration of natural sand above 8–9 g per 100 g of glass, the density of the resulting granular material increases intensively. Probably this phenomenon is due to active crystallization of glass and the destruction of cells in the process of gas formation. Based on the data obtained, it was decided to use waste glass as a raw material for further experiments, containing 7.5 g of impurities in the form of natural sand per 100 g of waste glass. After synthesis of granulated cellular material from this raw material, a fraction of granules of $0.85 < x < 2.0$ mm with a bulk density of 350 kg/m^3 was used for further experiments. The structure of these granules is similar for the structure of granular shown in Figure 3. These granules as "composite cellular granules" were used for the further experiments as a filler for preparation of raw ceramic bricks.

The granules prepared from pure rice husk ash without addition of waste glass powder were prepared (with a structure as at the Figure 1). It was separated by sieving the fraction of granules of $0.85 < x < 2.0$ mm with a bulk density of 110 kg/m^3. These granules as "polysilicate cellular granules" were used for the further experiments as a filler for preparation of raw ceramic bricks.

It can be assumed that by changing the ratio of granules of lightweight cellular aggregate and clay powder, one can change the density and strength of the resulting cellular ceramics.

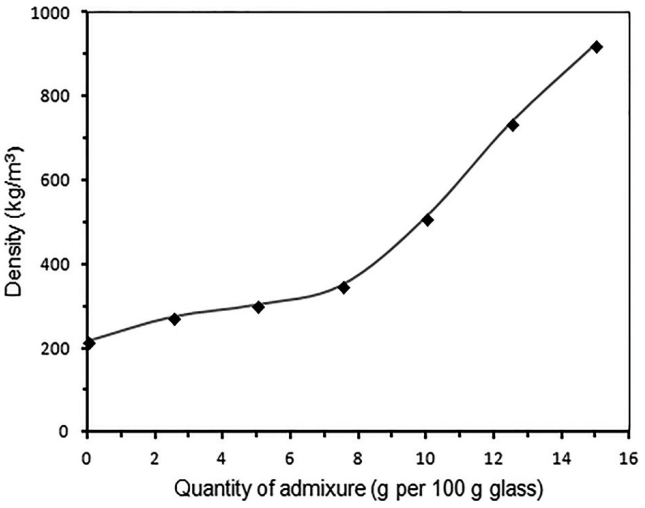

FIGURE 8 The dependence of cellular granulated material of fraction 0.85÷2.0 mm bulk density on the quantity of natural sand admixture in initial composition

TABLE 1 Bulk density of the resulting cellular granules

Granules size (mm)	>0.16 <0.32	>0.32 <0.63	>0.63 <0.85	>0.85 <1.3	>1.3 <2.0	>2.0 <2.5	>2.5 <5.0
Bulk density (kg/m^3)	352 ± 2	291 ± 2	260 ± 2	233 ± 2	211 ± 2	197 ± 2	184 ± 2

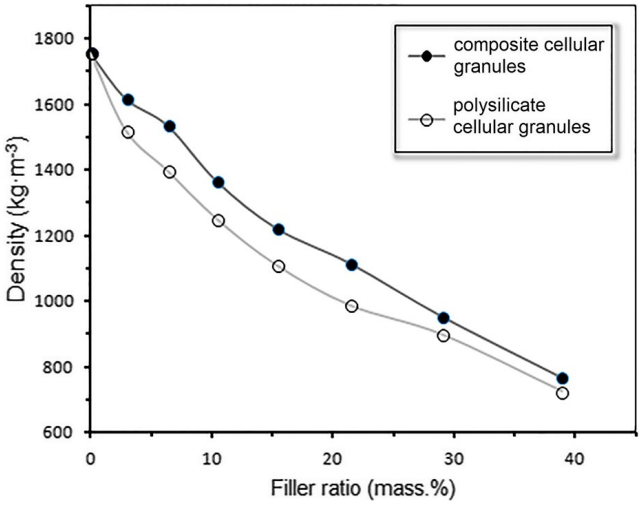

FIGURE 9 Dependence of the density of the resulting ceramics on the ratio of light weight fillers as composite cellular granules and polysilicate cellular granules [Color figure can be viewed at wileyonlinelibrary.com]

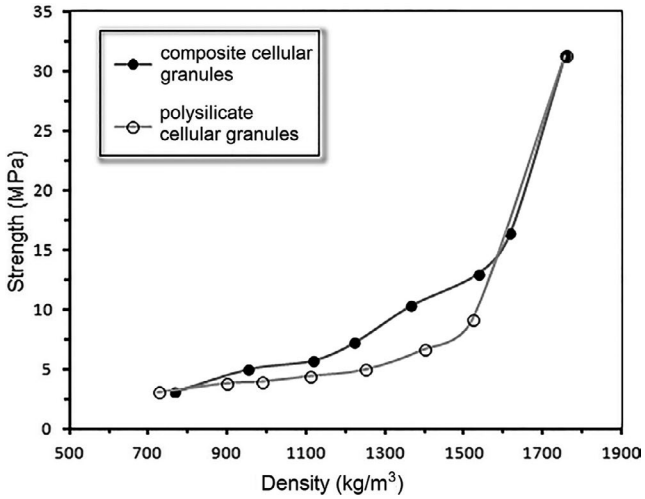

FIGURE 10 Dependence of compressive strength on the density of cellular ceramics with light weight fillers as composite cellular granules and polysilicate cellular granules

3.5 | Density of cellular ceramics

Lightweight glass granules melt and coalescence during heat treatment. Appearance of voids in the ceramic matrix at the places of granules leads to the formation of a cellular structure of the ceramic and a decrease in the density of the finished material. The dependence of the density of the resulting ceramics on the mass fraction of the granulated cellular aggregate in the original composition in terms of dry material is shown in Figure 9.

The resulting ceramic has a low density and isotropic structure, this fact distinguishes cellular ceramic from traditional lightweight ceramics obtained by extrusion. For example, ceramic bricks or tiles to obtain a comparable apparent density below 1200–1000 kg/m^3 are produced by extrusion through special spinneret for formation of parallel channels in the material. Anisotropic products obtained by the traditional method are cut difficulty for uniform parts for construction process and such products can be destroyed in areas with an increased concentration of defects during operation.

The resulting cellular ceramic has an isotropic cellular structure, which makes it possible to make construction products of any shape and allows convenient cutting.

3.6 | Compressive strength

Cellular ceramics have a compressive strength sufficient for using as a self-supporting material, even at low density, as shown in Figure 10.

So, for cellular ceramics obtained from lightweight glass-contained granules as a filler, the strength reaches 5 MPa at a density of 900–920 kg/m^3, that is considered acceptable for bricks or tiles. The same strength is achieved only for a material with a density higher than 1200–1300 kg/m^3 for cellular ceramics with lightweight filler made from rice husk ash.

From the results achieved it is possible to argue that waste glass contaminated with inorganic crystalline impurities up to 8–9 g per 100 g of glass and rice husk ash can be suitable raw materials for the production of lightweight cellular granular material. This granules manufacture can be in itself a technical solution for the disposal of contaminated waste glass. However, it seems more promising using of the resulting granular material as a filler in the production of lightweight cellular ceramics.

3.7 | Economic evaluation of waste glass reusing to cellular ceramics

Bulk materials usually have a price referred to the mass. For example, the price of crushed stone or natural sand is usually referred to a ton of material. The market price of crushed waste glass is 65–90 Euros per ton. It is much higher than the market price of natural bulk aggregates. So, it is obvious that the reusing of waste glass by replacing existing natural aggregates is economically unprofitable.

The economical view is also rueful in the case of reusing of waste glass for manufacture of granulated cellular glass from waste glass. Expanded clay at the market of lightweight bulk materials has the price per ton much lower than and the price of granulated cellular glass per ton. It is obvious that competitiveness of granulated cellular glass is also impossible in this market.

It can be concluded that the most economically effective is using of lightweight fillers in the production of lightweight ceramic. However, this solution for expanded clay is not technically justified due to intrinsic properties of expanded clay, such as the high softening temperatures of expanded clay and the inability of creation of voids inside the ceramic matrix. Another economic situation is formed if granulated cellular glass is used for creation of holes inside ceramics because the reference commercial field changes. In the case of ceramics, the market price is not related to the mass, but to the volume unit of the product. The price can be attributed to the volume as unit because the unit usually has the constant volume as bricks or tiles.

Granulated lightweight aggregate of different bulk density replaces part of the ceramics in the product and its unit cost is acceptable for economically justified use, even taking into account profits and overhead costs. So, reusing of amorphous silica waste for creation of porous ceramics turns out to be economically effective.

4 | CONCLUSIONS

The technology proposed in this paper for the production of granular cellular materials has the great advantage to be independent by the glass chemical composition, allowing the use of any type of glass with evident benefit from the logistic point of view. The solution of the recycling problem can be cost-effective when purchasing these materials after a pretreatment performed by processing enterprises at a price not lower than 65–90 Euros per ton.

The solution may be to create a technology aimed at using amorphous silica waste as a raw material and based on such unique properties of the material as the chemical ability to create hydrated products and the thermoplasticity of the resulting silicates. The technology allows to produce granulated cellular glass even using waste glass as a raw. The resulting granules, in turn, serve as a source for creating "holes" for the production of cellular ceramics.

The undoubted advantages of the proposed technology are the following:

- Possibility of its development at existing production facilities of ceramic products with minor modernization;
- Ecological benefits of using amorphous silica wastes, including glass waste and rice husk ash;
- Reduction of energy consumption and raw material costs per unit of production;
- Reduction of logistics costs.

Further researches discovery of the effectiveness of the proposed technological solution and for the development of resulting ceramic products are expected.

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