Porous magnesia compositions of a combined structure

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Abstract. In this research were developed heat-insulating magnesia compositions with technogenic fillers. A comparative analysis of the structures formed by different methods shows the high porosity of the compositions using a foaming agent, polystyrene pellets. Here was shown the expediency of obtaining porous compositions based on mixed magnesia binders with the addition of wastes of enrichment of skarn-magnetite ores (up to 30 %). The efficiency of the heat-shielding properties of materials is ensured by the creation of a highly porous combined structure by optimizing the formulation of the molding masses and by rational combination of various techniques of porosity. Effect of porosity methods on magnesia compositions structure was investigated. The conditions for formation of combined structures due to combination of cellular, granular and fibrous porosity were determined. Combined structures of various compositions based on technogenic fillers are characterized by porosity of 75 – 90%, density of 150 – 400 kg/m³ and coefficient of thermal conductivity of 0.04 – 0.08 W/(m K). Methods for preparing molding mixtures have been developed based on the primary contact of the components forming the matrix stability and providing a stable highly porous structure of the compositions. It is revealed that the magnesian compositions are distinguished by increased technology, ensuring the greatest strength of the porous materials.

Keywords: caustic magnesite, magnesia composites, foam concrete, porous granules.

1. Introduction

Increase in efficiency of thermal insulation materials is ensured by optimization of a structure [1 – 7]. Porosity is carried out by various methods: swelling due to gas-forming or foaming agents, loose packing of fibrous or granular particles, removal of a pore forming agent, and grouting of porous grains. Increase in closed pores improves heat-shielding properties of the structure. However, possibilities of separate methods of porosity are often limited by low strength of the formed structures or by the small number of pores. Combined materials are formed by combination of fibrous, granular and cellular structures [5 – 11]. Combination of structures allows combining advantages of one structure with advantages of another.

Magnesia binding materials are favourably distinguished by low energy intensity of production; ability of caustic magnesite to intensive hardening; high strength. Expressive adhesive ability makes it rational to use magnesia binding agents in materials of a combined structure [11 – 20].

2. Materials and methods of research

The compositions were prepared from a mixed binding agent, including caustic magnesite (30 – 50%) and a fine technogenic component (50 – 70%). A grouting fluid of molding masses is a solution of magnesium chloride. Technogenic fillers were used in the content of composition materials: fibrous - wood sawdust, sheep wool; porous – aluminous silicate microsphere (formed as a part of fly ash during high-temperature coal combustion) and regenerated expanded polystyrene granules (obtained during processing of packaging material). The properties of the composites were studied on samples
measuring 40x40x160 mm. The structure of the compositions was studied by electron microscopy.

3. Results and discussion
The object of research is porous magnesia compositions. The purpose of the work is to create magnesia heat-insulating materials by forming combined structures with an anthropogenic component.

In this work were developed highly effective thermal insulation materials by optimizing the formulation and regulation of the formation of a highly porous combined structure of magnesia compositions with technogenic fillers.

3.1 Effect of porosity method on formation of magnesia compositions structure
Cellular structure of magnesia materials is formed by swelling with the use of foam and forming agents. For production of foam, a protein foaming agent «Unipore» and a synthetic foaming agent «Fairy» were used. Foaming agents in the amount of 3% were loaded into MgCl₂ solution of various densities (1100 – 1300 kg/m³). Viscosity of MgCl₂ solutions increases with loading of «Unipore» and is reduced when using «Fairy». Surface tension is reduced by a factor of 2 when using «Unipore»; by a factor of 4 when using «Fairy». Viscosity of MgCl₂ solutions increases with salt concentration increasing. In the presence of «Fairy» foaming agent, MgCl₂ solutions do not show the ability to form foam. Stable fine-pored foam is formed on the basis of the foaming agent «Unipore» from a solution of MgCl₂ with density of 1200 – 1250 kg/m³.

Studies of porous magnesia compositions using «Unipore» foaming agent (Table 1, Figure 1) showed that increased porosity is achieved with silicate technogenic fillers (wastes of enrichment of skarn-magnetite ores, metallurgical slag). The content of fillers for foamed compositions with density of not more than 500 kg/m³ should be limited to 30%.

| Pore-forming agent                  | Mass flow diameter, mm | Composite density, kg/m³ | Composite compressive strength, MPa |
|-------------------------------------|------------------------|--------------------------|-------------------------------------|
| None                                | 250                    | 1500                     | 22.5                                |
| Foam generating agent               | 230                    | 580                      | 4.0                                 |
| Hydrogen peroxide                   | 240                    | 650                      | 4.6                                 |
| Ash microsphere                     | 270                    | 1350                     | 14.7                                |
| Expanded polystyrene granules       | 150                    | 470                      | 2.0                                 |

Figure 1. Effect of a pore-forming agent on the structure of composites

For pore-formation by gasification method, substances that ensure separation of the gas phase during the interaction with CaCO₃ are used: Al₂(SO₄)₃, AlCl₃, FeCl₃, ZnCl₂, MgCl₂.

The greatest volume of gas in magnesia compositions is formed when hydrogen peroxide H₂O₂ is introduced in the amount of 0.5 – 5.0%. Hydrogen peroxide provides formation of cells of increased size (Table 1, Figure 1).

The effect of porous particles injected into magnesia compositions to form a granular structure was
investigated (Table 1, Figure 1). Ash microsphere in the amount of 2 – 20% reduces density of the composition by 5 – 15%, forms a fine-grained structure. When the content of microsphere is 2 – 5% the mobility of the molding composition is increasing. Loading of 5 – 10% of expanded polystyrene (diameter of granules is 3 – 5 mm) ensures the formation of a coarse-grained structure of composites with density of 470 – 650 kg/m³.

A comparative analysis of the structures formed by different methods indicates high porosity of the compositions using a foaming agent, expanded polystyrene granules. Reasonability of obtaining porous compositions based on mixed magnesia binding agents with addition of enrichment wastes of skarn-magnetite ores (up to 30%) is shown.

Effect of addition of liquid thermal insulation on the properties of the compositions was studied (Table 2). The additive improves the stability of the foam: the time of syneresis increases. With the addition of 5 – 10% of the additive, the strength of the magnesia materials rises by 1.2 – 1.6 times, while the density of the compositions decreases by 11 – 27%. The additive helps to reduce the coefficient of thermal conductivity from 0.07 to 0.05 W/(m·°C), to reduce water absorption of cellular compositions by 12 – 17%. It has been found out that it is rational to load the additive before foaming of the raw suspension.

Mixed binding agents, containing 30 – 70% of filler, are not inferior to strength indicators of caustic magnesite, differing by delayed early hardening. Strength of cellular materials with technogenic filler is below the strength of foam magnesite. Foaming agents slow down hardening of magnesia binding agents and reduce the strength by 1.5 – 3.0 times. Increased sensitivity of mixed binding agents to presence of foaming agents is due to MgO activity decreasing and screening effect of the foaming agent on the technogenic filler.

| Additive, % | Foam syneresis, min | Density, kg/m³ | Compressive strength, MPa, at…days |
|-------------|---------------------|----------------|-----------------------------------|
|             |                     |                | 3                                 | 28 |
| Dense structure |                    |                |                                   |    |
| 0           | –                   | 1950           | 28                                | 47 |
| 5           | –                   | 1740           | 47                                | 56 |
| 10          | –                   | 1620           | 32                                | 48 |
| 15          | –                   | 1430           | 25                                | 32 |
| Cell structure |                    |                |                                   |    |
| 0           | 65                  | 570            | 2.5                               | 4.2|
| 5           | 78                  | 495            | 3.8                               | 5.2|
| 10          | 95                  | 420            | 2.7                               | 3.8|
| 15          | 105                 | 380            | 1.6                               | 2.7|

To reduce the negative effect of the foaming agent on hardening of magnesia compositions, a complex technological method is used, which involves activation of the binding agent and improvement of foam preparation. In order to increase the hydration ability the components of the mixed binding agent were separately and jointly subjected to mechanical activation.

With the same processing time for powders, the specific surface area of caustic magnesite increased from 350 to 530 m²/kg; filler – from 360 to 680 m²/kg. The highest values of a toughness index were achieved under mechanical activation of both components of the mixed binding agent. Activation of binding agents intensifies structure formation and reduces hardening time of compositions prior to acquisition of structural strength by 30 – 35%. When comparing structure and properties of compositions of different preparations, a method that provides a primary contact of a binding agent with a highly concentrated solution of MgCl₂ is preferred. This initiates hydration of
MgO₂, ahead of the foaming agent. Magnesia binders provide the possibility of obtaining low-density foam concrete. magnesia foam concrete is characterized by strength, which is 1.5 – 1.7 times higher than the strength of Portland cement foam (density of foam concrete is 500 kg/m³). High strength of magnesia cellular concrete is provided by magnesium hydroxychloride crystals, which form a reliable partition between the cells. The compositions are characterized by a uniform porosity with a cell size of not more than 1 mm. The crystalline base of the interporal partition material, consisting mainly of 5Mg(OH)₂·MgCl₂·8H₂O fibers, provides high strength to cellular compositions (Figure 2).

![Figure 2. Microstructure of magnesia composites](image)

Optimization of structure promotes increase of heat-protective properties of magnesia compositions. The coefficient of thermal conductivity of the compositions decreases from 0.07 to 0.06 W/(m·K).

### 3.2 Compositions of a combined structure

When H₂O₂ is added to the foam, pores of different types are formed in the structure of the composition: large gas generation cells and small foam pores located in dividing walls between large pores (Figure 3). The possibility of additional foam porosity and creation of a combined structure due to 5 – 20% porous granules is shown (Table 3).

![Figure 3. Microstructure of magnesia compositions of combined structure](image)

1 – foam formation; 2 – gas formation; 3 – foam formation + gas formation; 4 – foam formation + microsphere; 5 – foam formation + foam polystyrene granules; 6 – foam formation + alkali silicate granules
When foam polystyrene granules are loaded into the foam mass, the density decreases by a factor of 1.8. Alkali-silicate granules with bulk density of 150 kg/m³ were synthesized to create a cellular-granular structure. Loading of alkali-silicate aggregate reduces the density of the compositions by 33%.

Table 3. Comparative characteristics of porosity in magnesia composites

| Method of pores formation                              | Density, kg/m³ | Thermal conductivity, W/(m·°C) | Compressive strength, MPa |
|--------------------------------------------------------|----------------|-------------------------------|---------------------------|
| Foam formation                                         | 525            | 0.07                          | 4.3                       |
| Gas formation                                          | 650            | 0.09                          | 4.6                       |
| Foam formation + gas formation                         | 390            | 0.05                          | 2.2                       |
| Foam formation + microsphere                           | 435            | 0.08                          | 3.6                       |
| Foam formation + foam polystyrene granules             | 285            | 0.05                          | 1.0                       |
| Foam formation + alkali silicate granules              | 350            | 0.05                          | 3.2                       |
| Foam formation + gas formation + foam polystyrene granules | 220            | 0.04                          | 0.8                       |

Compositions on an integral filler «foam polystyrene – wood particles – ash microsphere» were offered. Optimizing the particle ratio allows obtaining the combined structure «packed» with different pores to the maximum (Figure 4). Compositions have density of 350 to 650 kg/m³ and compressive strength of 1 to 7 MPa. Substandard sheep wool is used as a fibrous component while combined structures creating. Technogenic fibers (3%) strengthen interporous cell walls (Figure 4).

![Figure 4. Microstructure of compositions with fibrous components](image)

1, 2 – microsphere + wood particles; 3 – foam formation + sheep wool fiber

The nature of the porosity of the compositions essentially depends on the mechanism of cells formation. Gas formation due to H₂O₂ in compositions of various composition forms large pores, separated by thick partitions. Foam formation forms cells, the size of which is almost two times less than the pores of gas formation. The introduction of the microsphere promotes the consolidation of the interporal partitions, the preservation of the closed character of the cells. The bulk of the fibrous filler is located inside the partitions separating the pores. Complex pores are accompanied by a decrease in the size of the pores of gas formation, the appearance of small foam cells in the interporous partitions. The increase in porosity increases the heat-protective properties of magnesia compositions.

A rational method for variational structure formation of magnesia compositions has been developed, which involves sequential laying of masses with different porosities. For the central layer of products, a molding mass with porous granules is proposed. When forming a variational structure,
multimodal porosity is formed, creating a heat-insulating barrier. Magnesia binder provides strong adhesion of various layers (Figure 5).

Compositions have density of 300 – 450 kg/m$^3$ and a thermal conductivity coefficient of 0.055 – 0.060 W/(m$^0$K). Calculation of the wall block for the bearing capacity, performed with the use of the software package «LIRA», confirmed the stability of the variational magnesia compositions.

The results of experimental research are the basis for technological design. Technological schemes for the production of heat-insulating products from porous magnesia composites with a density of 200 – 500 kg/m$^3$ and a coefficient of thermal conductivity of 0.05 – 0.08 W/(m$^0$K) have been developed.

4. Conclusions
Magnesia compositions containing as a shutter a solution of increased density salt, allow using a wide range of technological methods for porous structure formation.

The multicomponent composition of magnesia compositions provides opportunities for combining different ways of porous structure creating.

Magnesia molding compositions compare favourably with processability, show high adhesion to fillers of different composition and structure, and provide increased strength of porous materials.

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