Ash-and-Slag-Waste-based Porous Glass: Synthesis and Properties

I.S. Grushko

Abstract. In recent years, porous glass (sponge-glass) is becoming increasingly popular as an environmentally and hygienically safe non-flammable insulating material in the construction of civil and industrial buildings and structures. Composite materials with sponge-glass can be used for exterior insulation and facade finish. These materials are characterized by sufficiently high insulating effect, mechanical strength and chemical durability in combination with low cost of their production. Ash and slag waste from thermal power plants can be used as one of the main raw materials for the production of sponge-glass for construction purposes. The paper presents the results of research on the development and study of the properties of porous glass on the basis of ash and slag wastes of the Novotcherkasskaya GRES and bottled glass scrap: various compositions of the furnace charge have been synthesized, the influence of the fluxing agent and blowing agent on the functional properties of porous glass (density, porosity, strength and heat conduction) has been studied. Crystalline borax was used as the fluxing agent, and anthracite as the foaming agent. Standard methods were used for the study: electron microscopy methods, measurements of heat fluxes (tests were carried out in two modes: cooling and heating), determination of apparent density, etc., qualified equipment. The following was established in the course of study: the porosity of porous glass samples increases by more than two times with an increase in the anthracite additive; with an increase in the anthracite additive the strength of the porous glass decreases by more than 1.5 times; the optimal composition of the furnace charge, taking into account the effect of anthracite on the most important properties of the synthesized porous glass, is SHPS-B5 composition, which provides a sufficiently high porosity of 37.7% and a density of 466.8 kg/m³.

1. Introduction

In recent years the porous glass (foam glass) spread more and more due to its being used as an ecologically and hygienically safe incombustible heat-insulating material for building civil and industrial facilities. Composite materials with applied foam glass can be used for outer insulation and furnishing of buildings facades [1]. These materials are characterized by a pretty high heat-insulating ability, mechanical and chemical durability combined with a low manufacturing price. As one of the main raw components of foam glass manufacturing, ash and slag waste of TPSs can be used [2]. Using ash and slag waste could not only decrease foam glass based construction materials costs, but also move forward a solution of the ecological problem of utilizing big amounts of ash and slag waste which is accumulated around thermal power stations (TPS). That’s why it’s the current aim to develop a technology of foam glass manufacturing with ash and slag waste of the TPSs used as a raw material [3].
2. Results and discussion
Following parameters have a key value for the ash and slag foam glass being used as a heat-insulating material: apparent density (hereafter density), real porosity, thermal conductivity and compressive strength. For investigating the dependence of amount of the above pore former parameters, the following investigations were performed [4]:
- compositions with different anthracite and borax proportions were received based on an optimal composition of waste foam glass;
- values of density and porosity of received samples were estimated;
- results of the heat conductivity coefficient estimation and compressive strength of the test foam glass samples were received.

For solving the tasks set, following compositions for synthesizing of the waste glass based on charges with borax proportions from 1 to 7% were developed (table 1). All samples were synthesized by a temperature of 825 °C.

Table 1. Waste porous glass charges composition

| Composition No. | Proportions of components, % |
|-----------------|------------------------------|
|                 | Waste | Cullet | Borax* | Anthracite* |
| PCG-A1          | 30    | 70     | 1      | 5           |
| PCG-A2          | 30    | 70     | 2      | 5           |
| PCG-A3          | 30    | 70     | 3      | 5           |
| PCG-A4          | 30    | 70     | 4      | 5           |
| PCG-A5          | 30    | 70     | 5      | 5           |
| PCG-A6          | 30    | 70     | 6      | 5           |
| PCG-A7          | 30    | 70     | 7      | 5           |

* components’ proportion shown over 100% of charge

A visual inspection of the synthesized samples was made. Samples PCG-A1, PCG-A2, PCG-A3, PCG-A4 had clear geometrical edges, the lengthwise cut had a high density, almost no pores seemed to exist. Samples PCG-A5, PCG-A6, PCG-A7 weighed less, the lengthwise cut showed evenly located pores.

Considering the results, the other equal parameters and a rational use of raw materials (especially borax), the composition PCG-A5 was claimed as an optimal one.

Researches were performed on the effect of borax as both a melter and a foaming agent. Results of the investigation showed that under its composition of 5%, borax conditions high melting of the waste porous glass, which consequently can not provide the porous glass synthesis, which will be shown further. This is a convincing argument of lack of pores emergence while using borax. That’s why the further waste porous glass synthesis was performed by using anthracite only as a pore blowing agent and borax as a melter. According to these conclusions, waste porous glass compositions with different proportions of anthracite were developed, which are shown in the table 2.

Results of the porous glass synthesized samples microstructure research allow us to conclude the following: sample PCG-B1 (figure 1) has a dense structure, spherical pores. Number of pores is quite small relatively to the volume of the sample. Sample PCG-B2 (figure 2) also has a dense structure, pores have a bigger size compared to PCG-B1, but their number is also insufficient. Interporal partitions are dense. Sample PCG-B3 (figure 3) has a heterogeneous porosity, pores allocation isn’t even. Samples PCG-B4 and PCG-B5 (figures 4, 5) have a pretty homogenous structure, pores are closed and isolated from each other, even porosity. Samples PCG-B6 and PCG-B7 (figures 6, 7) have large closed and also connected spherical pores, interporal partitions are thin and can’t stand constructional loads. Increasing the anthracite proportion leads to an increase of pores’ size and its number, which should provide higher heat insulating properties of the synthesized material. The greatest interest according to results of the microscopic researches represent the samples PCG-B4 and PCG-B5.
Table 2. Waste porous glass charges composition (PCG)

| Waste porous glass charges composition | Proportions of components, % |
|----------------------------------------|------------------------------|
| PCG-B1                                 | Waste 30 | Cullet 70 | Borax* 5 | Anthracite* 1 |
| PCG-B2                                 | Waste 30 | Cullet 70 | Borax* 5 | Anthracite* 2 |
| PCG-B3                                 | Waste 30 | Cullet 70 | Borax* 5 | Anthracite* 3 |
| PCG-B4                                 | Waste 30 | Cullet 70 | Borax* 5 | Anthracite* 4 |
| PCG-B5                                 | Waste 30 | Cullet 70 | Borax* 5 | Anthracite* 5 |
| PCG-B6                                 | Waste 30 | Cullet 70 | Borax* 5 | Anthracite* 6 |
| PCG-B7                                 | Waste 30 | Cullet 70 | Borax* 5 | Anthracite* 7 |

* component’s proportion shown over 100% of charge

The microstructure of synthesized porous glasses is shown in pictures 1 – 7 (a- is an increase of 20X, b - is an increase of 540X).

![Figure 1](image1.png) ![Figure 2](image2.png)

**Figure 1.** Microstructure of the sample SHPS-B1

![Figure 3](image3.png) ![Figure 4](image4.png)

**Figure 2.** Microstructure of the sample SHPS-B2
Figure 3. Microstructure of the sample SHPS-B3

Figure 4. Microstructure of the sample SHPS-B4

Figure 5. Microstructure of the sample SHPS-B5
The synthesized glass properties research was also performed based on charges with anthracite proportions of 1-7% in the charges composition presented in the table 2. The results of calculations are presented in table 3.

The true porosity of the material is considered to be the degree of filling its volume with pores. Its value can be calculated with a following formula [5]:

\[ P = (1 - \rho_k/\rho_t)*100 \]  \hspace{1cm} (1)

where \( P \) is the true porosity, %;
\( \rho_k \) – material’s density, kg/ m³;
\( \rho_t \) – true material’s density, kg/ m³.

Density of the samples is calculated considering the GOST R EN 1602-2008 «Heat-insulating products, used in construction sphere. Method of estimating the “apparent density” according to the formula [5]:

\[ \rho_k = \frac{m}{V} \]  \hspace{1cm} (2)

where \( m \) is the mass of the materials, kg;
\( V \) – the volume of the material, pores and empty space included, m³.
Due to the fact that the quality of synthesized porous glass, characterized by its heat-insulating properties determined by the heat conductivity, we launched several researches on the subject of complex borax and anthracite proportions in the samples PCG-B1, PCG-B2, PCG-B3, PCG-B4 and PCG-B5.

For estimating the dependence of materials’ density and porosity on its heat-insulating properties, the synthesized samples [6] were investigated on the subject of heat conductivity.

**Table 3.** Results of density, porosity and compressive strength of the waste porous glass estimating.

| Name  | Density, kg/m³ | Porosity, % | Compressive strength, H/m² |
|-------|----------------|-------------|---------------------------|
| PCG-B1| 579            | 24.7        | 2.48                      |
|       | 573            | 26.0        | 2.44                      |
|       | 577            | 25.4        | 2.45                      |
|       | 579            | 24.7        | 2.48                      |
|       | 571            | 25.1        | 2.46                      |
| PCG-B2| 537            | 31.9        | 2.36                      |
|       | 526            | 33.1        | 2.31                      |
|       | 532            | 32.5        | 2.35                      |
|       | 539            | 31.0        | 2.38                      |
|       | 537            | 31.9        | 2.36                      |
| PCG-B3| 509            | 37.1        | 2.23                      |
|       | 521            | 36.0        | 2.26                      |
|       | 516            | 36.5        | 2.25                      |
|       | 521            | 36.0        | 2.26                      |
|       | 529            | 35.7        | 2.27                      |
| PCG-B4| 491            | 38.0        | 2.19                      |
|       | 497            | 37.7        | 2.21                      |
|       | 497            | 37.7        | 2.21                      |
|       | 504            | 37.3        | 2.22                      |
|       | 512            | 37.2        | 2.23                      |
| PCG-B5| 475            | 37.1        | 2.20                      |
|       | 463            | 38.0        | 2.17                      |
|       | 463            | 38.0        | 2.17                      |
|       | 470            | 37.5        | 2.18                      |
|       | 463            | 38.0        | 2.17                      |
| PCG-B6| 441            | 44.7        | 1.75                      |
|       | 417            | 46.9        | 1.70                      |
|       | 435            | 45.2        | 1.74                      |
|       | 429            | 46.4        | 1.73                      |
|       | 435            | 45.2        | 1.74                      |
| PCG-B7| 410            | 48.9        | 1.15                      |
|       | 401            | 49.7        | 1.13                      |
|       | 410            | 48.9        | 1.15                      |
|       | 414            | 47.4        | 1.16                      |
|       | 392            | 54.0        | 1.07                      |
For measuring the heat fluxes conducted through the samples we used the method of measuring the density of heat flows passing through the enclosing structures. Such a method allows to estimate the heat-technical properties of enclosing structures’ and construction material properly, and also to estimate the real heat losses through the external enclosing structures.

This work required a heat flow and temperature density measurer ITP-MG4.03/5(I) «Potok», № 1210, adequate with TC 7648-027-12585810-2008. Heat flow converter № 5191 with a converting coefficient of $K=26.94 \text{ W/(m}^2 \times \text{mW})$, sensors type – diameter of 27 mm, mode - observation.

For maintaining the needed temperature and humidity modes during the research, a climatic cell SM – 60/75-250 TVX was used.

Five waste porous glass samples with a different anthracite proportion were involved into the research, each of them had a porous structure. The research was performed in two modes: «cooling» and «heating» till -30°C and +50°C were reached, according to the requirements of the GOST 25380-82 «Method of measuring the density of heat flows passing through enclosing structures». Each sample had a thickness of 10 mm. Received data is presented below in the table 4.

**Table 4.** Results of the waste porous glass samples heat conductivity estimation.

| SampleNo. | Mode          | $q$, W/m² | $t_a$, °C | $t_n$, °C | $\lambda$, W/(m·°C) |
|-----------|---------------|-----------|-----------|-----------|----------------------|
|           | heating 50°C  | 80.6      | 32.6      | 38.1      | 0.147                |
|           |               | 82.0      | 32.4      | 37.9      | 0.149                |
|           |               | 81.2      | 33.1      | 38.6      | 0.148                |
|           |               | 81.7      | 32.9      | 38.3      | 0.151                |
|           |               | 80.9      | 32.6      | 38.1      | 0.147                |
| PCG-B1    | cooling -30°C | 148.7     | 22.4      | 6.1       | 0.091                |
|           |               | 150.1     | 21.7      | 5.4       | 0.092                |
|           |               | 154.3     | 21.0      | 5.1       | 0.097                |
|           |               | 151.8     | 21.4      | 5.0       | 0.093                |
|           |               | 149.5     | 22.1      | 5.9       | 0.092                |
|           | heating 50°C  | 70.9      | 28.1      | 34.7      | 0.107                |
|           |               | 71.8      | 28.2      | 34.8      | 0.109                |
|           |               | 71.9      | 28.2      | 34.8      | 0.109                |
|           |               | 72.4      | 28.4      | 34.7      | 0.115                |
| PCG-B2    | cooling -30°C | 70.1      | 28.5      | 34.9      | 0.110                |
|           |               | 133.0     | 18.1      | 3.5       | 0.091                |
|           |               | 136.5     | 17.8      | 3.2       | 0.093                |
|           |               | 136.7     | 17.9      | 3.5       | 0.095                |
|           |               | 134.0     | 17.8      | 3.6       | 0.094                |
|           |               | 133.7     | 18.0      | 3.7       | 0.093                |
|           | heating 50°C  | 55.2      | 24.1      | 29.2      | 0.108                |
|           |               | 56.3      | 24.2      | 29.4      | 0.108                |
|           |               | 55.9      | 23.9      | 30.0      | 0.092                |
|           |               | 57.3      | 23.6      | 32.0      | 0.068                |
|           |               | 56.2      | 23.6      | 31.4      | 0.072                |
| PCG-B3    | cooling -30°C | 54.5      | 23.3      | 11.7      | 0.047                |
|           |               | 53.3      | 23.4      | 11.8      | 0.046                |
|           |               | 52.8      | 23.5      | 12.6      | 0.048                |
|           |               | 48.5      | 23.5      | 11.9      | 0.042                |
|           |               | 46.1      | 23.7      | 12.3      | 0.040                |
### Table 5. Results of density, porosity and heat conductivity estimation.

| Sample No. | Anthracite’s proportion, % | ρ, kg/m³ | P, % | \( \Lambda_{av} \), W/(m·ºС) |
|------------|----------------------------|----------|------|--------------------------|
| PCG-B1     | 1                          | 575.8    | 25.2 | 1.121                    |
| PCG-B2     | 2                          | 534.2    | 32.1 | 0.102                    |
| PCG-B3     | 3                          | 519.2    | 36.3 | 0.067                    |
| PCG-B4     | 4                          | 500.2    | 37.6 | 0.060                    |
| PCG-B5     | 5                          | 466.8    | 37.7 | 0.062                    |
| PCG-B6     | 6                          | 431.4    | 45.7 | -                        |
| PCG-B7     | 7                          | 405.4    | 49.8 | -                        |

Received values were generalized and presented below in the table 5.

As can be seen from the table 5, by increasing the amount of anthracite in the charge from 1 % to 7 %, considering even properties, the porosity value increases from 25.2 % to 49.8 %. By decline of the density value and incline of the porosity the heat conductivity decreases. This happens because the heat flow goes not only through the material, but also through its pores filled with air. Due to air having an extremely low heat conductivity there emerges a significant resistance to the heat flow passing. In the presence of large mutually connected pores, the transfer of heat by the movement of air increases. A lack of connected pores also decreases the heat conductivity value. According to the results of this research we could estimate that the sample PCG-А5 represents the most optimal waste porous glass composition due to its lowest heat conductivity.

### 3. Conclusion

Based on the results of the complex of studies on the synthesis of porous glass based on ash and slag wastes, the following conclusions can be drawn.

1. The optimal composition of porous glass (SHPS-B5) as a component of the composite with the use of borax as a smelt, anthracite as a blowing agent has been developed.
2. The porosity of the samples increases with an increase in the anthracite additive by more than 2 times (Table 3). This shows that anthracite is an effective pore-former.
3. Dependence of the strength of glass on compression on the amount of anthracite is completely different. As can be seen from Table 3, with an increase in the anthracite additive, the strength value decreases by more than 1.5 times. Thus, the optimal composition of the charge, taking into account the effect of anthracite on the most important properties of the synthesized porous glass, is the composition of SHPS-B5, which provides a sufficiently high porosity of 37.7% and a density of 466.8 kg/m$^3$.

Acknowledgments
The article is prepared based on the results of a study carried out with the financial support of the Russian Foundation for Basic Research in the framework of the scientific project No. 16-33-60177 Mol_a_dk.

References
[1] Minko N.I., Puchka O.V., Evtushenko E.I., Nartsev V.M., Sergeyev S.V. Foamglass - a modern effective inorganic thermal insulation material // Fundamental research. - 2013. - No. 6.
[2] Shikhova V.A., Yatsenko E.A. Production of heat-insulating materials for construction purposes on the basis of waste from the fuel and energy complex. // Izvestiya Vysshikh Uchebnykh Zavedenii. The North Caucasus region. Series: Engineering sciences. - 2013. - No. 4.
[3] Smoliy V.A., Kosarev A.S., Yatsenko E.A. Cellular heat-insulating building glass materials based on waste from thermal power plants and ferrous metallurgy // Glass and ceramics. - 2017. - No. 2.
[4] Grushko I.S. Dependence of foam-slag glass parameters on furnace charge and technological additives // Scientific Review. - 2015. - № 6.
[5] GOST 2409-80 "Method for determination of apparent density, open and total porosity, water absorption".
[6] Research of the physicochemical regularities in the process of thermoplastic sintering and the formation of a cellular structure as a function of temperature-time regimes [Text]: report on R&D (concl.), RFBR project No. 13-03-90756 / 13 // Pr. manager. Grushko I.S. - St. Petersburg: 2015 - 230 pp.