Effect of alumina-silica microsphere additives on properties of ceramic wall products

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Abstract. Large size ceramic masonry products manufactured by forming and firing fusible clays are widely used. Their structure is presented with honeycomb porous walls which improve their thermal insulation performance. The movement of the thermal flow in this case is carried out by the maximum path from the inner to the outer surface. It leads to decrease the equivalent thermal insulation performance. The void ratio of this type of products is more than 50% and the density with voids is from 600 up to 800 kg/m\textsuperscript{3}. Voids in ceramic hollow products are filled with masonry mortar and it leads to decrease their thermal properties. In this paper the research of modified raw clay by alumina-silica hollow microspheres as pore forming agent is presented. The optimal composition and manufacturing technology of the product was established by applying mathematical experiment planning method. The obtained composite included microspheres with bulk density of 360 kg/m\textsuperscript{3} as a filler and raw clay with a true specific gravity of 2500 kg/m\textsuperscript{3} as a binder. The technology of manufacturing consisted of mixing thoroughly dry powdered clay with hollow microspheres with addition of water until a homogeneous mass, forming in the mold at the required pressure, release from the mold and firing with appropriate temperatures. The structure factor of strength and the structure factor of thermal conductivity as criteria for optimization of the properties were chosen. Effect of moisture on the thermal conductivity, sorption, vapor permeability, water absorption and adsorption rate were investigated. It was found that the thermal conductivity decreases with the use of alumina-silica hollow microspheres for every percent of the moisture content, which is significantly less than the similar ceramic materials. The obtained material has contact structure with a partial filling of intergranular space and it is associated with the firing character of its production. The way of optimization the material structure is to improve the packing density of the microspheres by controlling their size distribution and providing a thin uniform dispensing of the clay mass over the entire volume of composite.

1. Introduction
Market saturation of building materials and structures with increased energy efficiency is a huge challenge in all of the national economy sectors.
Large size ceramic masonry products manufactured by forming and firing fusible clays are widely used. Their structure is presented with honeycomb porous walls that improve their thermal insulation performance. The movement of the thermal flow in this case is carried out by the maximum path from the inner to the outer surface. It leads to decrease the equivalent thermal insulation performance [1, 2, 3, 4]. The void ratio of this type of products is more than 50% and the density with voids is from 600 up to 800 kg/m$^3$.

Thermal conductivity is one of the main functional properties of thermal insulation material can be determined by Fourier formula [5]:

$$\lambda = \frac{Q \cdot l}{F \cdot \tau \cdot \Delta t}$$

where: $\lambda$ – thermal conductivity, $Q$ – the amount of heat transferred, $F$ – cross-sectional area of the sample, $l$ – the sample length, $\tau$ – the time of heat transfer, $\Delta t$ – temperature difference on the surface of the sample.

The smaller the pore size the lower thermal conductivity of the material [6, 7, 8]. This is due to a lower convection of the gas in the pore, and to a decrease of thermal radiation influence. For the air pores of porous solid with the size of 0.1 mm $\lambda$ is equal to 0.024 W/(m·K), but for pores of 0.2 mm size $\lambda$ is equal to 0.031 W/(m·K).

The same material with the same density may have different thermal conductivity value, because of different pore structure [9, 10, 11].

The significant purpose is to improve the effective thermal insulation performance of the material with adjustable porosity based on alumina-silica microspheres additives with increased strength and reduced thermal conductivity [12, 13, 14, 15].

The idea of creation of a ceramic potsherd by introducing hollow microspheres with their optimal distribution in the material is proposed. Pyrogenic character of such materials creates good terms for their use to obtain porous ceramic products.

2. Materials and Methods

Alumina-silica microspheres are the inert light fraction of fly ash. They have size from 20...50 microns up to 400...500 microns with predominant diameter of the particles of 100...200 μm and wall thickness of 2...30 μm, bulk density of 350...400 kg/m$^3$, true density of wall thickness of 2500 kg/m$^3$.

The main component of the alumina-silica microspheres is silicon oxide SiO$_2$ (45...60%), alumina oxide Al$_2$O$_3$ (15...40%), iron oxide Fe$_2$O$_3$ (1...10%), calcium oxide CaO (1.5...4.5%), potassium oxide K$_2$O (2.0...4.5%) and the other oxides less than one percent.

The microspheres have low sorption capacity and it is less than 0.5% by mass. Their use as a filler in artificial building composites positively affects on their thermal and moisture characteristics. All these factors contribute the reduction of the moisture content and thermal conductivity gain for each percentage of moisture in materials. Sorption properties of microspheres are given in table 1.

| Table 1. Sorption properties of microspheres. |
|-----------------------------------------------|
| Value Parameters                               |
| Relative humidity ($\phi$), %                 |
| 40 60 80 90 97                                |
| Moisture sorption ($w$), %                    |
| 0.027 0.038 0.067 0.106 0.294                |

The modified composites consisted of:
- clay with solid density of 2500 kg/m$^3$ as a binder;
- alumina-silica additive with bulk density of 360 kg/m$^3$ as a filler;
- water.
The technology of obtaining a constructional material based on ceramic potsherd and hollow microspheres included the following stages. Firstly, dry powdered clay and microspheres were mixed. Then the water was added until homogeneous mass. The samples with size of 250x120x65 mm were formed in the mold at the required pressure, released from the mold and fired at the appropriate temperatures.

Clay firing was carried out according to the following sequence: raising the temperature from 20 to 100 °C in 15 minutes; temperature retardation at 100 °C for 10 minutes; raising the temperature up to 650 °C during 120 minutes; temperature retardation at 1050 °C for 120 minutes; and cooling.

The optimization of the mix was performed by using the empirical structure factor of strength and the empirical structure factor of thermal conductivity depended from density of the material.

| Name of composition | Content of microspheres in % by mass | Content of clay binder in % by mass | Forming pressure, kg/cm² |
|---------------------|-------------------------------------|-----------------------------------|--------------------------|
| MMC-1               | 65                                  | 35                                | 16                       |
| MMC-2               | 65                                  | 35                                | 32                       |
| MMC-3               | 70                                  | 30                                | 32                       |
| MMC-4               | 75                                  | 25                                | 32                       |
| MMC-5               | 65                                  | 35                                | 50                       |
| MMC-6               | 70                                  | 30                                | 50                       |
| MMC-7               | 75                                  | 25                                | 50                       |

3. Results
The results of the strength, density and frost resistance of the samples are presented in table 3.

| Name of composition | Density, kg/m³ | Compressive strength, MPa | Flexural strength, MPa | Compressive strength of wet samples, MPa | Compressive strength under 100 freeze-thaw cycles, MPa |
|---------------------|----------------|---------------------------|------------------------|------------------------------------------|-----------------------------------------------------|
| MMC-1               | 648            | 3.9                       | 1.2                    | 4.3                                      | 5.3                                                 |
| MMC-2               | 760            | 6.6                       | 1.6                    | 5.9                                      | 8.4                                                 |
| MMC-3               | 715            | 4.5                       | 2.8                    | 4.3                                      | 5.6                                                 |
| MMC-4               | 653            | 3.7                       | 3.4                    | 3.4                                      | 3.7                                                 |
| MMC-5               | 821            | 10.1                      | 3.2                    | 8.0                                      | 10.4                                                |
| MMC-6               | 795            | 8.6                       | 3.4                    | 6.6                                      | 8.1                                                 |
| MMC-7               | 773            | 6.7                       | 2.6                    | 5.0                                      | 7.0                                                 |

Table 2 and table 3 show the great influence of forming pressure and ratio of the components in the mix on density and strength of microsphere modified composites (MMC).

It was established the influence of the forming pressure (16 kg/cm²) on flexural strength of the MMC-1 which is significantly less than the strength of other compositions with similar properties (MMC-4).

Gradual pressure increases up to 32 kg/cm² for MMC-2 and 50 kg/cm² for MMC-5 at the same additive/binder ratio will allow to increase the strength in 1.7 and 2.6 times respectively while the density increase is only 1.17 and 1.27 times.
The increase the content of microspheres (sample MMC-2 and MMC-7) leads to decrease the strength which can be compensated by the raising of forming pressure. On the one hand it leads to increase the consumption of microspheres, reduce the part of the pores of the material which can be filled with water, enhance the thermophysical properties of the material when it moistened.

Water absorption of the samples was determined by lowering 1/2 of the sample in water for a day. Then the sample was hold full down until total saturation by weight.

The results for water absorption of the optimal composition (MMC-3) with microspheres and clay binder based on thermotechnical characteristics are presented in table 4.

| Type of water absorption | MMC-3 |
|--------------------------|-------|
| Water absorption, % by mass | 41.7  |
| Water absorption, kg/m³  | 294.8 |
| Water absorption, % by volume | 29.5  |

The water absorption coefficient for MMC-3 composition was equal to 72.9 kg/m²·h. The porosity of the sample MMC-3 was equal to 0.592 m³/m³ or 59.2%.

The sufficiently high water absorption of the material is explained by the characteristic of the pore space structure. The studied material has pores of irregular shape with smooth walls. Almost all the space is a single volume, easily filling with water. That could explain the high values of vapour permeability of the material.

The vapour permeability of microsphere back filling is equal to 0.17 mg/(m·h·Pa). The vapour permeability experiment results of firing materials based on microspheres are given in table 5.

| Vapour permeability of MMC-3. |
|-------------------------------|
| Vapour permeability in arid climate, mg/(m·h·Pa) | 0.111 |
| Vapour permeability in humid climate, mg/(m·h·Pa) | 0.106 |

The dependence of the thermal conductivity on the moisture content of the material is represented by the composition MMC-3 in figure 1.

\[
\text{Thermal conductivity, W/(m·K)} \quad \text{Humidity, %}
\]

**Figure 1.** Dependence of thermal conductivity on moisture content of MMC-3.

As you can see the thermal conductivity is almost linearly dependent on moisture.
The results of the study of pore structures using the electron microscope at the figure 2 are presented. The sample MMC-3 with 715 kg/m$^3$ and MMC-5 with 821 kg/m$^3$ were chosen.

![Figure 2](image2.png)  
**Figure 2.** The image of MMC-3 with magnification of 80 times.

![Figure 3](image3.png)  
**Figure 3.** The image of MMC-3 with magnification of 200 times.

As we can see on figure 2, at small magnifications the material has a homogeneous structure, with an even distribution of the filler. Macroscopic pores and other defects are absent. Attention is drawn to the narrow range of cell size distribution, as well as the large number of damaged microspheres at the fracture. This phenomenon is typical for materials based on porous aggregates, and, in most cases, indicates high matrix adhesion. The sample MMC-5 has the similar situation.

![Figure 4](image4.png)  
**Figure 4.** Microstructure of MMC-3 with magnification of 500 times.

![Figure 5](image5.png)  
**Figure 5.** Microstructure of MMC-3 with magnification of 1000 times.
With a larger increase in figures 3, 4, 5 and 6 the differences between the samples begin to appear. On the fracture of a material with a higher density of MMC-5 (figure 6), a greater amount of binder (burnt clay) is clearly visible. The binder distribution by the material volume is uniform, on the other hand the coating of the filler grains is not continuous. The binder is distributed on the surface of the particles here and there, and parts of the hardened clay that are comparable in size with the aggregate particles are present, which is especially noticeable in the MMC-5.

With a larger increase, we can see the destruction of the material passed through the microspheres without touching the elements of the composite matrix. In some cases, the damage of the aggregate particles located at some distance from the surface of the fracture is noticeable. The explanation for this can be the initial defectiveness of microspheres, and also their damage during the pressing process. It should be noted that the phenomenon is not massive.
In figure 8 and figure 9 the contact zone of the binder with the alumina-silica additives is clearly visible. There is a complete homogeneity of the given zone, the visible boundary of the materials is absent. The fragments surface of the material matrix is melted which indicates a deep calcination with the formation of a large amount of a liquid phase. All the data obtained in the study correspond with the main picture of the material properties.

4. Conclusions
The structure of the material can be characterized as a contact with the partial filling of the intergranular space, which is connected with the burning nature of its production, and with the absence of the flow of hydration processes.

The destruction of the alumina-silica filler particles and the type of contact zone explains the high strength of the material. It exceeds 2 times while amount of binder is 30 ... 35% with a proportional decrease of the microsphere content and an increase of density within acceptable limits.

Insufficiently uniform distribution of the clay binder on the surface of the material and the presence of large agglomerates results on the feasibility of increasing the dispersion of dry clay. This suggests the increase in dispersion of dry clay and the need to optimize the process of mixing the mass, the order of introducing the materials into the mixer. The additional resource for improving strength is more uniform distribution of the binder throughout the volume of the composite.

In accordance with the all obtained data the pore space of the material is formed by voids between the microsphere particles and the matrix fragments. The composite has interconnecting pore structure with irregular shape and dimension while microporosity is negligible. This explains the features of the hydrophysical properties of the material: low sorption and high water absorption.

Additional optimization of the structure may consist of increasing the packing density of the filler by controlling its granular composition and providing a thin layer and even distribution of the binder.

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References
[1] Rumyantsev B M and Zhukov A D 2012 Methodology for creating new building materials (Moscow: Moscow State University of Civil Engineering) p 11
[2] Bessonov I V and Sapelin A N 2012 J. Build. Mat. 6 26
[3] Bessonov I V, Zhukov A D, Sapelin A N and Mustafaev R M 2014 J. of Ind. and Civ. Eng. 6 58
[4] Zhukov A D, Bessonov I V, Sapelin A N, Naumova N V and Chkunin A S 2014 J. It. Sc. Rev. 2 155
[5] Bogoslovskiy V N 1982 Building Thermophysics (Moscow: Vysshaya Shkola Publishers) p 415
[6] Dong X, Hongyi J and Ming L 2018 J. Cer. Int. 44 2 1545
[7] Geng H, Hu X, Zhou J, Xu X, Wang M, Guo A, Du H and Liu J 2016 J. Cer. Int. 42 14 16071
[8] Suryavanshi A K, Swamy R N and Cardew G E 2002 J. Cem. and Conc. Res. 32 11 1783
[9] Inozemtcev A S and Korolev E V 2013 J Industrial and civil construction 10 80
[10] Kabirov R R, Garipov L N, Faseeva G R, Nafikov R M, Lapuk S E and Zakharov Y A 2017 J. Wast. Man. 60 230
[11] Hou Z, Zhang B, Zhang R and Liu L 2017 J. Cer.Int. 43 12 8809
[12] Yin Y, Zhang B Y, Zhang J H and Sun G L 2012 J. Constr. and Build. Mat. 30 80
[13] Wang Q, Chen J, Gui B, Zhai T and Yang D 2016 J. Cer. Int. 42 4 4886
[14] Song L, Li Z, Duan P, Huang M, Hao X and Yu Y 2017 J. Cer. Int. 43 6 5115
[15] Guo J - K, Li J and Kou H - M 2017 Modern Inorganic Synthetic Chemistry (Advanced Ceramic Materials) ed Xu R and Xu Y (Amsterdam: Elsevier) chapter 17 p 463