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Investigation of the Influence of Foaming Agents' Type and Ratio on the Foaming and Reactionary Abilities of Foamed Slag Glass

Elena Alfredovna Yatsenko, Boris Mikhailovich Goltsman, Victoria Aleksandrovna Smoliy, Andrey Sergeevich Kosarev and Roman Vladimirovich Bezuglov

Platov South-Russian State Polytechnic University (NPI), Russian Federation, 346428, Novocherkassk, Prosvescheniya Street, 132.

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Compositions of the foam glass based on thermal power plant's slag waste – foamed slag glass – have been developed. The most widespread foaming agents - anthracite, chalk, glycerol, graphite – have been chosen on the basis of published data. Synthesis of the samples at various temperatures has been conducted. Structure and properties of the obtained samples has been determined, the relationship between the type and amount of introduced foaming agents and changes in the structure and properties of the samples have been established. The best type of foaming agent for the synthesis of foamed slag glass has been selected.

Key words: Slag waste, Thermal insulation, Foam glass, Foaming agents.

Energy efficiency of buildings - current situation

The problem of over-consumption of natural energy resources is primarily connected with large heat losses when heating buildings due to the low thermal insulation properties of building materials used. Thus, it is necessary to use high-quality thermal insulating materials to minimize heat loss through the building envelope in civil and industrial construction, as well as in heat transportation systems.

The most widespread insulating materials nowadays are different organic polymer materials (polystyrene foam, polyurethane foam, products based on it), which have several advantages: low price, good insulating properties, low density. However, these materials also have some significant drawbacks - extreme flammability, emission of smoke and toxic compounds when burning, impossibility of utilization, low chemical resistance and service life, etc.

Thus, the search for effective environmentally safe incombustible thermal insulating materials is very important.

Foam glass - basic characteristics

Currently, one of the most promising thermal insulating materials is foam glass - cellular glass with foam structure. As a consequence of structure and composition, it has all advantages of glass: zero moisture- and vapor-permeability, complete fire safety, dimensional stability at high temperatures, resistance to rodents, insects and bacteria, ease of installation works, environmental friendliness, and many others. The service life of foam glass is virtually unlimited, and the physical properties do not change over time, as in conventional glass products. The main disadvantage of foam glass is its high price associated with the use of glass cullet as the main raw material. Studies on the replacement of glass to other materials are conducted all over the world,

* To whom all correspondence should be addressed.

and special attention is paid to various industrial wastes. Research works in this field are dedicated to the use of metallurgical slag[1-3], waste glass[4-7], coal combustion products[8-10] and even reservoir sediments[11].

Slag waste as the main raw material

The environmental deterioration in the modern world is one of the most urgent problems of mankind. This deterioration is due both thoughtless pollution by various domestic and industrial waste and excessive consumption of natural resources.

One of the most large-scale types of waste is waste of thermal power plants (TPP) which produce heat by coal combustion. Coal combustion by-products include a range of materials, the main of which is the slag - inorganic impurities in coal, which melt during combustion process and form a glassy material. Depending on coal combustion method, slag represents from 50 to 85% of all TPP waste[12].

The problem of waste management is particularly relevant for countries and regions with developed coal mining and processing industry. The overall ratio of waste generation and recycling in the Russian Federation is presented in Figure 1. And Novocherkassk State District Power Plant (NSDPP), the coal TPP that produces more than 90% of the Russian Southern Federal District's electricity, could be a good particular example. The volume of NSDPP's dumps for storing of produced waste is more than 40 million tons on the area of 250 hectares, and 0.8-1 million tons is produced annually.

The figure shows that the volume of slag recycling does not exceed 10%, and its main part is used as a filler in road construction. At the same time in USA this indicator is about 45%[13], and the leading slag application is blasting grit/roofing granules[14].

It should be noted that slag waste is an excellent secondary raw material that passed through primary heat treatment, and has stable chemical and mineralogical composition. The use of TPP slag waste in the production of glass materials is also justified by its amorphous structure, which is due to the principle of slag generation. When coal burns, refractory inorganic impurities are flowing under boiler (combustion chamber) as a melt, where sharply cooled to obtain glassy structure. The results of X-ray analysis of TPP slag is presented in Figure 2.

In this regard, we have developed the technology for producing foam glass with partial replacement of the initial glass cullet on the TPP slag waste to obtain *foamed slag glass*[15-16]. Number of optimal compositions has been established, and materials for constructive-insulating and insulating applications have been obtained on its basis. Amount of used slag was from 20 to 50 wt.%.

Influence of foaming agents on the structure and properties of foam glass

According to published data[17-19], traditional foaming agents in foam glass technologies are divided into two groups: carbon and carbonate. Carbon foaming agents include graphite, anthracite, soot, and other carbon-based materials. Furthermore, some organic compounds can be used as carbon agents. Pore formation during synthesis occurs due to the oxidation (combustion) of carbon according to the reaction (1). Resulting gas foams the material.

$$C + O_2 \rightarrow CO_2\uparrow \quad ...(1)$$

Carbonate foaming agents are most commonly presented by limestone and chalk, as the cheapest of carbonates. Other carbonate materials such as marble or even dolomite could also be used as carbonate foaming agents. Pore formation during synthesis occurs due to the gas generated by the thermal decomposition of carbonates according to the reaction (2).

$$CaCO_3 \rightarrow CaO + CO_2\uparrow \quad ...(2)$$

The use of various foaming agents leads to a different structure of the resulting material. So, for example, carbonate foaming agents lead to channel-like pores which give additional sound insulating properties to the material. However, no data related to the joint use of different foaming agents were found.

Thus, the aim of the research work is to study the influence of the foaming agents' type and amount on the structure and properties of foamed slag glass.

METHODS

Production of foamed slag glass samples was performed by standard powder method. Main materials (glass cullet, TPP slag waste, solid foaming agents) were first dried at 120 °C for further processing. The obtained dry materials were milled into powders passed through a No. 40 mesh [20]. The chemical composition of slag and glass was measured using an energy dispersive X-ray fluorescence spectrometer (ARLQUANT'X) and is represented in Table 1. Then, batches were made according to the established composition, wt.%: glass cullet - 70, slag waste - 20, composition of foaming agents - 10.

Then samples from prepared batches with additional two percent moistening were molded in cubes with edge length of 20 mm and weight of 10 g. Molded cubes were loaded into the furnace for heat treatment according to Figure 3.

When the air inside the furnace cooled to room temperature, the samples were removed from

Fig. 1. The ratio of generation and recycling of slag waste in the Russian Federation.

the furnace and passed through the mechanical treatment to obtain the straight parallelepiped form of samples. Then the mass of samples with specified shape was determined, and calculations of samples' volume, density and coefficients of foaming and porization were performed according to formulas (3) - (6), respectively. Then the obtained samples were sawed in half to determine its internal structure. Determination was carried out by optical microscopy using a monocular microscope Bresser Duolux.

Volume; $V = a \cdot b \cdot c$ ...(3)

Density; $D = M / V$ ...(4)

Coefficient of Foaming; $CF^T = V_R^T / V_I$ ...(5)

Coefficient of Porization; $CP^T = D_I / D_R^T$ ...(6)

where a – sample's length, cm; b – sample's width, cm; c – sample's height, cm; V – sample's volume, cm^3; M – sample's mass, g; V_R^T – sample's resulting volume after heat treatment at foaming temperature T, cm^3; V_I – sample's initial volume before heat treatment, 8 cm^3; D_I – sample's initial density before heat treatment, $D_I = Mm_I / V_I = 10 \cdot 10^{-3} / 8 \cdot 10^{-6} = 1250$ kg/m^3; D_R^T – sample's resulting density after heat treatment at foaming temperature T, kg/m^3.

Each recorded testing value was the mean of the results from five samples.

RESULTS

Synthesis of samples

According to the published data[17, 21], following foaming agents were selected for research work: anthracite, chalk, glycerol, graphite. It should be noted that among the chosen materials only one relates to the carbonate, and the others -

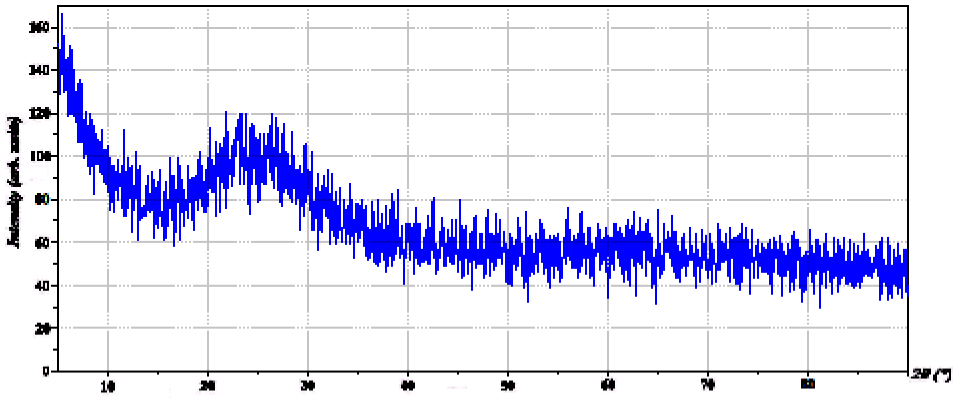
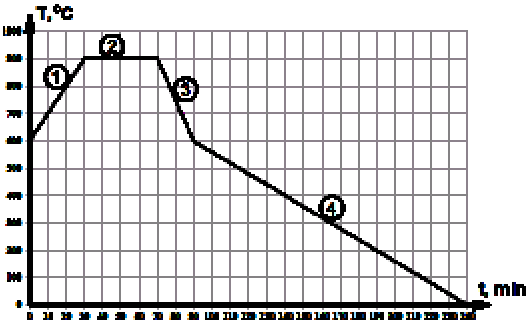


Fig. 2. XRD pattern of slag waste

to the carbon foaming agents. It can be explained primarily by the fact that the most common foaming agent in the production of industrial foam glass is anthracite - amorphous coal rock with carbon content of 92-98%. At the same time graphite is pure crystalline carbon. So, the compositions with mixtures of graphite and anthracite were not developed. Thus, the study will allow to determine the effect of not only chemical but also phase composition of foaming agents on the structure of foamed slag glass.

Glycerol, despite belonging to the carbon foaming agents by mechanism of action, has more complex structure, other aggregate state (liquid), physical and chemical properties, etc. So it can be attributed to a separate group of organic foaming agents. However, pure glycerol evaporates virtually



1 - heating, 2 - foaming 3 – rapid cooling with structure stabilization – quenching, 4 - slow cooling - annealing.
Fig. 3. Foamed slag glass synthetic schedule:

immediately after sample loaded into the furnace with the formation of densely sintered glassy sample. Therefore, sodium water glass, which forms eutectics at 700-900 °C that allows to stabilize structure of the material, was introduced in the foaming glycerol-based composition. Mixture “glycerol : water glass = 1 : 1”, hereinafter called “glycerol compound”, was used as foaming agent.

Single, double and triple mixtures with equal ratios of foaming agents in each mixture were developed for qualitative analysis of the influence of foaming components’ ratio on the properties of resulting material. Table 2 shows all developed compositions of foaming mixtures.

Further, five samples of each developed compositions were heat treated according to temperature-time modes (Figure 3) at a foaming temperature of 850, 875, 900, 925 °C. The internal structure of the obtained samples is given in Figure 4.

The influence of foaming agents on foaming ability

Estimation of the influence of foaming agents’ type and amount on the foaming ability was carried out using the coefficient of foaming (CF) - a parameter indicating an increase in volume of the sample after heat treatment. Coefficient of foaming was determined according to the formula (5) based on the mean volume values obtained in each series of samples and is represented in Table 3.

Table 3 clearly shows that the best type of foaming agent is glycerol compound, which

Table 1. Chemical composition of raw materials.

Material	Chemical composition*, wt.%						
	SiO_2	Al_2O_3	Fe_2O_3	CàO	MgO	K_2O	Na_2O
Slag	57.5	23.0	10.8	1.9	1.2	3.6	0.9
Glass	71.2	2.70	0.8	3.4	7.6	0.8	13.2

* Oxides content of which is less than 0.2 wt.% are not shown.

Table 2. Compositions of mixtures of foaming agents

Foaming agent	Amount of foaming agent, %, in the foaming composition, #										
	1	2	3	4	5	6	7	8	9	10	11
Anthracite	100	-	-	-	33	-	50	50	-	-	-
Chalk	-	100	-	-	33	33	50	-	50	50	-
Glycerol compound	-	-	100	-	33	33	-	50	50	-	50
Graphite	-	-	-	100	-	33	-	-	-	50	50

allows to obtain samples with CF = 5...6, i.e. increase in sample's volume after heat treatment is 5-6 times. Samples based on graphite foaming agent demonstrate the worst foaming ability (CF ≈ 1), i.e. samples did not increase in volume at all.

The influence of foaming agents on reactionary ability

Various foaming agents lead to the formation of different types of porosity. Consequently, it is impossible to establish the

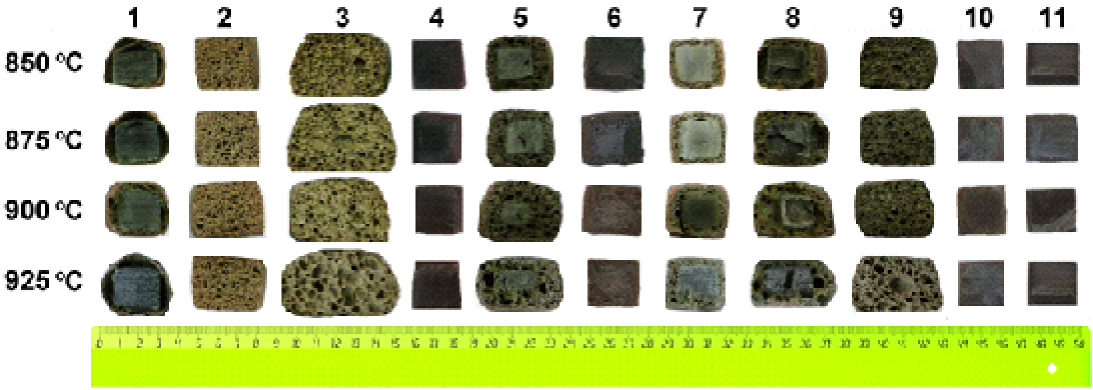


Fig. 4. Internal structure of the samples

Table 3. Mean volume and Coefficient of Foaming (CF) of compositions 1-11

# of composition	Mean volume of samples, cm³				Coefficient of Foaming (CF)			
	V_R^{850}	V_R^{875}	V_R^{900}	V_R^{925}	CF^{850}	CF^{875}	CF^{900}	CF^{925}
1	11,28	11,29	11,11	11,04	1,41	1,41	1,39	1,38
2	14,38	14,28	12,30	14,20	1,80	1,78	1,54	1,77
3	43,21	48,38	40,01	33,97	5,40	6,05	5,00	4,25
4	7,60	7,80	7,41	6,84	0,95	0,98	0,93	0,85
5	15,74	18,37	18,50	13,86	1,97	2,30	2,31	1,73
6	9,17	10,27	9,68	8,02	1,15	1,28	1,21	1,00
7	11,11	11,58	11,29	9,20	1,39	1,45	1,41	1,15
8	17,64	22,95	21,96	17,78	2,21	2,87	2,75	2,22
9	20,23	21,14	18,82	16,10	2,53	2,64	2,35	2,01
10	7,07	7,60	7,22	6,60	0,88	0,95	0,90	0,83
11	7,98	7,34	7,77	6,40	1,00	0,92	0,97	0,80

Table 4. Mean density and coefficient of porization (CP) of compositions 1-11

# of composition	Mean density of samples, kg/m³				Coefficient of porization (CP)			
	D_R^{850}	D_R^{875}	D_R^{900}	D_R^{925}	CP^{850}	CP^{875}	CP^{900}	CP^{925}
1	798	818	791	838	1,57	1,53	1,58	1,49
2	688	657	705	667	1,82	1,90	1,77	1,87
3	227	202	226	179	5,52	6,18	5,54	6,98
4	1249	1226	1228	1274	1,00	1,02	1,02	0,98
5	612	537	518	533	2,04	2,33	2,41	2,35
6	1002	914	927	899	1,25	1,37	1,35	1,39
7	850	843	879	937	1,47	1,48	1,42	1,33
8	530	434	417	425	2,36	2,88	2,99	2,94
9	482	453	494	506	2,59	2,76	2,53	2,47
10	1404	1291	1293	1264	0,89	0,97	0,97	0,99
11	1234	1292	1206	1288	1,01	0,97	1,04	0,97

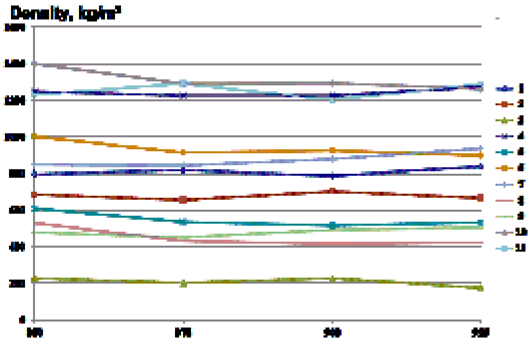


Fig. 5. The dependence of density on the foaming mixture's composition

quantitative and qualitative characteristics of porosity of materials developed on the basis of mixtures of different foaming agents. This factor also complicates determination of reactionary ability, i.e. area of unreacted zones and quality of reacted zones of the sample by boiling method.

Thus, the evaluation of the influence of foaming agents' type and amount on the reactionary ability of the material was determined based on two parameters:

- Determination of reaction completeness, i.e. determination of the presence of unreacted zones in the bulk of the sintered material, which can be seen by the results of the internal structure determination in Figure 4;
- Coefficient of reactionary ability – coefficient of porization (CP), which shows sample's density decrease after heat treatment due to the reactions of pore formation. Investigation included determination of density before and after treatment according to formula (3). Then coefficients of porization were calculated according to formula (6) based on the mean density values obtained in each series of samples. The results of determinations are shown in Table 4 and Figure 5.

The resulting density curves can be clearly divided into 4 groups:

1) density of more than 1000 kg/m^3;
2) density in the range of 700-1000 kg/m^3;
3) density in the range of 400-700 kg/m^3;
4) density of less than 400 kg/m^3.

Group 1 samples (compositions 4, 10, 11) comprise from 5 to 10 wt. % of graphite. Samples show almost complete absence of foaming processes with formation of densely sintered material (Figure 4) with density of about 1200 kg/m^3.

Group 2 samples also contain graphite (composition 6). In addition, this Group includes samples based on anthracite (composition 1, 7), which, despite better indicators of pore formation (700-800 kg/m^3) than graphite (1200-1300 kg/m^3), forms similar densely sintered core during heat treatment, that significantly increases samples' density and degrades the insulation properties.

Compositions with chalk as a main foaming agent (compositions 2, 5, 9) predominate in Group 3. Obviously, chalk is better, than graphite and anthracite, foaming agent which forms a homogeneous and defect-free structure, but the size and distribution of pores cause insufficient density level.

Finally, Group 4 includes only composition 3, wherein the foaming process is performed entirely by glycerol compound. Samples based on it have the best structure with uniformly distributed pores of approximately equal size, without defects and inhomogeneities.

Table 4 shows that the composition 3 on the basis of glycerol compound has the best performance in terms of reactionary ability. Coefficient of porization CP of this composition is 5.5 ... 7, that corresponds to approximately sixfold reduction in density. The above analysis of structure indicates no unreacted zones in these samples, and the structure formed during heat treatment has an extremely high stability.

DISCUSSION

Performed experiments allow to arrange foaming agents in ascending order of activity: graphite → anthracite → chalk → glycerol compound. Thus both graphite- and anthracite-based samples show almost complete absence of the porous structure that caused density of more than 1200 and 800 kg/m^3, respectively, and coefficients of foaming and porization are equal to 1. This complex of parameters makes these foaming agents unsuitable for the developed technology. Chalk showed average results of foaming. Samples with its use have densities of about 500 kg/m^3, which is still insufficient indicator. Further, the size and distribution of pores that led to CF and CP of less than 2, also does not satisfied the requirements. Best foaming composition is glycerol compound. Samples with its use have densities of about 200 kg/m^3, coefficients of foaming and porization of about 5...7 and large uniformly distributed pores, which is a sign of good insulation properties.

Direct correlation between reactionary ability of foaming agents and its decomposition temperature has been noted. Thus, the combustion temperature of graphite in the air is about 1000 °C. Anthracite burns at 700-750 °C, and glycerol - at 290 °C. Therefore, it can be assumed that the low reactionary ability of graphite and anthracite can be enhanced by the introduction of flux materials, which reduce the melting point of the mass and accelerate the foaming process.

The only exception from this dependence is chalk with decomposition temperature of 900-1000 °C. However, its reactionary ability is higher than both graphite and anthracite. It can be explained by the fact that thermal decomposition is only one of the processes occurring in the mass of foamed slag glass during heating. In addition, there are reactions between the components of the batch, where chalk acts as fluxing agent of second type, i.e. a material having high melting point, but forming easily fusible compounds with components of the batch[21]. Therefore, reaction (2) is more correctly expressed as the reaction (7):

$$CaCO_3 + SiO_2 = CaSiO_3 + CO_2\uparrow \qquad ...(7)$$

The density and structure uniformity of the material is directly related to the type and amount of introduced foaming components. Introduction of anthracite and graphite steadily results in the formation of densely sintered core. Moreover, the greater the amount of foaming agent has been introduced, the greater the volume of core has been formed. Thus, reduced density of compositions 5, 6 is due to low (3.33 wt.%) amount of anthracite and graphite, respectively. Thereby it became possible to assign these compositions to the groups of lower density.

It can also be assumed that the best indicators of samples based on glycerol compound are due to its liquid state. That is why it became possible to form uniformly distributed droplets (without additional grinding) which promote homogenization of the structure.

CONCLUSION

TPP slag waste can be used as a partial replacement of glass in the production of foam glass to obtain foamed slag glass. Carbonate (chalk), inorganic carbon (graphite, anthracite) and organic (glycerol) materials have been used as foaming agents. The influence of the type and amount of introduced foaming agents on the structure of the material has been established. Direct relationship between the foaming and reactionary ability of foaming agents and their decomposition temperature has also been identified. The optimum foaming agent to create foamed slag glass is glycerol compound, which provides the best structure and properties of the samples. Established dependences allow to proceed to the industrial tests of obtained materials and its commercialization.

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