Low-vacuum Thermal Insulation Panels based on Silicon Dioxide Powders

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Abstract. The composition and technology of obtaining low-vacuum thermal insulation panels with a powder filler of silicon dioxide and infrared silencer have been developed. The thermal conductivity of the low vacuum insulated products with the use of synthetic silica dioxide and micro-silica - waste production with the addition of titanium dioxide at moderate temperatures with samples of 37.5°C and 1.0°C is investigated. The results of electron microscopy of materials studied are presented. The optimal amount of additive-infrared silencer is determined. It has been found out that low-vacuum products based on micro-silica with an optimal amount of additives have a thermal conductivity lower than that of the air at lower temperatures.

1 Introduction

The problem of energy expenditure reducing is topical in connection with regular and very fast energy recourses prices growth. According to the concept of long-term development of the Russian Federation [1], special attention should be paid to innovative research of efficient energy-saving systems for various fields of industry, construction, housing and communal services, etc. Room heat energy loss is because of high coefficient of filler structures thermal conductivity and ventilation. These factors have not been taken into account in construction before because energy carriers were relatively cheap but in the process of being more expensive there was a problem of room energy efficiency. Earlier building heating insulation was formed by wall thickness increasing but at present time there is no need to do it with modern heat insulating materials appearing. These materials are light, frost resistant and they are used not only in new buildings construction but in old ones reconstruction. The modern market offers a wide range of thermal insulation materials for building envelopes, which can significantly reduce the loss of thermal energy during their operation. The use of vacuum insulation panels (VIP) [2-4] seems to be promising keeping in mind the global trend of reducing energy consumption by buildings.

Production of slabs from loose and powder materials by means of vacuuming technology is a promising technology for the manufacture of slab insulation. Vacuuming helps to ensure durability as a result of reducing the negative impact caused by the effect of condensation of water vapor [5]. High – porous materials – poly-disperse granular powders are used as the main component of filling vacuum insulation panels. Physical bases of thermal conductivity of the powders are discussed in details in publications of G. N. Dulnev [6, 7]. Thermal conductivity of dispersed systems is determined by many factors: the thermal conductivity of the solid frame material, the type and convection of gas in the pore space, its pressure, radiation, the porosity of the frame and its individual particles, as well as the thermal conductivity of the contact between these particles [4, 7, 8, 9, 10].

The creation of vacuum heat insulating panels is strictly based on laws of Physics proving that pressure absence or decreasing inside porous material increases its heat insulating properties.

The investigated low vacuum insulating panel is produced on the basis of open porous structure filler put in gas resisting casing and has three main components -“Filler" which provides mechanical strength and heat insulating properties by free gas flow (air molecules) preventing and thus decreasing heat transfer ability through air conductivity convective component. Theoretically the basic material must have open cell structure with very small size of pores and infrared radiation;

-“Gas impermeable barrier” which serves as a barrier for air and steam and is a casing for the main material. Vacuum panels heat properties and their durability depend on those characteristics.

-“Infrared jammer” added to the filler to decrease thermal conductivity ray component.

The produced FRONT-VIP vacuum insulation panel of VACU-ISOTEC KG Company (Radeberg, Germany) [11] has a filler in the form of highly dispersed silicon dioxide. As a VIP filler, pyrogenic silica is also used, obtained by flame hydrolysis of high purity tetrachloride silicon [11]. However, the pyrogenic silica has a complex production technology and high cost. Therefore, its
replacement, without performance degradation, by micro-
silica is economically and technologically justified.

The TURNA company offers TURVAC Si™ vacuum panels on the base of aerogel, packed in a low-
permeability multilayer foil, which increases the service
life according to the company, to 40...60 years. Low
thermal conductivity (<0.0045 W/(m·K) at 20 mm
thickness) is provided by internal pressure of < 5 mbar
(<500 Pa) [12].

VA-Q-tec AG (Würzburg, Germany) offers vacuum
insulation panels for va-q-vip B and va-q-vip F
construction having a thermal conductivity of 0.007 and
0.008 W/(m·K) at a thickness of 20 mm and 10...15mm
respectively. Internal pressure is <5 mbar, which may
have an increase in 1 mbar per year. The thermal
conductivity of the depressurized panel increases to 0.02
W/(m·K) [13].

Thus, the most promising fillers for the VIPs are poly-
disperse powders consisting of amorphous porous
particles of nano - and submicron size with a developed
surface area and a network of voids of different size.

VIPs are widely used in refrigeration, but their use in
construction is constrained by their high cost, which is
formed, among the other factors, by the need for high
vacuum and reliable sealing, which in turn involves the
use of high-quality expensive materials. In this regard,
the urgent task is to expand the range of the filler based
on local materials and improve the technology of their
production from the standpoint of economic.

2 Initial materials

Silica fume is formed as a by-product of the production
of silicon, ferrochrome and other silicon alloys in electric
arc furnaces as a result of cooling and filtration of furnace
gases. Production of silicon alloys is energy-intensive, so
such enterprises are usually located where there are
sufficient electric power sources [14]. The structure and
properties of amorphous silicon dioxide of various
origins are well studied. This material has been used for
the manufacture of ceramics, flame retardant compounds,
plasticizers, as a filler in polymer composites. This
material is most widely used in the manufacture of
concretes and mortar. A number of countries, including
Japan, Australia, France, Brazil, etc. have developed
standards for the use of silicon dioxide in concretes and
mortars. In the standards EN 13263-1:2005+A1:2009
Silica Fume for Concrete. Definitions, Requirements and
Conformity Criteria and ASTM C1240 - 15 Standard
Specification for Silica Fume Used in Cementitious
Mixtures the basic requirements are presented for silica
fume, as a component of cement materials [15,16,17].

In contribution [9] on the base of data of measurement
of a large set of samples it is shown that SiO2 spheres are
not continuous, but consist of several densely packed
spheres of a smaller size. It is suggested that small
spheres may have a similar substructure. The result of
this arrangement of spherical silicon dioxide particles
will be the presence of tetrahedral and octahedral voids of
various sizes: ~ 40...80 nm (large voids of the first order),
7...14 nm (medium voids of the second order) and 2...4
nm (small voids of the third order) (classification of the
authors [18]).

The structure of spherical particles of amorphous
silica was studied by electron microscopy [19]. The
authors have managed to show that relatively large (~
1000 nm) spherical silica particles consist of smaller
secondary particles with a diameter of ~ 100 nm, which
in turn are composed of primary particles of ~ 5...10 nm.
In this case, large SiO2 particles can contain a central
nucleus consisting of primary particles and surrounded by
several rows of secondary particles.

According to H. Giesche [20], the size of sub-
particles of spherical particles of silicon dioxide is
markedly less than 10 nm and can vary from sample to
sample, being not always recorded by electron
microscopy. In [21] a shell model for the structure of
particles of amorphous silica obtained by the method of
Stober – Fink – Bohn is shown. According to the authors,
the SiO2 particle consists of a central nucleus composed
of primary particles with a diameter of 5...10 nm, and the
shells consisting of layers of secondary particles with a
size of 20...40 nm, covered with layers of primary
particles. The variants of the distribution of primary
particles in the shells and the topology of the pore system
arising at the same time are considered. Fractal and pore
structures of silica particles are largely determined by the
synthesis conditions and parameters of the medium in
which it occurs [22].

![Figure 1. Microphotography of the particles of amorphous silica fume with an increase in 35000X.](image)

3 Methods

Differential thermal analysis was conducted with the help
of machine "STA-TG / DSK" of brand "STA 449 F 1
Jupiter". Curve lines DSK DTG and TG in the
temperature interval of 25–1000°C were got for every
kind of sample. Heating and cooling speed is, 10°C/min.;
X-ray diffraction analysis was performed by diffract
meter "D 8 ADVANCE". Investigation of samples
microstructure was made with the help of scanning
electron microscope "JEOL JSM 700 1F". Thermal
conductivity measurement of vacuum insulating panels
worked by the authors out was performed by the
stationary heat flux method applying thermal conductivity measurer "TCM MG 4 250".

We have conducted studies of the structure and properties of synthetic silica and micro silica - waste production. The study of the structure of the surface of the particles of silica fume was carried out by electron microscopy at a magnification of 50,000 and 35,000 times. On microphotography (Fig. 1) it can be seen that SiO2 spheres are not solid, but consist of several densely packed spheres of smaller size. Small spheres can have a similar substructure. The result of this arrangement of spherical particles of silicon dioxide is the presence of tetrahedral and octahedral voids of various sizes: ~40...80 nm, 7...14 nm and 2,...4 nm. The obtained results agree with the data of [20, 23, 24] contributions, in which the shell model of the structure of amorphous silicon dioxide particles is discussed.

Investigation of synthetic silicon dioxide microphotography (Fig 2.) has shown that the size of the spherical particles of silicon dioxide is much smaller than 10 nm and can vary from sample to sample, being not always recorded by electron microscopy. This conclusion is consistent with the results of R. Ailer [25], who believes that the size of the sub-particles is less than 5 nm. Agglomerates of amorphous silicon dioxide particles are observed in the form of diffuse sphere-like formations.

X-ray diffraction analysis points that silica mainly consist of X-ray amorphous phase and blurry peak shows it in the area 180...300. Crystal phase in the silica sample is actually absent and it is represented by β-quarts (d=0,425; d=0,335; d=0,245; d=0,154), carborundum (d=0,251; d=0,154) and graphite (d=0,335) fig.3.

Conducted research of COVELOS 35/01T synthetic silica and micro-silica of the aluminum plant confirm the existence of a developed pore structure of the particles of poly-disperse powder, which corresponds to a system with a large specific surface. The content of a large number of nanometer sized particles and pores make it possible to use these materials as a filler of vacuum insulation panels.

### 4 Vacuuming composition and technology

On the basis of amorphous micro- silica, synthetic silica and special additives, low-vacuum thermal insulation panels (VIPs) have been manufactured. The VIPs (Figure 5) have, as a rule, a flat parallelepiped form, but can be made in more complicated forms.
The panels consist of an impermeable shell made of metalized polymer composite and the inner membrane layer made of fiberglass. The barrier frame made of gas-filled polymer was used as a shape forming element. The panels were filled with synthetic amorphous silicon dioxide and micro-silica - a waste of industry with addition and without addition of the infrared silencer for which titanium dioxide was chosen. Fillers were thoroughly mixed by sieving through a sieve and dried to a constant mass. The samples vacuuming were conducted at a pressure of 0.085 MPa. The hermiticity of the samples was provided by sealing the edges around the perimeter of the sample immediately after completion of the vacuuming process in a normal vacuum-packaging device.

5 Thermal conductivity tests and discussion of results

The VIPs thermal conductivity was determined at steady-state heat flow at medium temperatures plus 1°C and plus 37.5°C. The test results are shown in Figures 6 and 7.

![Figure 6](image6.png)

**Figure 6.** Thermal conductivity of the VIP samples at an average sample temperature of 1°C.

![Figure 7](image7.png)

**Figure 7.** Thermal conductivity of the VIP samples at an average sample temperature of 37.5°C.

The figures clearly show that thermal conductivity of the compositions based on synthetic silicon dioxide is lower than that of the micro – silica - waste of production. Lowering the average temperature of the samples during testing reduces thermal conductivity. This is mainly due to the fact that lowering the temperature reduces the thermal conductivity of the remaining air. The pressure of 0.085 MPa in the manufacture of samples from the studied compositions of materials does not provide a significant reduction in thermal conductivity. The use of titanium dioxide becomes effective when its content is in the amount of 10 ... 15% compared to the weight of the filler. This effect is observed both for the samples of micro-silica and for synthetic silicon dioxide at elevated (plus 37.5°C) and low (plus 1°C) average temperatures. The thermal conductivity of the VIPs filled with micro-silica with the addition of titanium dioxide has a thermal conductivity lower than that of the air. Due to impermeability VIP do not change their heat insulating properties operating in high humid environment. The performed investigations of micro silica prove developed porous particle structure of polydespersed powders that corresponds the system with large specific surface. Disperse micro silica is aluminum plant industrial wastes can be used to produce low vacuum insulating panels VIP. Prospectively industry wastes applying can become the basis of high quality low net cost VIP manufacturing.

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