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Research paper

Using quartzofeldspathic waste to obtain foamed glass material

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Abstract

The present paper proposes a method for the processing of mine refuse non-ferrous metal ore in the production of foamed glass. The subject of this research is a low-temperature frit synthesis (<900 °C), allowing for the high-temperature glass melting process to be avoided. The technology for the production of frit without complete melting of the batch and without using glass-making units offers a considerable reduction in energy consumption and air pollution. It was found that material samples obtained with a density of up to 250 kg/m^3 are of rigidity (up to 1.7 MPa) in comparison with the conventional foamed glass (1 MPa). This increased rigidity was due to the presence of crystalline phase particles in its interpore partition of less than 2 μm in size. Material with a density of 300 kg/cm^3 is recommended for thermal insulation for the industrial and construction sectors. At densities above 300 kg/cm^3 and a strength of 2.5 MPa, the purpose becomes heat-insulating construction material. The proposed method for obtaining a porous material from waste widens our choice of raw materials for foamed glass, whilst saving resources and energy.

Keywords: Quartzofeldspathic waste; Low-temperature frit; Foamed glass material

1. Introduction

Feldspar is widely used in glass, ceramic and other industries, as well as in the manufacturing of abrasive materials, mastics and as a drilling fluid filler. In addition to deposits, feldspar can also be found in non-ferrous metal ore processing, where it appears in the form of feldspathic waste. The waste from the beneficiation of metal ore can also be used in the manufacturing of construction materials. The given area of application will depend on both the waste composition and the features of other ingredients. Individual cases must be based on research into the preparation of content and processes.

The waste from non-ferrous metal ore beneficiation, whether copper, lead-zinc, molybdenum or other, constitutes large tonnage recoverable waste which, if not used, would pollute the environment. Therefore, the issue of their usage draws considerable attention. For example, the mass of tailings from the production of 1 tonne of copper reaches 5.6 tonnes, while the production of nickel from oxide ore yields almost 100 tonnes. Currently each year, metallurgical slag amounts to hundreds of millions of tonnes all over the world, whereas the worldwide production of mining products and fuels is greater than 150 billion tonnes per year [1–5]. Pollution of the environment with industrial waste is one of the most important problems of the modern world [6–8]. Industrial waste disposal is necessary not only for the reduction of dangerous environmental pollution, but also for the generation of economic benefits. The use of sludge and tailings from various processes as an alternative raw material is regarded as the most promising method of reducing the production costs of various materials [9,10]. The present article considers the issue of obtaining foamed glass from quartzofeldspathic waste, generated by non-ferrous metal ore beneficiation.

The conventional raw material from which foamed glass used to be extracted has been secondary glass waste or other specially melted glass. Glass waste, the potential of which in terms of foamed glass is limited, can now be gradually replaced by industrial or off-grade waste. There are examples of the production of light porous fillers from clay, shale rock, perlite and vermiculite, as well as certain types of waste [11–13]. Research in this area is one of the most rapidly growing fields. Furthermore, the issue of the reduction of energy consumption

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is also attracting growing attention. There is practical interest in obtaining foam glass from other types of man-made materials using low-temperature processes, without relying on conventional high-temperature melting techniques. For the development and application of these materials, it is necessary to bring together the technological and operational properties of materials, as well as their composition.

The objective of this work is to synthesise frit, from waste of non-ferrous metal ore obtained from beneficiation, and use it to produce foamed glass, using the low-temperature process (<900 °C). The technology for the production of frit without complete melting of the batch and without using glass-melting processes offers a considerable reduction in energy consumption and air pollution.

2. Materials and methods

2.1. Materials

The subject of the research is quartzofeldspathic refuse, obtained through beneficiation, in the form of copper-zinc ore from the Zhezkazganskoe mine in Kazakhstan, as well as beneficiation waste from molybdenum ore, from the Sorskoe complex in Russia. The chemical and granulometric composition of the waste is indicated in Table 1.

The chemical composition of the waste differs from that of graded quartz sands, normally used for glass melting, as they contain less glass-forming SiO_2 and more Al_2O_3, Fe_2O_3. Both types of waste are aluminosilicates. According to the results of chemical analysis, the wastes do not correspond to the sand grade [normally] used in the production of foam glass, cans and bottles, half-white glass, insulation or pipes. The elevated levels of oxides contained in glass and the quality of main components, such as CaO, MgO, K_2O, Na_2O, must be taken into account when calculating the batch composition. The chemical composition of the waste indicates possible suitability for producing foamed glass from frit.

In addition to the chemical composition, another important requirement for raw materials suitable for low-temperature synthesis of frit is its dispersiveness, where the average particle size must not be lower than 100 µm. The assessment of granulometric composition of quartzofeldspathic waste indicated that the material obtained from beneficiation of the ores originating from Zhezkazganskoe deposits are a fine grain material, which could be used in frit synthesis. The waste from the beneficiation of ore originating from Sorskoe deposits, on the other hand, must undergo additional pulverisation.

2.2. Experimental method

The study of the material's phase composition as well as finished materials was conducted using X-ray diffraction on a DRON-3M in copper radiation, whilst the quantitative X-ray diffraction analysis was performed using Match! software. The physical and chemical processes that occur during the heat treatment of the batch were studied using differential thermal analysis (combined TGA/DSC/DTA analyser SDT Q600). The study of the macro- and microstructures of the porous samples was performed on a digital microscope (USB Digital Microscope) and scanning electron microscope (JCM-6000) with an attachment for energy dispersive analysis.

Radiological measurements, conducted using the "RKS-01-SOLO" radiometer-dosimeter, indicated that the radiation from this material does not exceed the natural background radiation level, constituting 0.07 µSv/h. The effective activity of the radionuclides, measured using the "Progress-2000" gamma spectrometer, amounted to 241 Bq/kg, which also does not exceed the level of safety for construction materials (370 Bq/kg).

3. Results and discussion

The work produced frit at a temperature of 800–900 °C based on a two-stage process developed for this purpose [14]. During the first stage, frit was synthesised by thermal processing of the initial batch from waste. In the second stage, the frit was ground, with the addition of a blowing agent; the mixture was then granulated and foamed. The two-stage technology allows us to gradually optimise the structure and properties of the material. At the first stage, we solve the problem of synthesising frit with certain characteristics, as they can be regulated by certain recipe and technology factors. The main features of material macrostructure are manipulated in the second stage.

When selecting the chemical composition of frit for low-temperature processing, the following factors were taken into

Table 1
Chemical and granulometric composition of ore beneficiation waste.

Chemical composition										
Ore deposits	Content of oxides, %									
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	Cr_2O_3	TiO_2	SO_3
Zhezkazganskoe	68.38	17.04	3.81	3.02	1.79	3.49	1.65	0.14	0.50	0.18
Sorskoe	63.58	16.33	4.28	4.83	2.06	4.38	3.85	–	0.59	0.10

Granulometric composition					
Particle size, mm	Fraction content, %				
	<0.056	0.056–0.16	0.16–0.35	0.35–1.63	1.63–3.5
Sorskoe	2.1	11.2	45.3	38.2	3.2
Zhezkazganskoe	87.0	13.0	0	0	0

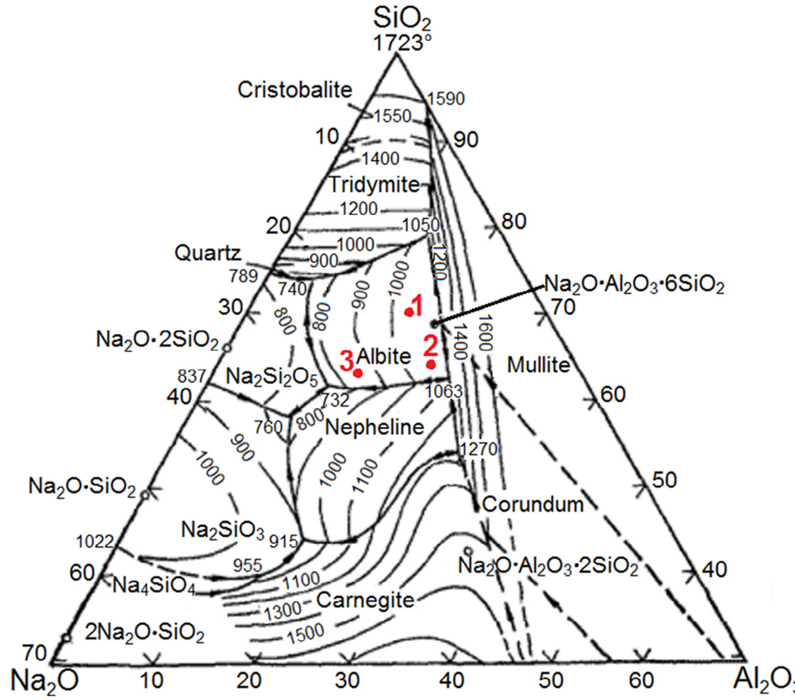
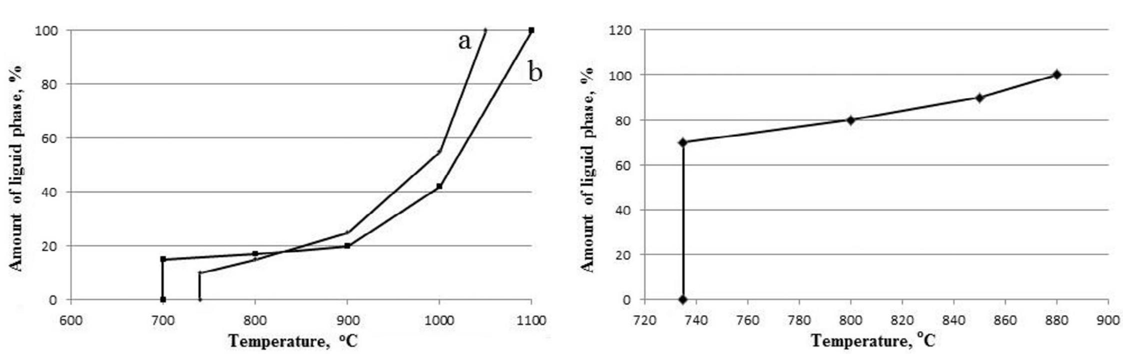


Fig. 1. The composition range for beneficiation waste and frit on the system diagram: Na_2O–Al_2O_3–SiO_2: (1) Zhezkazganskoe; (2) Sorskoe; (3) frit.

account. The composition of the batch must have sufficient glass-forming particles (60–75 wt. %) and alkali metal oxides (13–22 wt. %). The quantity of melt formed at temperatures up to 900 °C must make up more than 70%, which was established by the existing data [15]. The volume of crystalline particles, preserved in low-temperature frit, must not exceed 25%. The content of the active oxidising agent SO_3, used by the foaming reaction, must be at least 0.15%. An important part of the selection is the low-crystallisation capacity of the glass, since uncontrolled crystallisation will have a negative impact on the finished foam glass.

Since quartzofeldspathic waste consists of aluminosilicates, the following system constitution diagram was selected: Na_2O–Al_2O_3–SiO_2. The waste composition was broken down into three components, indicated as white feldspar on the diagram, and has a complete melting point of 1100 °C in the case of Zhezkazganskoe waste and 1200 °C for Sorskoe waste (Fig. 1, points 1 and 2). The calculated melting curve of the waste indicates that 70% of the melt is achieved at a temperature of above 1025 °C (Fig. 2, 1). This does not meet the requirements and indicates that it is necessary to add a low-melting component in the form of soda ash. The batch that corresponds to the requirements is composed of waste (80%) and soda ash (20%). The batch provides the following frit composition by wt. %: SiO_2: 60.88; Na_2O: 16.23; Al_2O_3: 15.21; Fe_2O_3: 3.40; CaO: 2.69; MgO: 1.59. The figurative composition point is also found in the albite field, and has a complete melting point of 880 °C (Fig. 1, point 3). The melting curve of the composition shows



(1) (2)

Fig. 2. The melting curves for beneficiation waste (1) and batch (2): (a) Zhezkazganskoe; (b) Sorskoe.

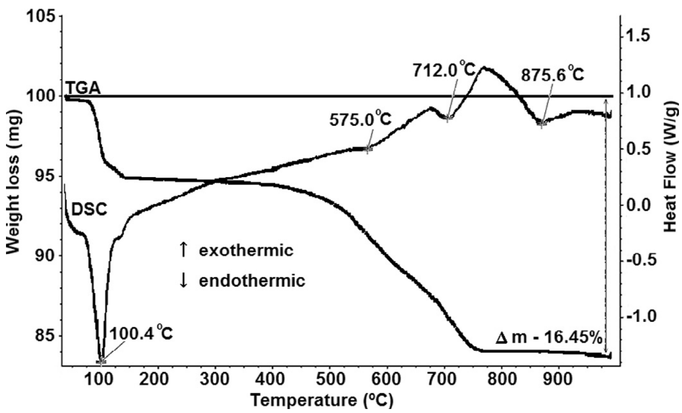


Fig. 3. TG, DTG curves of the two-component blend with the composition ratio: waste: 80 wt. % and soda ash: 20 wt. %.

that, at a melting temperature of 730 °C, the melt content is 70% (Fig. 2, 2).

Foamed glass can be obtained from glass which, at temperatures of 800–900 °C, has a viscosity of 10^5–10^7 Pa·c. Using the SciGlass Professional software for the analysis of content of the frit, temperatures were calculated for their corresponding viscosity values. It was found that the frit content can reach the required viscosity of 10^6 Pa·c at a foaming temperature of 800–900 °C.

Consequently, theoretical calculations indicate that the sample batch content provides the required quantity of melt (over 70%) at temperatures of up to 900 °C and the required degree of viscosity of 10^6 Pa·c at foaming temperature. Ore beneficiation waste from Zhezkazganskoe requires no additional processing in contrast to that originating from Sorskoe deposits, which needs to be pulverised further. Details of the experiment's results for foamed glass material, obtained from waste from ore beneficiation from Zhezkazganskoe, are indicated below.

Based on differential-thermal analysis (Fig. 3) it was demonstrated that the heating curve of the waste of a selected content presents some endothermic effects, reflected in the removal of hygroscopic water (100 °C), eutectic melting, and double salts (712 and 876 °C). A slight endothermic effect at 575 °C corresponds to polymorphic conversion of quartz. The main mass losses occur in the temperature range of 500–750 °C, which is consistent with silicate formation (1). At a temperature of 750 °C the thermogravimetric curve becomes horizontal, indicating the complete binding of sodium carbonate and the completion of silicate forming reactions.

$$nSiO_2 + Na_2CO_3 \rightarrow Na_2O \cdot nSiO_2 + CO_2\uparrow \quad (1)$$

The content of quartzofeldspathic waste allows for the use of a two-component batch, in contrast to the conventional, siliceous material, which requires alkaline metal carbonates. Low-temperature processing of the batch is sufficient for the glass-forming process. In the melt, produced at 875 °C residual quartz and white feldspar, contained in the initial waste, are dissolved.

Based on the results of X-ray diffraction analysis of the frit, synthesised at 800, 900, 1000 °C, it was observed that all X-ray images (Fig. 4) indicate an amorphous ring and maximum reflections resulting from crystalline phase. Crystalline phase is reflected in residual quartz (d = 0.334; 0.245; 0.228; 0.212 nm) as well as white feldspar (d = 0.321; 0.411; 0.295 nm). Increasing the batch processing temperature from 800 to 1000 °C leads to an increase in the amount of the glass phase from 75 to 85%. A quantification X-ray analysis indicated different content of crystalline particles, depending on the temperature of frit synthesis and the exposure (Fig. 5). As the synthesis temperature increases from 800 to 1000 °C, and with isothermal holding from 5 to 15 minutes, the amount of crystalline phase dropped from 25% (800 °C, 10 min) to 17% (1000 °C, 10 min). Consequently, the frit content and the low-temperature process were found to provide sufficient quantity of melt.

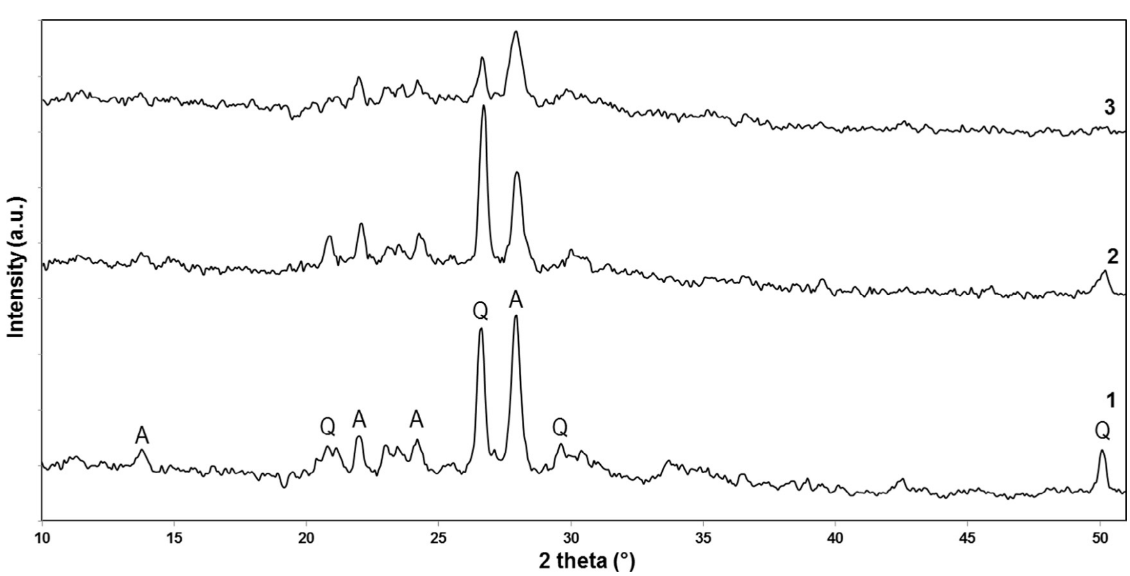


Fig. 4. X-ray images of frit, obtained at temperatures: (1) 800 °C; (2) 900 °C; (3) 1000°C (Q, quartz; A, white feldspar).

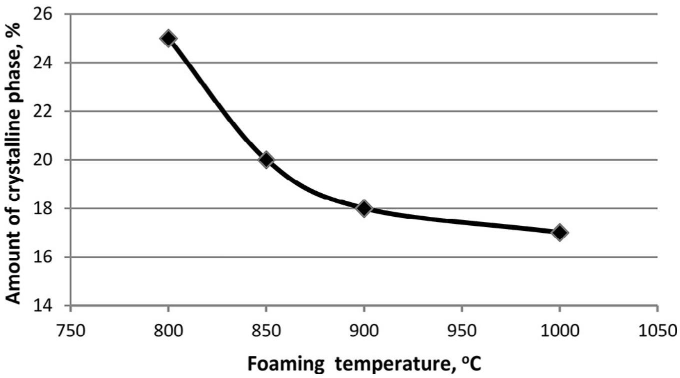


Fig. 5. Dependence of crystalline phase on frit synthesis temperature based on X-ray diffraction analysis.

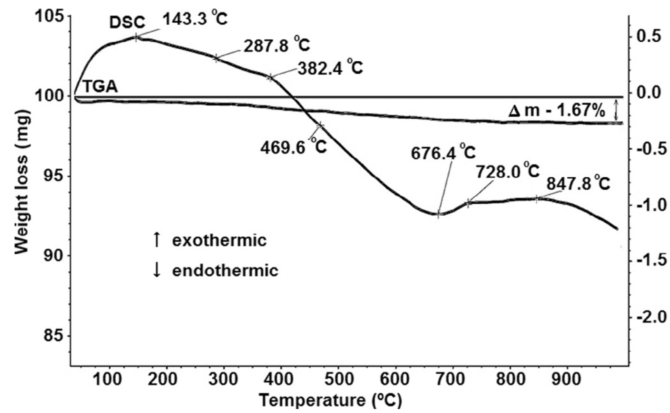


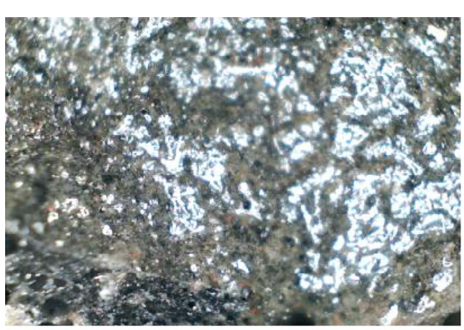
Fig. 7. TG, DTG curves of heating the frit, obtained at 900 °C.

The foaming mixture was prepared from milled frit (specific surface area of 500 cm^2/kg) by mixing with gas-forming agent in the amount of 0.5 wt. Carbon black with a specific surface area of 16 000 m^2/kg and a bulk density of 320 kg/m^3 was used as a foaming agent. Granulation was performed on a pan granulator, using a 15% solution of sodium silicate as a binder. The resulting granules were dried in air and foamed at temperatures of 800–900 °C.

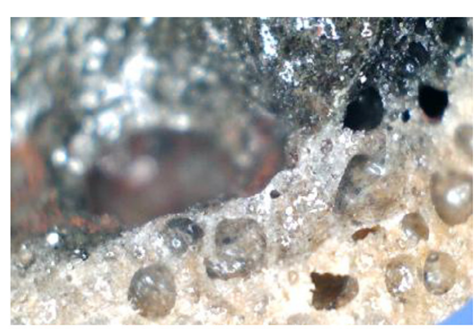
It was found that frit synthesised at 800 °C, regardless of the sufficient amount of the glass phase, does not yield quality porous material. Melt of this composition is highly viscous due to the significant amount of the crystalline phase, at 25%. Samples of foam material were collected from frit, at a temperature of 800 °C, their structure being indicated in Fig. 6. Foaming granules from this type of frit leads to a porous structure only on the surface layer, whereas within the granule the material is monolithic. Consequently, further studies were conducted with frit synthesised at a temperature of 900 °C. The thermogram of this frit did not display any clearly expressed exothermic effects, which indicates that crystallisation processes are absent (Fig. 7). The endothermic effect at 674 °C corresponds to the frit melting point. The weight loss associated with the allocation of the remaining CO_2 does not exceed 2%, which indicates that the silicate formation processes are sufficiently complete at the first stage of the frit synthesis.

The quantity of the crystalline phase in the finished foam product will depend on the foaming temperature and the exposure. As mentioned before, the crystalline phase of frit is reflected in the existence of residual quartz and albite and with a reduced amount of foaming material, from 18 to 10% minimum (900 °C, 10 minutes) (Table 2). The temperature regime in foaming also affects the formation of the material's porous structure. With a relatively high foaming point of 900 °C the structure is not homogeneous and the average pore size tends to increase to 4 mm. A homogeneous structure cannot be created at a foaming temperature of 800 °C. Samples obtained at a foaming temperature of 850 °C with an exposure of 10–15 minutes were found to have a high degree of homogeneity in their pore structure. The macrostructure of samples is illustrated in Fig. 8.

Depending on the amount of the crystalline phase and its composition, the chemical composition of the glass phase will also change, affecting its viscosity. The calculation of the foaming temperature for the melt, corresponding to viscosity $Lg(\eta) = 6$ indicates that, in the case of frits not including a crystalline phase, the melt viscosity temperature can have a maximum value of 875 °C. With the increase in the volume of crystalline phase in the overall amount of glass mass the temperature, corresponding to viscosity of $Lg(\eta) = 6$, tends to drop to 855 °C (Fig. 9). This temperature corresponds to the frit glass phase, synthesised at 900 °C.



a



b

Fig. 6. The macrostructure of the material obtained from frit (by synthesis at 800 °C), following foaming, at a temperature of 900 °C for 15 minutes: (a) particle centre, (b) particle periphery.

Table 2
The amount of crystalline phase in foam material samples, obtained at different foaming temperatures and their macrostructural features.

Foaming mode		Volume of crystalline phase, %	Average pore size in mm	Uniformity of dispersion of pores in the volume
Temperature, °C	Foaming time, min			
850	5	16	0.5	Uniform
	10	15	1.0	Uniform
	15	12	2.0	Uniform
900	5	15	3.0	Non-uniform
	10	10	4.0	Non-uniform

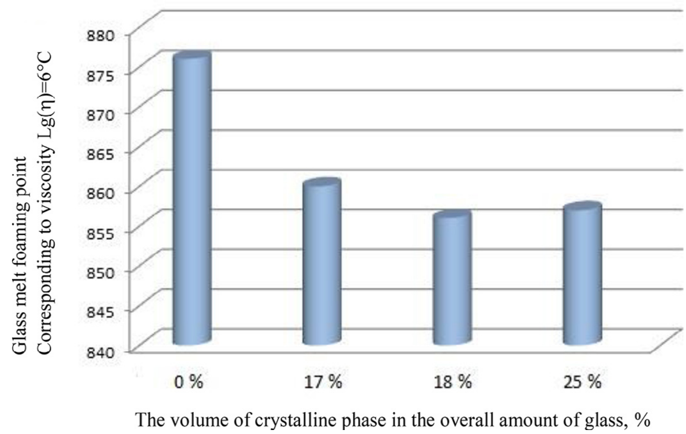


Fig. 9. Dependence of foaming temperature of the glass phase melt, with viscosity of Lg(η) = 6 on the volume of residual crystalline phase in the frit.

Physical and mechanical properties of finished samples obtained from low-temperature frit also depend on the foaming regime (Table 3). With the increase in foaming temperature from 800 to 900 °C the average density of the material is reduced from 650 to 250 kg/mm^3. At low foaming temperatures the granulated material corresponds to heavy expanded clay. Furthermore, the foam material has low water saturation (less than 1%) compared to expanded clay. At foaming temperature of 850 °C the foaming material has a similar density to that of foam glass obtained from glass waste. At high foaming temperatures (900 °C) the material becomes very similar to foamed glass, however with a porous structure, which affects its rigidity. The most rigid proved to be the samples obtained at 850 °C (exposure 10 minutes), which exceed the rigidity of foamed glass, allowing the resulting material to be used in construction and thermal insulation.

So the best foaming regime is based on a temperature of 850 ºC and exposure of 10 minutes. In this mode, the samples have the microstructure shown in Fig. 10. With a magnification of fifty thousand times, we can see that along the major pores that are 0.5 mm, the interpore partition has very small pores of less than 0.01 mm. In the interpore partition of the finished material, crystalline phase particles can be seen, measuring less than 2 µm (Fig. 10b). Based on the results of X-ray diffractional analysis, the composition of crystalline phase particles includes oxides, in % of the vol.: SiO_2: 53; Na_2O: 20; Al_2O_3: 11; CaO: 4; K_2O: 2; Fe_2O_3: 7; MgO: 3. This composition corresponds to the composition of solid albite solution, which was also confirmed by X-ray diffraction analysis.

4. Conclusions

This paper proposes a method for the processing of nonferrous metal waste in the production of foamed glass. We determined the composition of batch, from quartzofeldspathic waste and by synthesising frit at low-temperature. The technology for the production of frit without complete melting of the batch and without using glass-making units, offers a considerable reduction in energy consumption and air pollution. At a temperature of 850 °C granulated foam was obtained from frit, with a volume density of 194–224 kg/mm^3. In contrast to conventional foamed glass, this material is highly rigid (1.7 MPa compared to 1 MPa). Material with a density of 300 kg/cm^3 is recommended for thermal insulation for the industrial and construction sectors. At densities above 300 kg/cm^3 and a strength of 2.5 MPa, the purpose becomes heat-insulating construction material. As far as basic properties are concerned, the material meets the requirements for an effective porous filler. As a result of the conducted studies, we propose this resource and energy efficient method of using waste from beneficiation of

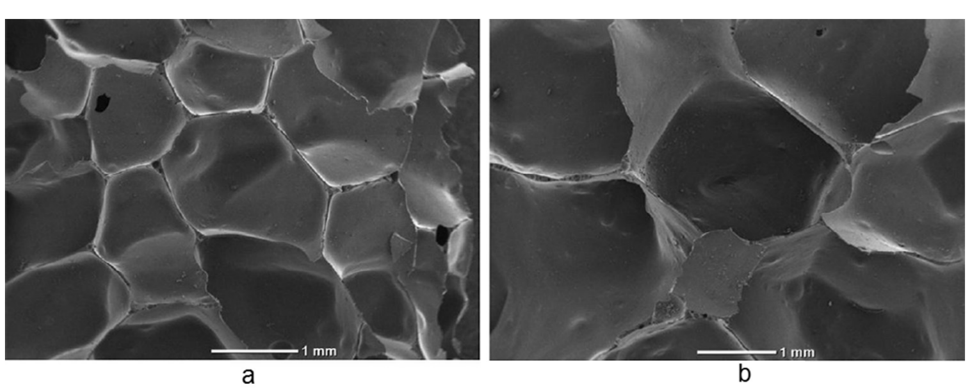
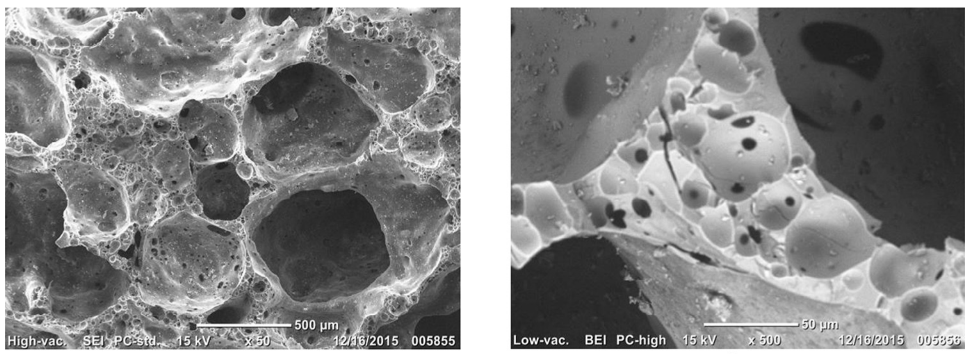


Fig. 8. The macrostructure of the samples, obtained at a foaming temperature of 850 °C with an exposure of (×50): (a) 10 min; (b) 15 min.

Table 3
The main physical and mechanical characteristics of the produced material.

Foaming regime		Max. compressive strength, MPa	Density, kg/m^3		Thermal conductivity, $W/(m \cdot K)$	Water absorption, %
Temperature, °C	Exposure, min		Average	Bulk		
800	10	6.6	650	398	0.123	0.2
800	15	4.5	500	294	0.091	0.2
850	5	3.5	380	224	0.087	0.7
850	10	3.0	350	206	0.085	0.8
850	15	2.8	330	194	0.083	0.9
900	5	2.2	299	176	0.080	0.9
900	10	1.7	250	147	0.070	0.9



a b

Fig. 10. SEM micrographs and EDAX analysis of samples (foaming temperature of 850 °C, 10 min): (a) porous structure; (b) partition structure.

copper–zinc ore, further extending the choice of raw materials for foam glass materials.

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