Porous materials based on foaming solutions obtained from industrial waste

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Abstract. This study analyzes foam concrete production efficiency. Research has shown the possibility of using a newly-designed protein-based foaming agent to produce porous materials using gypsum and cement binders. The protein foaming agent is obtained by alkaline hydrolysis of a raw mixture consisting of industrial waste in an electromagnetic field. The mixture consists of spent biomass of the Aspergillus niger fungus and dust from burning furnaces used in cement production. Varying the content of the foaming agent allows obtaining gypsum binder-based foam concretes with the density of 200-500 kg/m$^3$ and compressive strength of 0.1-1.0 MPa, which can be used for thermal and sound insulation of building interiors. Cement binders were used to obtain structural and thermal insulation materials with the density of 300-950 kg/m$^3$ and compressive strength of 0.9-9.0 MPa. The maximum operating temperature of cement-based foam concretes is 500°C because it provides the shrinkage of less than 2%.

1. Introduction

The intensive growth of industrial production and the increase in energy consumption have predefined the steady growth of prices for basic energy carriers in Russia, as well as abroad. According to the research [1], approximately 40% of energy consumption in both Europe and Russia accounts for heating buildings and other structures. It is known [2] that the average heat loss through doors and windows is 37%, 35% - through outside walls, 13% - through basement floors, and 15% - through attic floors. This leads to the necessity of increasing the quality of the manufactured envelope constructions of residential and civic buildings and increasing their thermal resistance, which will ensure a reduction in energy consumption during the operation of buildings and an improvement of people's living conditions. This problem can be solved by using multi-layer envelope constructions with externally and internally located efficient heat insulators based on mineral wool, expanded polystyrene, and foam concretes. Selection of a particular material is conditioned not only by its high thermophysical characteristics, but also by its sufficient durability and environmental friendliness. Another thing to consider is the power demand for its production. From this point of view, the optimal solution is using cellular concretes, particularly foam concretes.

Foam concrete belongs to the group of efficient cellular-structured materials. It provides articles with a large proportion (up to 85% of the total volume of material) of fine and medium air cells sized up to 1-3mm that shape due to hardening the porous mix that consists of binder substances, finely-dispersed aggregate, water, and foaming additive.
Foam concretes are used to manufacture solid homogeneous structures that simultaneously meet the requirements of bearing capability, heat and sound insulation, and fire safety. This combination of advantages makes foam concrete a technologically and economically preferable building material in both residential and industrial constructions.

Organizing the process of production of porous concrete requires less investment than that for lightweight aggregates, as well as lightweight concretes and constructions based on them [3]. Aside from that, a low-output mobile facility to produce foam concretes can be deployed immediately on the construction site.

Manufacturing foam concrete requires conventional raw materials and equipment, and heat treatment is carried out under air pressure. This is why the cost of foam concrete articles is 1.2-1.5 times lower compared to that of autoclaved aerated concrete blocks given there are equal physical and mechanical properties [4].

Compared to other building materials, the ratio of foam concrete volume to raw material volume is the highest (Fig. 1). Thus, for the foam concrete with the average density of 400 kg/m$^3$, pore volume is 80% and solid content is 20% respectively.

![Figure 1. Volumes of input material and raw material for various building materials: 1 – concrete; 2 – silicate hollow rock; 3 – brick with vertical hollows; 4 – silicate rock with vertical hollows; 5 – lightweight concrete hollow rock; 6 – porous brick with vertical hollows; 7 – foam concrete.](image)

This way, using low amounts of raw material allows obtaining material that combines low density, high thermal insulation properties, and sufficient strength.

Currently, there is not a comprehensive methodology of selecting the composition of the raw mixture to obtain foam concretes of various density. This is explained by the fact that the basic physical and mechanical properties of the output materials depend on a range of factors: chemical nature of the foaming agent, foaming method, raw material component characteristics, type and mineralogical composition of the binder, etc. Binders and foaming agents have the decisive effect on the characteristics of foam concretes [5, 6]. Foam needs to be considered as a simple aggregate that is characterized by its specific surface area, expansion ratio, stability, effect on the raw mixture components, etc.

All foaming agents used in building production techniques are subdivided into synthetic and protein-based. Synthetic agents are the most popularly used due to consistency of their composition, resistance to fermentation and, consequently, longer shelf life. Protein-based foaming agents are obtained from plant and animal waste, as a result of alkaline hydrolysis of animal blood and cereal products [7 - 9]. This results in their inconsistency of composition and limited shelf life of the end product. However, unlike synthetic solutions, protein-based agents allow one to increase the volume of the air entrained in the foam concrete mixture up to 80-90% [10], to obtain stable foam mass with a
high expansion ratio, and to prevent segregation of foam concrete systems, which ensures the high strength characteristics of low-density cellular concretes [10, 11].

For this reason, development of new types of protein-based foaming agents, study of their basic features, and design of porous materials of various purpose on their basis are relevant problems.

Previous researches show the possibility of obtaining protein foaming agents from industrial waste: spent slurry from microbiological production and dust from burning furnaces used in cement production plants [12 - 14]. The goal of this study is to design the composition of foam concretes based on the newly-designed protein-based foaming agent using cement and gypsum binder solutions. The following problems were solved to achieve this goal:

- studying the influence of the newly-developed foam agent on the structure and physical and mechanical properties of the obtained foam concretes;
- determining the maximum operating temperatures of foam concretes obtained using cement-based binders.

2. Materials and methods

The experimental studies involved the following raw materials:

- Portland cement of PTs400DO GOST 30515-97-brand manufactured by Oskolcement Plant, Stary Oskol, Russia;
- gypsum binder of G-5 GOST 125-79-brand manufactured by Khabezskiy Gipsovyy Zavod (Khabez Gypsum Plant), Russia;
- calcium hydroxide produced by JSC Stroimaterialy containing 84% of active (CaO+MgO) according to GOST 9179, Belgorod, Russia.

The protein foaming agent was obtained through alkaline hydrolysis of spent biomass of Aspergillus niger fungus from citric acid production in CJSC Tsitrobel, Belgorod, Russia. The optimal ratio of the basic components of the raw mix were: water: mycelium: alkaline component = 500: 100: 28 with respect to mass, and the alkaline hydrolysis conditions were: microwave power of 700 Wt, processing time of 20 minutes. These were previously determined [12-14] and used in this research.

The use of microwave field for the process of hydrolysis was conditioned by the presence of dipoles (protein and water molecules) in the processed mix. Microwave radiation ensures the increase in velocity and the degree of denaturation of compound biopolymers (protein molecules to simpler ones), i.e. amino acids, and the degree of their emission into the foaming agent solution [13], which allows one to significantly shorten the time of hydrolysis (six times), and, consequently, the energy consumption of obtaining the foaming agent while keeping its properties the same.

The alkali component (AC) was the mixture of calcium hydroxide and the cement dust formed from the spent gas of burning furnaces used for cement production (ZAO Belgorod Cement, Belgorod, Russia). According to the chemical composition presented in Table 1, the main component of the cement dust is calcium oxide with a significant content of sulphates and chlorides.

| Table 1. Chemical composition of dust during burning stage, mass % |
|-----------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| Fe₂O₃ | CaO  | SiO₂ | Al₂O₃ | MgO  | K₂O  | Na₂O | SO₃ | Cl⁻ |
| 2.35  | 38.49| 13.00| 3.13  | 0.50 | 5.25 | 0.25 | 2.13| 2.24| 2.24|
| 7.11  | 53.54| 14.27| 6.20  | 6.32 | 10.23| 0.77 | 2.30| 3.26| 2.24|

According to the research undertaken [14], the main minerals of the cement dust are calcium carbonate, burned clay, potassium compounds (potassium sulphates, carbonates, and chlorides), clinker minerals, and calcium hydroxide, which provide the alkaline pH level of the aqueous extract of 12.57. This is what determined the use of cement dust from blast furnaces as the main component of the raw mixture to obtain the foaming agent. The basic properties of the obtained foaming agents are shown in Table 2.
Table 2. Change of basic characteristics of foam during partial replacement of calcium hydroxide with cement dust without stabilizing additives.

| Series No. | Cement dust content in AC, % | Critical micelle formation range (CMF), % | Expansion factor | Foam stability, min. |
|------------|------------------------------|------------------------------------------|------------------|---------------------|
| 1          | 0                            | 1.0 – 1.75                               | 20.0             | 10.0                |
| 2          | 5                            | 1.75 – 2.0                               | 16.0             | 10.0                |
| 3          | 10                           | 1.75 – 2.0                               | 12.4             | 7.0                 |
| 4          | 15                           | 1.75 – 2.0                               | 12.2             | 4.0                 |

Further research involved foaming agent No. 2 containing 5% of cement dust with AC and the concentration of the working mixture of 2.56%.

Foam concretes were prepared in the following way. The foaming agent was mixed in a paddle mixer with the speed of 1200 RPM for 5 minutes, thus obtaining the foam that was then mixed with previously prepared gypsum or cement paste. After mixing the components, the obtained foam mass was pored into moulds. Further setting and curing the binder fixed the structure of the material. Before determining their physical and mechanical characteristics, gypsum-based materials were dried until constant mass under the temperature of 55°C, while the cement-based ones were subjected to steam curing under the isothermal temperature of 95°C. Gypsum paste was produced under the W/G (water/gypsum) ratio of 0.48, and the cement paste was produced under the W/C (water/cement) ratio of 0.4.

3. Research results and discussion.

In the technology of producing porous building materials, the use of the newly-designed protein-based foaming agent in the proportion of 10 to 50% from the mass of gypsum binders allowed one to obtain foam concretes with the density of 200 to 500 kg/m³ and compressive strength of 0.1 to 1.0 MPa (Fig. 2).

Evaluating the nature of the porosity of the obtained materials by optical microscopy revealed the presence of evenly dispersed in volume closed isolated spherical pores, whose size varied based on the density of concrete from 0.1 to 1.2 mm, and whose interpore partitions were represented by a solid and homogeneous composite with minimal capillary porosity (Fig. 3).

The obtained physical and mathematical characteristics of gypsum foam materials allow recommending them for use in monolithic construction for thermal and sound insulation of building interiors.

![Figure 2](image-url)
Furthermore, the technique is recommended for producing unique articles in factory environment because it provides the sufficient compressive strength of up to 1.0 MPa with the density of 200 kg/m$^3$, which ensures the articles' safe transportation.

Use of cement binders allows increasing the range of the physical and mechanical properties of the obtained foam concretes. Foaming agent content within the range from 5 to 30% from the mass of cement ensures the variation of the material's density from 300 to 950 kg/m$^3$ with the variation of compressive strength from 0.9 to 9.0 MPa (Fig. 4). In addition, foam concrete develops a macrostructure with isolated porosity, which is reflected in its sorption humidity. Under the relative humidity of 97%, the samples' weight gain during the first days of the tests does not happen intensively, which proves the material's closed porosity and, consequently, increased heat and thermal insulation capabilities.

The foaming agent spending factor of 5 to 15% (to cement mass) ensures obtaining of structural porous materials with the compressive strength of 8.56 to 4 MPa (Fig. 4). There forms a macrostructure with evenly distributed pores sized up to 0.5 mm and maximally approaching the spherical shape. Interpore partitions are dense, containing no defects, and are up to 0.8 mm thick. With this kind of setting, pores make up the volumetric porosity within the range of 60-70% and the density of foam concretes of 950 to 600 kg/m$^3$.

Increasing the content of the foaming agent leads to maximum entrainment of air into the raw mixture, which facilitates the highly-porous structure of the obtained material and, consequently, the reduction of its density. With the foaming agent spending factor of 20 to 30 % (to cement mass), strength properties of the materials rapidly change and vary within the range of 1.78 to 1 MPa with the density of 500 to 300 kg/m$^3$ (Fig. the 4), which allows one to classify them as thermal insulating.

It is known that the tightest layout of globous bodies of the same diameter (in this case, foam bubbles) is achieved by their hexagonal arrangement. Thus, foam concrete with the density of 300 kg/m$^3$ is characterized by the presence of pores sized 1.2-1.7 mm, whose shape is approximated to hexagonal (Fig. 5).
In order to determine the maximum operating temperature of the obtained foam concretes based on cement binders, research was carried out to assess the linear setting of the samples processed under the temperatures from 100 to 600°C. The results, presented in Fig 6, have shown that the obtained porous materials can be recommended for use under the temperatures of up to 500°C as they are characterized by the shrinkage of less than 2%.

4. Conclusion
The research has shown the possibility of using the newly-designed protein-based foaming agent based on industrial waste: spent biomass of the *Aspergillus niger* fungus and dust from burning furnaces used in cement production, to produce porous materials using gypsum and cement binders. Varying the content of the foaming agent allows obtaining gypsum binder-based foam concretes with the density from 200 to 500 kg/m³ and compressive strength from 0.1 to 1.0 MPa, which can be used for thermal and sound insulation of building interiors.
Cement binders allow obtaining structural and thermal insulation materials with the density of 300 to 950 kg/m³ and compressive strength from 0.9 to 9.0 MPa. The maximum operating temperature of cement-based foam concretes is 500°C because it provides the shrinkage of less than 2%.

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