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Porous inorganic materials for fire protection of industrial structures

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Abstract. The necessity to study the thermophysical properties of porous inorganic materials is due to the wide use of thin-walled structures, the fire protective coating of which is performed when use porous materials. One of the most dangerous physical influence, leading to the destruction of thin-walled constructions in a fire, is a rapid increase in the temperatures of the combustion products in the fire zone. For a fire fencing, just 20÷30 minutes after its start, the temperature of the products in the combustion zone can reach 800÷900 °C, while the temperature can increase under more favorable conditions for the combustion process of air exchange. For open fires, when the air exchange conditions are not limited, the temperature of the combustion products can quickly reach 1100 °C of more. In the article, analyzing the effect on the porous materials of high-temperature combustion products, high humidity, direct exposure to water, as well as the process of phase of phase transitions of moisture contained in capillaries and its possible consequences. Presented and analyzing the influence of the process of thermal radiation inside gas-filled cellular structures on the heat-conducting properties of porous material based on perlite and expanded vermiculite. The results of an experiment to study the dependence of the thermal conductivity coefficient of expanded vermiculite on the specific particle size density and pressure suggest that with an increase in the temperature of the combustion products a thin-walled fire protection layer made of fibrous materials (for example, perlite and expanded vermiculite) with a decrease in the size of the solid fraction, the thermal conductivity coefficient of expanded vermiculite increases to a greater extent than of perlite, nab a certain tendency is observed to increase the share of the convective component in the thermal conductivity of expanded fire-protective materials as the particle sizes of their solid fraction decrease.

1. Introduction

The object of the present research is the heat and physical properties of porous inorganic materials used for fire protection of building structures. This article used the analysis data of M.V. Gravit et al. On the possible use of components of external substances in improving the fire safety of buildings [1–5], fire protection of high-rise buildings [6, 7, 8, 9], as well as options for increasing strength properties of concrete under fire conditions, which were considered in [10–13] by V.I. Korsun et.al., and concrete protection methods studied in the works [14, 15, 16, 17] of N.I. Vatin et.al.

The relevance of research is due to the fact that the current state of development of modern industrial technologies suggest supporting the required level of fire safety of building and structures since the consequences of their collapse as a result of a fire can lead to significant material losses, personal injury and even death [18].

In the construction of industrial facilities, there is a wide use of reinforced concrete reinforced concrete reinforced cement fiber-reinforced concrete and metal constructions, the value of the fire resistance limit of which usually did not exceed the values of 30-40 minutes [19, 20]. To slow down the

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heating of such structures allows the use of various fire-retardant coating based on the use of relatively inexpensive materials, primary perlite and expanded vermiculite [21–28].

The aim of the research is to assess the possibility of using porous inorganic materials to increase the level of fire protection of building structures, the achievement of which involves solving the following tasks.

- analysis of the process of heating porous inorganic materials in a fire and assessment of the ratio between different types of heat exchange;
- dependence identification between heat-conducting properties of porous inorganic materials and grain sizes;
- studying of the effect on the heat-conducting properties of porous inorganic materials of moisture, accumulated during fire fighting.

2. Methods

For scientific research, experimental data were collected and analyzed from domestic and foreign literary sources, as well as experimental studies of the thermal conductivity of composite materials made on the basis of expanded vermiculite in a temperature range of 50-400 °C. The temperature dependences of the thermal conductivity of these materials were obtained by using the IT-λ-400 meter, which is based on the method of monotonous heating. The thermal circuit of the applied method is shown in Fig. 1.

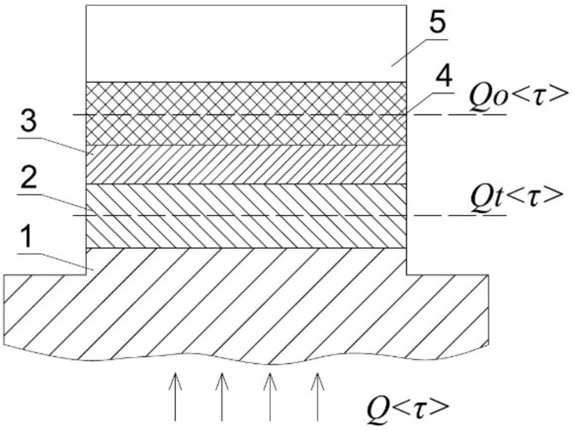

Figure 1. Thermal circuit: 1 – base; 2 – plate; 3 – contact plate; 4 – sample; 5 – core.

The heat flux Q coming from the base 1 passes through the cross section of the plate 2, is partially absorbed by it, and then goes on the monotonous heating of the plate 3, sample 4 Q and rod 5. The lateral surfaces of the rod, sample, and plates 2 and 3 also are thermally insulated.

The rod and contact plate are made of a material with a high thermal conductivity, so the temperature differences on them are insignificant.

The geometric parameters of the system are chosen so that the flows accumulated by the sample and plate are an order of magnitude smaller than those absorbed by the rod. In this case, the temperature field of sample 4 and plate 2 are close to linear and stationary. The theoretical justification of the applied method for measuring thermal conductivity is described in detail in the literature [29].

3. Results and Discussion

The initial stage of the process of passing through the mass of fire during the fire is characterized by its non-stationary nature, while the characteristics of the temperature field of the thin-walled structure are a function of not only spatial coordinates but also time.

The magnitude of the heating rate of such a structure is determined by the ability of its material to conduct heat, which is characterized by the coefficient of thermal conductivity of the material λ (W/(M°C)) and its temperature coefficient of thermal conductivity β (W/(M°C^2)), the effect of which is significant at a fire temperatures. In addition, the heating rate of a thin-walled structure will depend on the ability of the material to accumulate thermal energy, which can be characterized by the heat capacity of the entire material of the structure C (kJ/°C), which is numerically equal to the product of the material ρ (kg/m^3) by the specific (mass) heat capacity of c (kJ/(kg°C)).Thus, effective fire protection of thin-walled structures in a fire is possible when using materials with a relatively small coefficient of thermal conductivity, the value of which is determined by a large number of factors, such as the average density of the material, its true porosity, size and shape of these pores, moisture content of the material. In addition, the composition and radiative ability of the grains of the material, and of course the average temperature of heating the material, are significant factors.

In the process of heat transfer in an array of porous materials used for fire protection of thin-walled structures in a fire, several components are involved:

- The process of thermal conductivity with direct contact of the structural particles of the solid phase of the porous material.
- The process of free (natural) convention when moving gas molecules in the free space between the structural particles of the solid phase of a porous material.
- The process of radiant heat exchange between the internal surfaces of the structural particles of the solid phase of a porous material [20, 26].

The intensity of heat transfer processes in an array of porous material for fire protection of thin-walled structures is largely determined by the presence of moisture located in the pores of the material, which is caused by both atmospheric conditions (to less extent) and water ingress during the supply of trunks during fire fighting (to greater extent). If the temperature reaches the boiling point of water under the given atmospheric conditions on the heated surface of the fire-retardant layer, then in the capillaries of the array of porous material a phase transition from a liquid to a vapor begins to occur.

Part of the heat of fire heat is used for this, proportional to the specific heat of vaporization of water, equal to 2200 kJ/kg. As the fireproof layer of the porous material warms up, moisture diffuses in the direction of the heated surface, while moisture drops in the depth of the material array, and a dry surface zone forms near the heated surface. Considering that the steam flow during the movement in the opposite direction of heat as it warms up will absorb part of the energy, fire, the heating process of a thin-walled structure can slow down [23, 28]. In this case, the vapor formed in the array of the fire-retardant layer can cause delamination of this layer from the surface of the protected thin-walled structure, which can be identified as a destructive effect.

However, for flame retardant materials such as perlite and expanded vermiculite, the high porosity provides them with good heat-insulating ability. The dependence of the thermal conductivity coefficient of various types of expanded vermiculite on the composition of the fraction is shown in Fig. 2 [19].

The dependence of the coefficient of thermal conductivity of expanded vermiculite on the fractional composition:

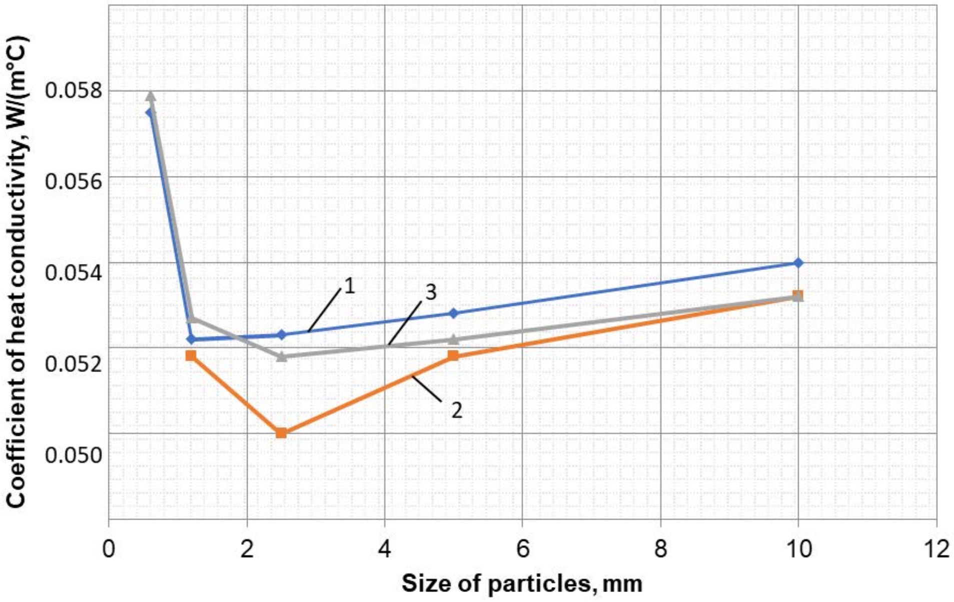

Figure 2. Dependence of expanded vermiculite heat conductivity coefficient from fractional composition: 1. Kovdor hydrophlogopite , sample 1; 2. Kovdor hydrophlogopite , sample 2; 3. Inaglinsky vermiculite.

For the provided samples of fireproof porous materials, the values of the thermal conductivity coefficient fluctuate in the range of 4÷8 %, which follows their analysis of the graphic dependences in Fig. 2

and Fig. 3. A slight increase in the coefficient of thermal conductivity with an increase in the size of structural particles can be explained by the intensification of the process of convective heat transfer in the free space between the structural particles of the solid phase of the porous material associated with the transaction from a free convention in thin layers to a free convention in a large volume. With linear particle sizes less than 0.6 mm, the proportion of gangue decreases, the density of the porous fire-retardant material increases, and the proportion of heat transfer increases due to the process of heat conduction in a solid body.

The shape of the particles making up the porous fire retardant material is also important.

The measurements give reason to argue that the heat-conducting properties of porous materials formed on the basis of lamellar particles are slightly less than those properties of materials whose properties of materials whose particles are closer to the circulations may be the one-sided orientation of lamellar particles, which determines the nature of their contact and the heat flux propagates in vermiculite backfill perpendicular to the sintering plane of lamellar particles.

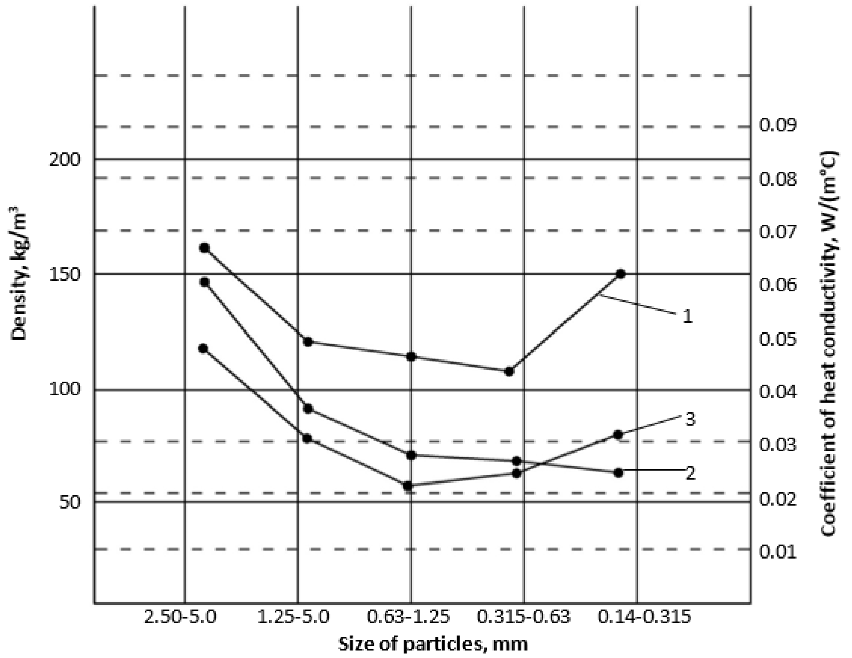

Figure 3. The dependence of the coefficient of thermal conductivity (1) and density and expanded vermiculite (2) and perlite (3) on the particle size.

Graphical Content Analysis the thermal conductivity coefficient and the density and density of expanded vermiculite and perlite on the particle size shown in Fig. 3 make it possible to conclude that the particle size of the solid formation affects the value of the thermal conductivity of perlite.

The experimental data on the thermal conductivity coefficients of porous fire-retardant materials given in [19, 21, 25, 28] are not unambiguous, since the measurements were carried out by different methods, as well as under different atmospheric conditions, for different sizes of solid grains and different characteristics of porosity. This is due to the different nature of heat transfer in the space between the structural particles of the solid phase of the porous material.

It is generally considered that for a porous material its heat-conducting properties of air, since for the solid components of porous materials their thermal conductivity coefficients usually exceed such values for gases, including air.

This statement follows from then proposal that the linear pore sizes of flame retardant materials significantly exceed the mean free path of air molecules under normal conditions. However, in a fire, the thermodynamic parameters in the space between the structural particles of the solid phase of the porous material differ significantly from normal conditions. In this case, for a finely dispersed porous material, the value of its thermal conductivity coefficient can be even less than the thermal conductivity coefficient of air at the same temperature.

Table 1 shows the experimental date obtained for the thermal conductivity of a foreign material, which is silicic acids reduced to a porous state with linear pore sizes of $18 \cdot 10^{-8}$ mm and solid grain sizes of $2.5 \cdot 10^{-8}$ mm.

The values of the thermal conductivity of the domestic material “White Soot BS-280” measured at various temperatures are also given, with the average free path of air molecules for normal atmospheric conditions being assumed to be $10000 \cdot 10^{-8}$ mm.

Table 1. Heat conductivity coefficients of finely dispersed materials depending on temperature.

Material	Heat conductivity coefficient, W/(m°C)	
	At temperature 0 °C	At temperature 50 °C
Santosel	0.0209	0.0239
White soot BS-280	0.01	0.02
Air at normal pressure	0.0237	0.0270

The experiments with silica aerogel with different dispersion characteristics made it possible to prove that the value of the thermal conductivity can decrease to 0.0032 W/(m°C), which is about 10 times less than the thermal conductivity of air measured for normal atmospheric pressure [8].

Increased porosity of flame retardant materials can be achieved by using some features of the shape and structural particles. From the number of thin-walled structure of porous materials is a conglomerate of relatively small ball formation with a diameter of 5÷20 nm. Such materials include silicic acid airgel, white carbon black, “Aerosila” material.

Perlite and expanded vermiculite, the structure of which is cellular in nature, can be attributed to another group, and an empirical equation (1) is proposed to determine the value of the thermal conductivity of such materials:

$$\lambda = \lambda_v \left[1 + \left(\frac{3}{2}(1-P) + 11(1-P)^4 \right) - \frac{1}{2.69 + 0.31 \lambda_m / \lambda_v} \right], \quad (1)$$

P is the fraction of the volume of voids between particles of solid reck.

λ_v is air conductivity coefficient

λ_m is thermal conductivity of solid particles.

One of the most important indicators of the fire-retardant properties of porous materials such as perlite and expanded vermiculite is the thermal conductivity coefficient, so when choosing the right material for fire protection of thin-walled structures, it is necessary to take into account the dependence of the thermal conductivity coefficient of the average heating temperature.

Such experiments were carried out in the work for a temperature range of 200÷600 °C.

Measurements showed that the greatest dependence of the thermal conductivity on temperature is observed in the foam asbestos M-25, which is an ultra-light heat-insulating material: the value of the coefficient of thermal conductivity during heating increased 6 times. For expanded M-150 vermiculite, this dependence is not so pronounced: the values of the thermal conductivity coefficient only doubled [27].

As applied to the properties of foam asbestos, such a significant increase in the coefficient of thermal conductivity can be explained by the presence of significant number of large communicative gaps, in which there are conditions for the development of convective flows of the air. Almost all fibrous heat-insulating materials have a similar structure, therefore, as the temperature of the combustion products increases, which is typical for the initial stage of a fire, therefore, fire protection made of foam asbestos is less effective than fire protection made of perlite and expanded vermiculite. The surface of the expanded vermiculite has a characteristic golden color, which reduces the emissivity of this fire protection material to approximately $C \approx 0.6$ Wt/(m^{2}K^4), which is significantly less than the emissivity of the AHT $C_0 = 5.67/$ Wt/(m^{2}K^4), which can explain the relatively weaker dependence of the thermal conductivity of this material from temperature [20].

A relatively small fraction of the radiation component in the effective heat conductivity of fire retardant thin-walled structures expanding coatings is due to the presence of many tiny thermal screens that formed by porous structure of the substance. They weaken the radiation component of the heat flux aimed at thin-walled structure heating. Therefore, it is desirable to use materials with a small emitting and high reflectivity for fire protection.

They measured reflection coefficients of the surfaces of perlite and expanded vermiculite by a spectrophotometer to evaluate emission factors, and then calculated emissivity value assuming that there is no transmittance.

In case of open fires combustion products temperature can quickly reach 1100 °C and higher, so the fire protection material surface reflectance should be measured for the visible spectrum of the heat fire radiation (λ = 400÷700 nm).

The measuring results of the reflection coefficients of the surfaces of clean and painted black expanded perlite and expanded vermiculite for the visible range of heat radiation of fire are shown on Fig. 4 [23].

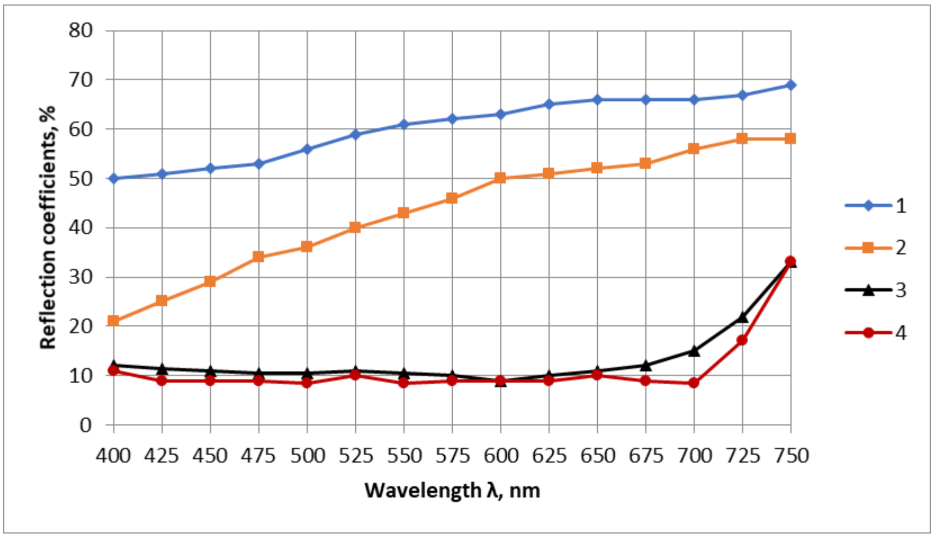

Figure 4. Dependence of reflection coefficient of vermiculite (perlite) from wavelength: 1 – expanded vermiculite, 2 – expanded perlite, 3 – "black" expanded vermiculite, 4 – "black" expanded perlite.

On the basis of measurements results of expanded vermiculite heat conductivity coefficient in Table 2 it is possible to conclude that there is an unambiguous dependence between color of material, condition of its external surface relief (value of reflection coefficient) and value of heat conductivity coefficient of the studied material [20].

Table 2. Coefficients of heat conductivity of black and golden expanded vermiculite.

Color of vermiculite	Fraction size, mm	Density, kg/m^3	Coefficient of heat conductivity, W/(m°C)	
			Probe method	Bicalorimeter
golden	2.5÷5.0	145	0.073	0.080
black			0.085	0.086
golden	1.25÷2.5	175	0.066	0.080
black			0.076	0.085
golden	0.63÷1.25	200	0.072	0.079
black			0.080	0.088

The procedure for detecting the convective component in the thermal conductivity of a porous material is based on determining the difference in values at normal pressure and in vacuum, however, if this deforms the structure of the material cells, this can significantly affect the error, and in the case of significant deformations, such measurements are useless. The fraction of the convective component in the coefficient of the thermal conductivity of the porous materials in % can be calculated using equation (2).

$$\Delta\lambda = \frac{\lambda - \lambda_{vac}}{\lambda} \times 100, \qquad (2)$$

where λ is heat conductivity coefficients of material at atmospheric pressure, W/(m°C);

λ_{vac} is heat conductivity of material in vacuum, W/(m°C),

Table 3 presents the dependences of the thermal conductivity of the expanded aggregates on the bulk density, grain size and color, and air pressure [27].

Table 3. Dependence of the coefficient of thermal conductivity of expanded perlite on the bulk density of particle size and air pressure.

Parameters	Size of solid fraction, mm			
	1.25÷2.5	0.63÷1.25	0.315÷0.63	0.16÷0.315
Poured density, kg/m^3	87	70	65	125
Heat conductivity coefficient at atmospheric pressure, W/(m°C)	0.058	0.054	0.049	0.072
Heat conductivity coefficient in vacuum, W/(m°C)	0.043	0.033	0.025	0.029

The proportion of the convective component of the heat transfer process in the body of expanded fire-retardant materials having a porosity in the body of expanded fire-retardant materials having a porosity in the range 82÷97.5 % can vary in a significant range of perlite: 25.9÷63.5 % and 6.7÷37.1 % of vermiculite, Table 4 [25].

Table 4. The proportion of convective component in the heat transfer of expanded fire-retardant materials.

Material	Particle size of solid fraction, mm			
	1.25÷2.5	0.63÷1.25	6.315÷0.63	0.14÷0.315
Expanded vermiculite	6.7	16.8	16.2	37.1
Expanded perlite	25.9	39.4	40.9	63.5

Increasing of fire resistance of LSTC elements can be carried out not only by using additional fire protection, but also by selecting products that are already part of this construction. As a study of the temperature dependence of the thermal conductivity of composite materials made on the basis of expanded vermiculite, the samples presented in Table 5 were considered and are demonstrated in Table 5.

Table 5. Test samples.

No. sample's	Structure	Density, kg/m^3
1	Vermiculite, wollastonite, liquid glass	360
2		540
3		700

When researching the temperature dependence of thermal conductivity, an IT-λ-400 thermal conductivity gauge was used in the monotonous heating mode.

It was suggested that the oxides in the composition of vermiculite in the temperature range from 0 °C to 400 °C have a decreasing dependence, then it is possible that the thermal conductivity of the material will decrease with increasing temperature. Table 6 and Fig. 5 show the results of studies of the temperature dependence of the thermal conductivity of composite materials, made on the basis of expanded vermiculite, obtained using a thermal conductivity meter. IT-λ-400, in monotonous mode.

Table 6. The dependence of the thermal conductivity of the composite material on temperature and density.

t,°C	λ, W/(m°C)		
	Material No.1	Material No.2	Material No.3
50	0.291	0.304	0.352
75	0.289	0.302	0.349
100	0.288	0.301	0.346
125	0.287	0.300	0.346
150	0.288	0.301	0.346
175	0.290	0.303	0.347
200	0.293	0.308	0.348
225	0.296	0.312	0.352
250	0.300	0.316	0.356
275	0.304	0.327	0.362
300	0.310	0.335	0.368
325	0.316	0.346	0.375
350	0.322	0.353	0.384
375	0.328	0.366	0.394
400	0.331	0.379	0.404

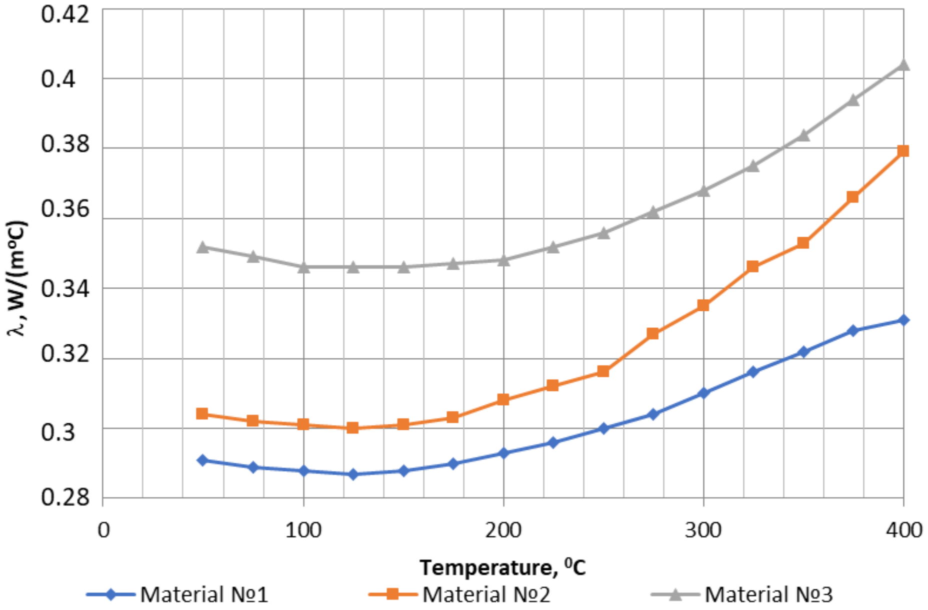

Figure 5 The dependence of the thermal conductivity of vermiculite products on temperature and density.

The experiment showed that the expected results coincide with those expected in the temperature range from 50 °C to 170 °C. Then the thermal conductivity increases monotonically. The distortion of the results can be explained by the radiant component of the thermal conductivity, which begins to increase sharply from 170 °C. With an increase in the density of materials, the thermal conductivity increases.

4. Conclusions

The problem of the working out and research of flame retardants with increased heat-protective properties, as you know, is very relevant. In the light of this problem, the low density and thermal conductivity of intumescent and fire-retardant compositions allow them to be classified as promising materials in the manufacture of heat-resistant and fire-retardant insulation.

In the framework of the presented work, a study was made of the temperature dependence of the thermal conductivity of a composer based on vermiculite, and the studies of domestic and foreign experts in this field were analyzed.

The results of the study confirm the legitimacy of the use of fire-retardant intumescent coating, since with an increase in the temperature of the combustion products the thin-walled fire protection layer made of fibrous materials does not work as effectively as fire protection from porous materials (for example, perlite or expanded vermiculite), as well as, that:

- With a decrease in the size of the solid fraction, the thermal conductivity coefficient of expanded vermiculite increases to a greater extent than that of perlite.
- There is a certain tendency towards an increase in the share of the convective component in the thermal conductivity of expanded fire-retardant materials as the particle sizes of their solid fraction decrease.

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