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Selection of composition and development of the method of production of a new heat insulation system for protection of equipment operating at temperatures up to 700˚ C.

Sergey Vadimovich Levitin*, Olga Vitalievna Shorsheva, Natalya Aramovna Loginova, Evgenii Evgenievich Lapin, and Artem Vyacheslavovich Ryzhenkov.

National Research University «Moscow Power Engineering Institute», Russian Federation, 111250, Moscow, Krasnokazarmennaya Street, 14

ABSTRACT

The absence of reliable technical solutions with regards to heat insulation of the equipment of thermal power plants and/or industrial equipment operating at temperatures up to 700˚C suggests that the development of novel high-temperature thermal insulation systems has good prospects for the future.

This article offers an algorithm for selection of an optimal composition of a novel hollow glass microsphere heat insulation system and depicts the main phases of its creation. It also presents a general method of fabrication of thermal insulation panels of complex geometric shapes with metal coating for reflection of infrared radiation.

Keywords: high-temperature thermal insulation, hollow glass microspheres, thermal conductivity, heat insulation system, compression, curing, metal layer, *reactive magnetron* sputtering.

Corresponding author

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INTRODUCTION

In order to reduce heat losses during operation of heat power plants and industrial equipment at temperatures up to 700 ˚C one should use high performance heat insulation coatings.

The fabrication of high-temperature heat insulation such as stone wool, basalt superfine fibers, foamed vermiculite, chamotte, perlite and asbestos involves the use of various inorganic binders and (fibrous and dispersing) fillers that can operate at high temperatures (maximum at 700˚C) .

All of them have both advantages and disadvantages; for instance, asbestos is banned in the European Union because it causes cancer [1]; materials made from foamed perlite are not efficient if exposed to high humidity; materials made from chamotte have high thermal conductivity and therefore are heavy and clumsy. A major disadvantage of fiber-filled materials is the impairment of thermal insulation properties occurring when water penetrates into spaces between the fibers. In case of vibration at temperatures ~ 400 ˚C mineral fibers embrittle and clump and as a result do not meet the requirements imposed on thermal conductivity and service life. This leads to significant heat losses and high repair, maintenance and replacement expenses during the entire service life [2.3].

In this connection there exists an urgent necessity to develop a novel thermal insulation system that would ensure high thermal insulation properties and at the same time possess none of the above-mentioned disadvantages.

The last few years have seen the growing interest in the use of hollow microspheres as dispersing fillers of various materials. Because of their low thermal conductivity, low density and high thermal resistance there are good prospects for their use as fillers in a new generation of high temperature thermal insulation.

MATERIALS, EQUIPMENT AND METHOD OF FABRICATION

When selecting the composition of a thermal insulation system one should take into consideration high operating temperatures (up to 700˚ C); therefore the materials are for the most part selected based on their thermal resistance and thermal conductivity. A thermal insulation system has two main components: an inorganic binder and a dispersing filler.

It is very important to choose an adequate binder that would not lose its properties during a long operation at high temperatures. In the first phase of our research we studied the properties of the following binders: aluminum boron phosphate, aluminum chromophosphate, refractory cement and kaolin clay (China clay). We have investigated rheological characteristics of mixtures composed of binders and microspheres mixed in volumetric proportions from 1:1 to 1:10.

The experiments showed that the refractory cement and the kaolin clay have low spatial filling index (up to 1:3) and high density (≥1 g/cm^3). This exerts negative influence on the thermal conductivity of the obtained thermal insulation material, and for this reason we did not investigate the properties of these binders any longer. The physical and chemical properties of aluminum boron phosphate are similar to those of aluminum chromophosphate; however, a material comprising the first of them proved to be less heat resistant; that is why, upon analyzing the results of experiments, we have chosen the aluminum chromophosphate binder, i.e. a water solution of the orthophosphoric acid, its chrome and aluminum salts, chrome oxides and aluminum oxides.

Initially a microsphere is a quasi-liquid medium; its excessive proportion in the mixture can cause phase inversion [4], i.e. the microsphere will become the main medium determining the characteristics of the flow. In this case the mechanical properties of the materials produced from such mixtures are worsened. The optimal solution (i.e. a compromise between conflicting requirements imposed on thermal conductivity, thermal resistance and mechanical strength) seems to be creation of materials from components mixed in a volumetric proportion that is close to that one, at which the phase inversion occurs, but not equal to it. Thus, the maximum proportion between the mixed aluminum chromophosphate binder and the microspheres, at which the mechanical properties are still not worsened, is 1 : 8. Therefore for meeting the specified

characteristics the materials should be produced from a molding mixture, whose above-mentioned components are mixed in a volumetric proportion in the range from 1: 4 to 1:8.

Hollow glass microspheres were used as a dispersing filler. These microspheres have low bulk density (0.11 g/cm^3) and a low thermal conductivity coefficient (0.55 W/m*K). Besides, their ultimate isostatic crush strength is equal to 5 MPa and this circumstance is especially important if materials are fabricated through compression molding because of the high probability of crush of lighter and more fragile microspheres during compression resulting in worsening of strength, thermal and other physical properties.

The primary tests of laboratory samples of a thermal insulation material for mechanical and thermal-physical properties have shown good results. The thermal conductivity of the laboratory samples was equal to 0.089 W/m*K (at 20˚C), the compressive strength being equal to 0.15 MPa and density – to 0.20 g/cm^3. However during the fabrication of the first batch of full-size panels of the thermal insulation system a problem arose: the material became unstable at the stage of curing and the panels were broken and split at the stage of thermal treatment. The only possible explanation of this phenomenon is the presence of water in the aluminum chromophosphate binder: at the temperatures over 100˚C the water contained in the material boils and as the vapor has no way out, it splits the panels from inside.

In order to fix this problem we have added to the molding mixture an additional organic binder that is cured by a catalyst; this enabled us to cure the molded panel at room temperature and at a later stage, when the main binder was cured, the structural integrity of the material was not affected. When selecting a binder, we took into consideration both its thermal resistance and thermal stability. The available options included epoxy, polyester and carbamide resins, but they have rather low thermal resistance at 150-200˚C : in this temperature range they undergo plastic deformation and polyester and carbamide resins are thermally destructed. The optimal option is to use carbamide-furan resin, i.e. the product of polycondensation of carbamide, formaldehyde and furfuryl alcohol in water medium [5] in combination with an acidic curing catalyst. This resin is used in foundries as a component of sand-resin mixtures when making sand casting molds. It has high thermal resistance (up to 350˚C), high resistance to heat shocks and low rate of thermal destruction [6].

mixture of orthophosphoric acid and sulfuric acid can be used as a catalyst for curing this resin; however, as the orthophosphoric acid is one of the components of the main binder, the consumption of this curing catalyst decreases from the recommended 40% down to 10% of the mass of the resin. Thus, during the process of the molded panel curing a part of the orthophosphoric acid, being a component of the aluminum chromophosphate binder, is consumed as a curing catalyst. For this reason the mold mixture was prepared in three stages, so that premature (before the formation of the panel) curing of the resin was prevented.

When the panels were being formed, both the magnitude of the pressing force and the regime of vibration-induced shrinkage played a significant role. The experiments provide evidence that the optimal pressure exerted simultaneously with vibration is 15-20 atmospheres. If the pressure is higher, it happens that upon removal of the load and taking away the matrix the formed panel displayed a significant relaxation behavior that impaired the structural homogenity and later resulted in development of cracks both on the surface and inside the panels.

In case of facilities operating at high temperatures one should reduce heat losses occurring through radiation; the intensity of the latter rises as the fourth power of the absolute temperature of the heated surface. A possible solution is to protect the surface of the heat insulation material with a shielding layer made from materials with low-emission properties and a high reflective index in the infra-red range.

With this purpose in mind we have covered the butt sides of the panels with metal layers; however, the (“own”) surface of the panels was rather rough and this roughness resulted in a low reflective index. In order to obtain a smooth surface we applied a solution of an organosilicon polymer to the butt sides of the panels.

When the binder is vaporized, the polymer forms an even, smooth surface; the metal layer is formed later.

For formation of metal layers on the surface of the panels we have used ionic and plasma deposition techniques; one of their advantages is the use of magnetron systems operating in the continuous double discharge mode.

The high level of influence exerted by ions on the surface of the growing film (that is characterized by both, the ratio of the flux of ions to the flux of deposited atoms and the energy of interacting ions) enables deposition of coatings through reactive magnetron sputtering at low (≤100˚C) temperatures of the products' surfaces [7].

We have chosen chrome as the metal to be sputtered. In the infra-red range its reflective index is lower than that of aluminum, but in contrast to aluminum chrome is heat-resistant in the range of temperatures up to 700˚C.

In order to lay the novel thermal insulation panels in a firm and reliable manner we have chosen a special composition of glues that are available in the market. When selecting the glue, we took into consideration the maximum temperature at which it can be used and its tear strength, as well as the list of the materials to be glued. We have conducted tests using the following glues: К84, Alsiblock-H, Alsiblock-D and КМХ-1 (КМКh-1) and КМХ-2 (КМКh-2) produced by the company 'Gzhel Ceramics' . The glued joints of the thermal insulation system were tested for tear strength before and after thermal treatment at 700˚C during 10 hours. The glues were applied to the laboratory samples of the thermal insulation system in accordance with the user's manuals. Table 1 shows the results of the tests.

Table 1. Strength of glued joints of the thermal insulation system.

Glue brand	Tear strength before thermal treatment, MPa	Tear strength after thermal treatment, MPa
К84	1.1	0.09
Alsiblock-H	3.2	2.4
Alsiblock-D	3.1	0.9
КМХ-1 (КМКh-1)	4.3	2.7
КМХ-2 (КМКh-2)	4.4	2.6

The tests have shown that Alsiblock-H, КМХ-1 (КМКh-1) and КМХ-2 (КМКh-2) were the best-performing glues. However, the КМХ-2 (КМКh-2) glue, which is comprised of two components, does not meet the requirements imposed on the quality of glue seams, because its dispersed phase comprises coarse particles with diameters of up to 1 mm and therefore the glue seam is too thick; in case of tongue and groove the panels were not appropriately joined. Despite the results of the tests, the Alsiblock-H glue exhibited poor ageing resistance: ten days after the heat treatment the strength of the glued joint decreased by 90%. Thus, based on these data, we have selected the КМХ-2 (КМКh-2) glue as our main glue.

We have selected proper equipment for fabrication of thermal insulation panels based on the suggested design of manufacturing processes, including preparation of a viscous mold mixture, its compression and further thermal treatment of the panels at high temperatures.

For preparation of the mold mixture we have used a planetary mixer with detachable blades, whose rotational speed could be varied in the range from 172 to 530 revolutions per minute.

The thermal insulation panels were formed with the use of a hydraulic press equipped with a vibrating motor that produces pressure in the range from 15 to 75 atmospheres.

The panels were dried and cured in a chamber of an electric furnace, whose volume was equal to 1.5 m^3.

The panels were shaped with the use of a 'matrix' of an intricate shape: its side walls have detachable ridges ('tongues') so that the side walls of the panels also have ridges ('tongues') and slots (grooves) for tongue and groove joints; the bottom of the matrix has a (detachable) ridge for formation of a longitudinal slot (groove), and the die is designed to form a longitudinal ridge (tongue) [tongue and groove joint] (figure 1)/

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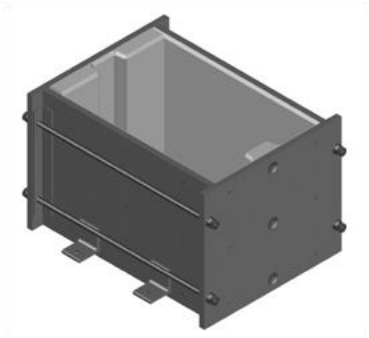

Figure 1. Shape of the matrix.

This design of the panels prevents thermal bridging on all of the sides and therefore reduces heat losses in the thermal insulation system.

A TECHNOLOGY OF FORMATION OF HEAT INSULATION PANELS

The mold mixture for fabrication of thermal insulation panel is prepared in three stages. At the first stage we prepared the mixture comprised of microspheres, aluminum chromophosphate and an acidic curing catalyst; then the mixture was taken away from the mixer and put into a closed – top container. At the second stage we prepared mixtures comprising microspheres and urea-formaldehyde resin. At the third stage we homogenized both mixtures via adding portions of the first mixture to the second mixture with gradual increase of the mixer's rotational speed.

Then we loaded the obtained mold mixture into the matrix of the vibrating press and turned on the vibrating motor for a short time so that the mixture shrank due to vibration. After that the mixture was exposed to both pressure (the die's pressure being equal to 15 atmospheres) and vibration during 5-7 seconds and thus it was compressed. Upon the compression of the mixture the matrix and the die were lifted and the semi-finished panel was taken away. It remained at room temperature during 12 hours for catalytic polymerization of the resin. Then it was put into a chamber of a furnace that was isolated from the ambient air for curing in an oxygen-free medium with the following stage heating: 200˚C during 1 hour, then 700˚C during 5 hours. Upon completion of the curing process the furnace was switched off and the semi-finished panel remained inside it for smooth cooling during 10 hours.

The obtained mold mixture had high dynamic viscosity (at the level of 3 Pa*sec); this resulted in an inhomogeneous volumetric distribution of the density because when being exposed to low pressure the mixture was unilaterally compressed and therefore the densification was not homogeneous and as a result there were defects on the lower side of the panel. In order to eliminate this negative effect caused by unilateral compression we have installed a spring support at the bottom of the matrix in order to generate a force in the direction opposite to the direction of the pressure exerted by the die. This solution enabled achievement of a homogeneous volumetric distribution of the mixture's density and prevented formation of defects.

Table 2 presents the results of the experiments, which have shown that in terms of strength characteristics and thermal conductivity the optimal proportion between the volumes of aluminum chromophosphate and urea-formaldehyde resin was 7:3 and the optimal proportion between the volumes of binders and glass microspheres was 1:6. At the same time the minimal duration of the curing of a panel at room temperature must be at least 12 hours.

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Table 2. Physical and chemical parameters of thermal insulation panels produced from mold mixtures with different composition

Proportion between volumes of binders and microspheres, l/l	Volume fractions of binders, %	Thermal conductivity, W/m*K	Ultimate compressive strength, Mpa	Density, g/cm^3
1:5	50:50	0,121	1.1	0,38
	70:30	0,094	0,97	0,31
	90:10	0,090	0,70	0,27
1:6	50:50	0,11	0,91	0,28
	70:30	0,089	0,75	0,25
	90:10	0,075	0,56	0,21
1:8	50:50	0,097	0,79	0,24
	70:30	0,079	0,65	0,22
	90:10	0,071	0,49	0,21

The process of the curing of the mold mixture occurs in several stages, i.e. it is a combination of a number of consecutive and parallel reactions:

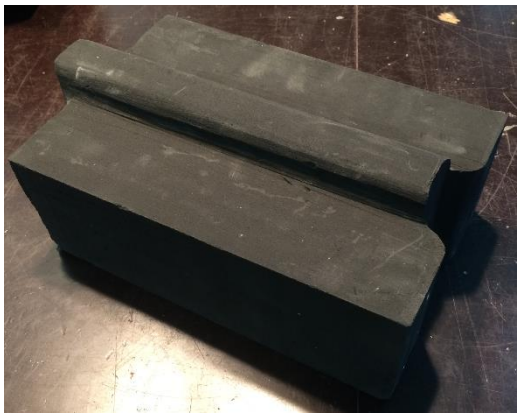
- *at the temperatures in the range from 150˚*C *to 200˚C*:
polymerization of the residual monomer(s) contained in the resin with formation of a cross-linked polymer [8]; in this temperature range the water is vaporized and crystallohydrates in the aluminum chromophosphate binder undergo decomposition [9];

- *at the temperatures in the range from 400˚*C *to 500˚C*:
start of the process of curing of aluminum chromophosphate with formation of polyphosphates and oxides of metals and final removal of the crystallization water [10]; the carbonization of the carbamide-furan resin starts in this temperature range [11, 12];

- *at the temperatures of 700˚C*:
final carbonization of the resin with formation of a carbonic structure [13]; crystals of pyrophosphate of aluminum are released from aluminum chromophosphate [14].

An important feature of the curing process is the presence of acidic medium. The first thermal treatment was carried out in an enclosed volume that was isolated from the ambient air in order to reduce the formation of amorphous carbon. This solution allowed us to increase the strength of the panels.

For making the mounting of the novel thermal insulation system easy the fabricated panels were designed with ridges (tongues) and slots (grooves) for tongue and groove joints(figure 2a, b). Such a design of panels makes the mounting easy, reduces heat losses in the vicinity of joints and increases the overall strength of the system.



a)

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b)

Figure 2. Photos of thermal insulation panels:
a) general aspect of a panel;
b) joining panels.

A solution of heat-resistant organosilicon polymer was applied to the butts of a finished cured panel in order to have smooth surfaces. Then a (chrome-oxide-based) metal coating was deposited on the surface through ionic and plasma sputtering.

CONCLUSIONS

Today there exist no environmentally-friendly reliable thermal insulation systems that could protect surface of the equipment of thermal power plants and/or industrial equipment operating at temperatures up to 700˚C and would have both high strength characteristics and a low thermal conductivity coefficient.

In order to eliminate disadvantages associated with traditional thermal insulation materials one can use a novel thermal insulation system in the form of thermal insulation panels comprising hollow microspheres; the properties of such an insulation depend on the kind and size of the microspheres; this system is characterized by low thermal conductivity, high heat resistance (at temperatures up to 2300˚C) , high level of chemical durability and low density (from 110 kg/m^3) and therefore such a design ensures light weight and a rather small size of the entire system [15, 16].

Based on the results of our research and tests, we have chosen the aluminum chromophosphate binder, i.e. a water solution of the orthophosphoric acid, its chrome & aluminum salts, chrome oxides and aluminum oxides. We found out that, when fabricating a thermal insulation system, there are good reasons to add to the molding mixture an additional organic binder that is cured by a catalyst (carbamide-furan resin) that enables curing at room temperatures so that at a later stage, when the main binder is cured, the structural integrity of the material is not affected.

In order to reduce heat losses via thermal (infrared) radiation we have applied a metal coating to the butt sides of thermal insulation panels using ionic and plasma sputtering techniques.

We found out that KMX-2 (KMKh-2) glue produced by the company 'Gzhel Ceramics' is the best-performing glue enabling a strong and reliable laying of the novel thermal insulation panels.

We have also selected technological equipment for fabrication of thermal insulation systems including equipment for preparation of viscous mold mixture, its compression and further thermal treatment at high temperatures; we have also selected production cycles and process conditions.

As a result we have selected the composition and developed a method of production of a novel thermal insulation system comprising hollow microspheres, i.e. a new ultralightweight material with density of 0.28 g/cm^3, for protection of the equipment of thermal power plants and/or industrial equipment operating at temperatures up to 700˚C.

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REFERENCES

[1] Skrineckaya, A.G., Shipika, A.S. et al. (2012). Analysis of the influence of the asbestos products on human health and environment in various countries. *Proceedings of 5.th regional Conferernce, Donetsk, DonNTU*, pp. 83-87.
[2] Berlin, Al.Al. (1995). Composite polymeric materials. *Soros educational journal*, #1, pp.57-65.
[3] Makarov, V.P., Nedzelskiy, I.A. (2012). Complex biopoplymer binders for fabrication of panels from stone wool . *News of KRSU*, V. 12, # 6, pp. 102-105.
[4] Oganesian, E.T. (2002). Chemistry. A brief dictionary. *Chemistry, Moscow*, p.512.
[5] László-Hedvig, Z., Szesztay, M. (1999). Furan resins (2-furfuryl alcohol based), *in: J.C. Salamone (Ed.), The Polymeric Materials Encyclopaedia: Synthesis, Properties and Applications, CRC Press, Boca Raton, FL*, pp. 548–549.
[6] Fink, J. K. (2013). Reactive Polymers Fundamentals and Applications (Second Edition). *A Concise Guide to Industrial Polymers. A volume in Plastics Design Library*, *Chapter 7 – Furan Resins*, pp. 203-215.
[7] Ryzhenkov, V.A., Kachalin, G.V., Mednikov, A.F. (2013). Prospects for use of ionic and plasma deposited coatings for improving the reliability and extending the service life of friction joints of equipment used in the fuel and power sector. *Nadezhnost' i Bezopasnost' Energetiki,* # 1(20), pp. 41-44.
[8] Mamatov Yu.M. (1974). Furan resins. Fabrication and applications. *Moscow*, pp.73-75.
[9] Kukuj D.M., Andrianov N.V. (2005). Theory and technologies used in foundry engineering. Mold materials and mixtures. Artificial drying of rocks. *Schoolbook, Minsk, BNTU*, pp. 27-31.
[10] D'Jvoize, F. (1961). Bull. Soc. Chem. France, # 12, pp. 2227-2229.
[11] Mamatov Yu.M. (1975). Polymeric materials produced from furan resins and their applications. *Moscow*, p.97.
[12] Ahamad, T., Alshehri, S. M. (2014). Thermal degradation and evolved gas analysis: A polymeric blend of urea formaldehyde (UF) and epoxy (DGEBA) resin. *Arabian Journal of Chemistry*, V. 7, # 6. p. 1140–1147.
[13] Kuznetcova, I.B., Krol, M.S. (1975). Reference book on plastic materials. *Moscow*, V. 2, p. 331-334.
[14] Sychev, M.M. (1986). Inorganic glues. *Chemistry, Leningrad,* 2th edition, p.152.
[15] Bing, Li. (2011). Effect of microstructure and physical parameters of hollow glass microsphere on insulation performance. *Material Letters*, V. 65, # 12, p. 1992-1994.
[16] Katz, H.S., Milewski, J.V. (1978). Handbook of fillers and reinforcements for plastics. *New York: Van Nostrand Reinhold Co.,* p. 652.