

THERMOPHYSICAL PROPERTIES OF POROUS MATERIALS

Abstract: *The study of the porosity of thermal insulation made of refractory materials is an important task for the power industry, since the thermal conductivity of porous materials depends on the shape and especially the location of the pores. An analytical review of existing technologies shows that research in this area is not enough to simulate the process of heat and mass transfer in porous alumina material. Experimental determination of the characteristics of heat and mass transfer in porous materials during the formation of a porous structure is a pressing scientific problem. This article analyzes the influence of the composition of materials on the formation of pores, as well as the effect of various impurities and temperature on the thermal conductivity of the material.*

Keywords: *porous materials, composite insulation materials, alkaline silicate, thermal bloating.*

Statement of the problem

Investigation and control of the processes of structure formation of materials are difficult tasks, which are still unsolved. Clear understanding of the mechanism of structure formation makes it possible to develop a methodological basis of new technologies, including the technology of production of thermal insulating materials with predictable thermal properties.

However, the ways of formation physical properties of the material were not found. A lot of experimental data show the relationship between the porosity of the material and its thermal properties [7, 9, 13]. It is obvious that the structure of the materials, in particular the porosity, determines their properties. But in the mentioned works this impact is shown in different ways. For example, in the [13] the thermal conductivity of Fe (58.19 W/(m·K)) and of clay (3.26 W/(m·K)) differ by 18, but the thermal conductivity of insulation structures, which are made from granules of Fe and granules of clay with the same porosity are almost equal – 0.0403 W/(m·K) and 0.0402 W/(m·K). Such results show that not only porosity, but also size and shape of the pores affect the properties of the material. Since any material has an own characteristic distribution of the pore size, it is obvious that various researchers obtained conflicting information about the nature of the influence of pore size on the thermal properties of these materials. Current technologies of structure formation do not provide the prediction of the geometric structure, which means that there is no possibility to predict the properties of materials.

Literary analysis and the problem statement

In [4, 7, 9, 13] the dependence of the thermal properties of porous materials on a structure was discussed, but recommendations about optimal structure were not given. In [2, 3, 5] the dependence of the mechanical properties on a structure of porous materials was analyzed and recommendations about structure formation with predicted properties were given, but there was no information about the thermal properties.

In [6] the influence of internal pore pressure on closed-cell elastomeric foams was explored. Changes of internal pore pressure with different hydrostatic loads were considered. Obtained results show that this pressure can significantly change macroscopic reaction and stability of closed-cell elastomeric foams. Also it shows that elastomeric foams with internal pore pressure have a higher stiffness, even with atmospheric pressure, than without it. But the method of calculating the internal pore pressure was not given. Also pressure was taken only as a function of density. In [14] changes of the structure with a closed porosity under compression and extension, with different initial pressures in the pores, were researched. Experiment results show, that internal pressure has a positive effect under compression and negative under extension. The impact of deformation on the structures with closed porosity can lead to high initial pressure in the pores, which increases the total energy absorption and stiffness of the material under the process of deformation. But nothing was said about the methods of achieving certain pressure in the pores of the material and its calculation.

In [1] the micromechanical analysis of the porous material with internal pressure in the pores was made, the polymer BX-265 was taken as experimental material. The influence of initial pore pressure on the predicted elongation of the sample and the influence of the applied load (with pressure in the pores and without it) on the predicted break of the sample were shown. But nothing was said about the calculation methods of internal pore pressure.

In [12] the dependencies of thermal characteristics from the structure of materials were compiled and the task of the controlled pore formation by adjustable heat treatment of the raw gel-like mixture was formulated. In [8, 10, 11] the main physicochemical formation processes of the gas-vapor area (pores) were analyzed, which were taken as a basis in this work.

All mentioned works have one main idea that materials structure affects their properties. But there are no practical recommendations about formation of specific material structure.

Above information cannot be generalized, because it's contradictory. That's why existing technologies of the thermal swelling (structure formation) can't give the required structure.

The purpose and objectives of the research

The purpose of this work is the research of regularities of gas-vapor phase formation in liquid mixtures, which are in a state of thermodynamic equilibrium.

To achieve this purpose, next objectives must be solved:

- to simulate the condition of thermodynamic phase equilibrium in the liquid mixture to control the process of pore formation;
- to determine the energy parameters of the swelling process (the pressure of the pore former agent gas inside the closed spherical pore, the conditions of thermal balance);
- to determine the overheating temperature of the liquid mixture to assess the growth dynamics of the gas-vapor area;
- to research the growth dynamics of the gas-vapor phase (pores).

Materials and methods of research

Carrying out the practical research into raw mass, we added the chamotte clay or pure structural clay, the composition of which is shown in the Table 1.

The research was performed by the use of differential thermal analysis (DTA) of the thermal bloating process for the raw mixture.

TABLE 1. The chemical composition of fire-clay

No.	Clay	The content of oxides, %									
		SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	CaO	MgO	K ₂ O	Na ₂ O	SO ₃	Lost on ignition
1.	Structural clay	44.59-54.14	27.13-35.85	1.48-2.47	1.14-1.97	0.38-0.81	0.23-0.42	0.21-0.60	0.25-0.45	1.34-3.62	11.48-13.86
2.	Chamotte clay	46.80	36.80	1.58	-	0.20	0.76	0.34	0.18	-	13.6

Trails are performed at a constant rise of temperature with recording the temperature difference on the chart paper as a function of temperature. The result is a curve DTA (Figs. 1-4). At processing the experiment's results, the horizontal axis should be graded by temperature. According to the position of peak of the endothermic process, the temperature interval of phase transitions can be found.

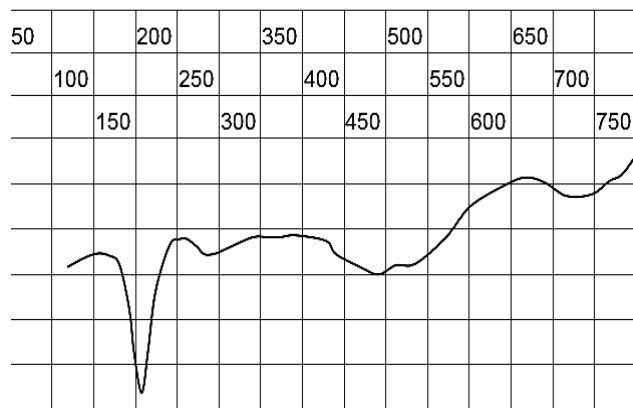


FIGURE 1. DTA of raw material mixture with a content of 75 mass fractions of clay No. 1 (Table 1)

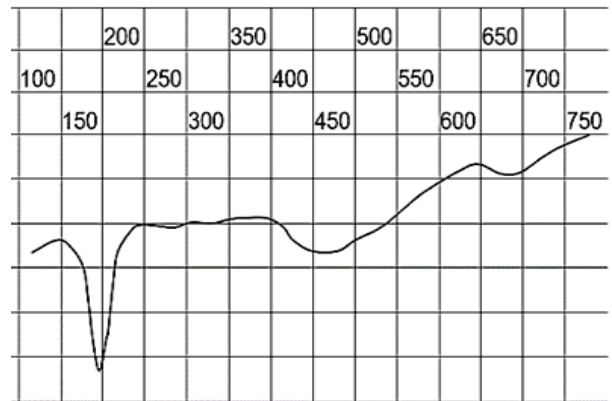


FIGURE 2. DTA of raw material mixture with a content of 75 mass fractions of clay No. 2 (Table 1)

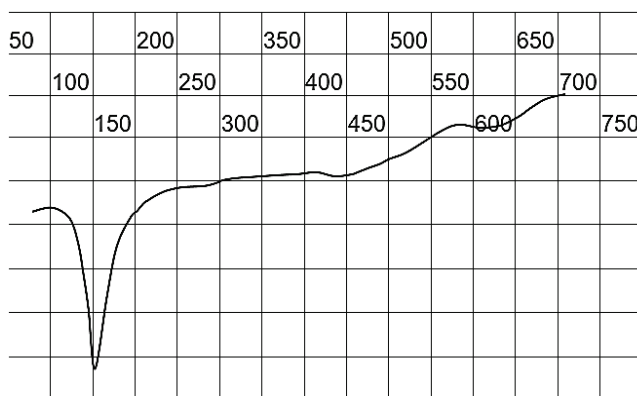


FIGURE 3. DTA of raw material mixture with a content of 160 mass fractions of clay No. 1 (Table 1)

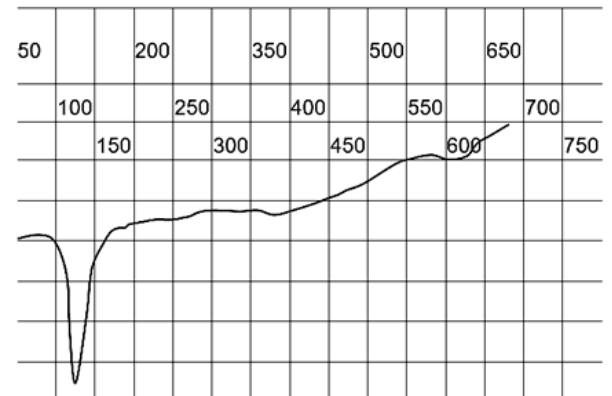


FIGURE 4. DTA of raw material mixture with a content of 160 mass fractions of clay No. 2 (Table 1)

Changes, which had the place during the heating, showed three endothermic effects: 146, 450, and 720. A large endothermic effect due to the removal of absorbed water is at 146°C, and the observed step at 300°C on the curve says about removal of interpacket water. The second effect (450-550°C) corresponds to the removal of the constitutional water (bound into the form of OH). The endothermic effect at 720°C, it explains the removal of OH-ions. As it can be seen from the data chart, the optimum temperature range for dehydration of the mixture is within 146-720°C. It should be defined the connection of temperature intervals with the structure of bloated material, and, consequently, with the

useful application properties (strength, conductivity, heat resistance, water absorption). For this, changing the composition of the initial mixture, the measurements were repeated under method presented above.

On the obtained DTA curves for all experimental samples in the investigated temperature intervals a number of phenomena associated with thermal effects is observed:

- up to 100°C – evaporation of chemically unbound water;
- 100°C, ..., 170°C – a sudden loss of mass and strongly expressed endothermic effect that is related to the partial dehydration of gel and phases of different composition;
- 450°C, ..., 550°C – endothermic effect that corresponds to the decomposition of portlandite with water vapor emission;
- 700°C, ..., 900°C – a minor loss of mass and weak endothermic effect, which is related to the decomposition of carbonate minerals (calcite, dolomite), and late-stage dehydration of gel and hydro aluminates.

The morphology and porosity of the samples were determined by optical methods. According to this method, the macroscopic parameters of porosity inside metric interval with a lower bound of 10 μm and upper bound of 5 mm are determined. The specified interval characterizes the strength parameters of the substance and parameters of heat and mass transfer.

The characteristic feature of the obtained data is that graphs for different types of clay are almost the same. Significant differences are in reading for different temperature minimums. So, for the first endothermic minimum, we received the bloated material with small and almost spherical pores [2, 6]. Most of them had a minimum size. The bloating of the raw material mixture in the second endothermic minimum provides a mixed porosity (spherical cellular and channel). The material becomes less solid. When there is bloating in the conditions of the third endothermic minimum the channel porosity is mainly formed. This material has the lowest strength. You should expect the reducing in thermal conductivity with increasing temperature of bloating.

The obtained material has a low thermal conductivity even at temperatures of 1000-1200°C (Fig. 1). The thermal conductivity of the material was determined by thermal conductivity meter IT – λ – 400. Samples with a cylindrical form (height 5 mm, diameter 15 mm) were put inside the meter and were processed by temperature influence from 200°C to 700°C.

In this temperature range, the thermal conductivity of the material was determined according to the standard method, which is described in the device manual.

Figure 5 shows the experimental dependence of thermal conductivity on the temperature of the material, for technologies of which the main technological stages were simulated.

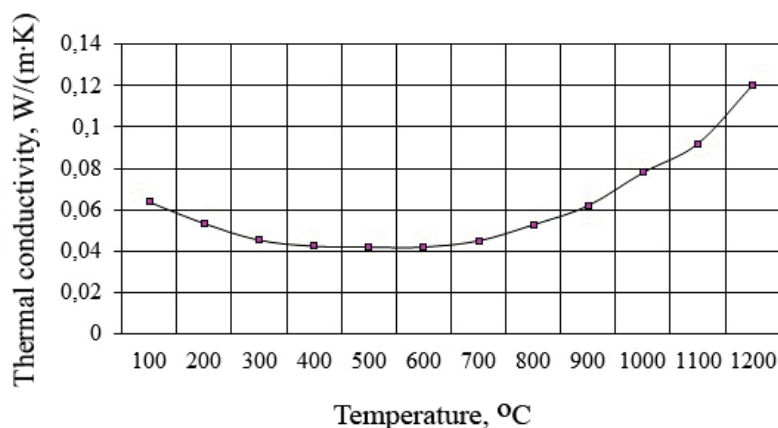


FIGURE 5. Dependence of thermal conductivity on the temperature

Equilibrium conditions of the pore agent in the material, during the formation of the porous structure

As the dynamic characteristic, which determines the direction of size changes in vapor pore, tension difference was taken, which was caused by the pressure in the vapor area and by the resistance of the boundary surface of the pore. The equation, which characterizes the dynamics of growth or reduction of the vapor bubble [12]:

$$\frac{dw}{d\tau} = -\frac{1.5\rho w^2 + P_g - P_n(T)}{\rho_g R} = -\frac{1.5\rho w^2}{\rho_g R} + \frac{P_n(T) - P_g}{\rho_g R} \quad (1)$$

where:

w – speed of growth of the vapor bubble;

τ – time of bubble growth;

ρ – density;

P_g – pressure inside the vapor area;

P_n – pressure in the surrounding liquid;

T – temperature;

R – radius of the vapor bubble.

Increasing, decreasing and stabilization of the bubble sizes can be represented by three cases:

$$\left\{ \begin{array}{l} w = \frac{\alpha \left[(w_0 - \alpha) e^{\frac{1.5\rho\tau}{\rho R}} + w_0 + \alpha \right]}{w_0 + \alpha - (w_0 - \alpha) e^{\frac{1.5\rho\tau}{\rho R}}}; \\ \alpha = \sqrt{\frac{P_n(T) - P_g}{1.5\rho}}; \\ \frac{P_n(T) - P_g}{1.5\rho} > 0; \\ \\ w = \frac{\sqrt{\left| \frac{1.5\rho}{P_n(T) - P_g} \right|} w_0 - \operatorname{tg} \frac{\rho\tau}{\rho_g R}}{\sqrt{\left| \frac{1.5\rho}{P_n(T) - P_g} \right|} + \left| \frac{1.5\rho}{P_n(T) - P_g} \right| w_0 \operatorname{tg} \frac{\rho\tau}{\rho_g R}}; \frac{P_n(T) - P_g}{1.5\rho} < 0; \\ \\ w = \frac{w_0 \rho_g R}{1.5\rho w_0 \tau - \rho_g R}; \\ P_n(T) - P_g = 0 \end{array} \right. \quad (2)$$

In the last case, when $P_n(T) - P_g = 0$ – the gas-vapor area (pore) doesn't change in volume. In the technological aspect, relations between energetic parameters, which characterize the predicted pore size (average), were achieved. Therefore, thermophysical parameters also were achieved, including thermal conductivity.

The equation for finding the speed of size changing of the pore, can be written as:

$$\frac{dR}{d\tau} = \frac{w_0 \rho_g R}{1.5 \rho w_0 \tau - \rho_g R} \quad (3)$$

where w_0 is the initial velocity of the boundary of the vapor region (accept 1).

When solving the equation (3), duration of the swelling process can be found. Since the average value of the pore size is one of the main factors, which determine thermophysical properties of the sample, it this method gives a chance to predict the discussed properties (Fig. 6).

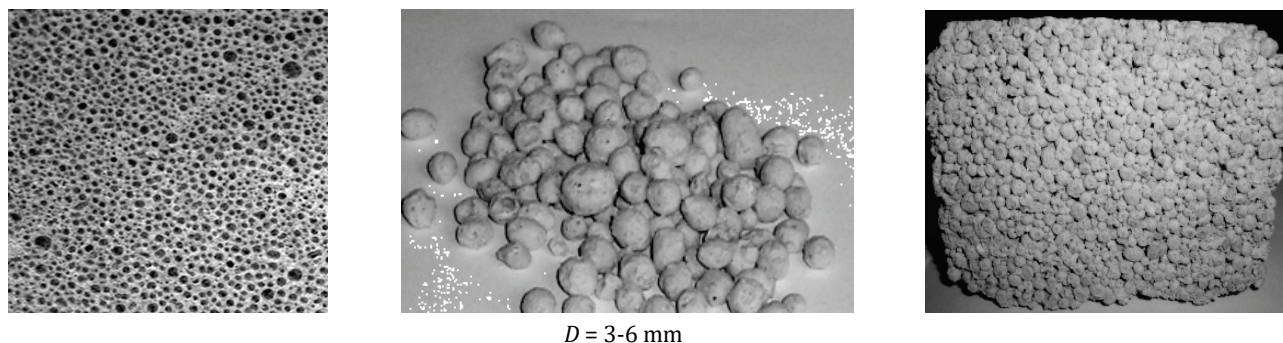


FIGURE 6. New materials for thermal protection of buildings

Conclusions

The solution of creating new porous thermal insulation materials and technologies of their production is inextricably related to scientific research in energy transferring of porous structure during the stages of bloating, hardening and drying under the condition of providing the lowest thermal conductivity and density.

The indicated material properties are determined by a rate of their porosity, the ratio of micro and macro porosities, properties of interporous material that form a kind of supporting structure, which in its turn is determined by the production technology, type of raw materials and conditions of their preparation. All mentioned above impose the special requirements to the formation of material structure to ensure its relatively high strength and durability.

With the help of differential thermal analysis, the modes of heat treatment have been studied; the rational parameters of thermal bloating has been defined that allows to implement the process with minimal energy consumption and the predicted thermal properties of obtained materials.

Conflicts of Interest: The author declares no conflict of interest.

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