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# OBTAINING POROUS THERMAL INSULATING MATERIALS BASED ON ASH FROM THERMAL POWER PLANTS

***Abstract:*** *We report results of research into processes of formation of porous structure by the method of thermal bloating of the gellike mixture of raw materials. Regularities of the course of physicalchemical transformations are considered in the material when it is heated; as a result, we established the initial water content in the raw mixture, optimal for the formation of xerogel, and the residual water content in gel, sufficient for effective bloating. We proposed the optimized composition of the raw mixture that employs maximally permissible amount of ash as a mineral filler; the thermal modes of bloating are studied. Based on the data obtained, a new technology for the production of porous thermal insulation materials is created. New porous thermal insulation materials were obtained using soluble glass as a binding component; foaming agent; regulator of hardening rate of the mixture. The basic thermophysical properties were determined.*

***Keywords:*** *fly ash; thermal power plants; technology; thermophysical characteristics; building material.*

## Introduction

The impact of thermal power plants (TPP) on the environment depends largely on the type of fuel. Coal is most polluted of all energy sources and making the largest contribution to global climate change. In coal power plants account for the biggest share of greenhouse gas emissions in the energy sector, as they have the highest rate of release of carbon dioxide per unit of electricity produced compared with all other fossil fuels. When burning coal into the atmosphere large quantities of solid particles containing not burned carbon oxides and heavy metals emitted as carbon monoxide (CO) and toxic organic compounds, including dioxins and benzopyrene, have carcinogenic effect, fly ash, sulfur and sulfuric anhydride, nitrogen oxides, some amount of fluoride and gaseous products of incomplete combustion. So especially harmful condensation power plants working on low-grade fuels. Among these stations applies Burshtyn TPP.

Solid waste production BTPP is the main fuel slag and ash. Laboratory studies show that in 2015 was formed 526,335 tons of ash and 125,583 tons of slag, which in large near BTPP form parts of ash dumps (Fig. 1).

Most European TPP do not form ash dumps because their rational use, given the content of the ash, useful for technologies manufacturing of building material chemical elements.

***FIGURE 1.*** *Burshtyn TPP (ash storage No. 3)*

## Analysis of recent sources research and publications

In the publications [1-10] shows the advantages of using high-calcium ash in the production of cellular concrete. The use of ashes in the production of cellular concrete in reality presented in various versions, from using it as a main component to the introduction of ash in the raw material as an additive. Since the high-calcium ash has all the source characteristics of materials for the production of cellular concrete (dispersion and binder potential) to the same cellular structure softens degradation expansion ash pore space without developing cracks.

The main barrier using ash as a raw material for the production of building materials is its content of free calcium and magnesium oxides in a state of burnout. Other impediment – is the wide range the composition of highly-calcium ash defining significant fluctuations in the properties (strength, medium density, frost resistance, etc.) of the finished material.

According to literature data, it was found that neutralize the negative impact of CaO ash possible in different ways: physical, chemical, and by sharing with cement or other "diluents".

For the production of high-quality non-autoclave gas concrete, complex and energy-intensive solutions should be used:

- Constantly changing technological modes in accordance with fluctuations in the properties of ash. Thus, in [2] established the optimum mixing time ash and water mass, depending on the timing of grasp the
- All the researchers recommend the use of compulsory steaming and grind in some decisions of high-calcium ash [3] or drying of products [4].

At the same time, some researchers are concerned with the question the use of high-calcium ash for the production of cellular concrete, not only take into account the factor of variability of composition and properties of the ash. Therefore, developed technology, ash gas concrete are characterized by a significant percentage of defective products due to variations in the properties of finished products, and other problems. The latter is often impossible to organize a sustainable manufacturing process using raw materials with a large variation of its composition and properties without correction (composition mass, technological processes parameters, etc.). In addition, the proposed technology is almost impossible to use in small production.

Therefore it is necessary to develop such schemes, the production of non-autoclaved gas concrete based on high-calcium ash TPP that will provide a stable material with high construction and technical properties on technology that does not require steaming, grind and other difficult-to-small enterprises process stages.

You should also explore the possibility of obtaining materials with different structures, for example with a porous structure. These materials can be analogs of foam concrete or porous insulation materials.

## Emphasis previously unsolved parts of the general problem

For production non-autoclave cellular concrete, including small enterprises – the most rapidly developing sector of wall materials today. Classical technology of these concrete is based mostly on cement and sand unground. The use of ash TPP for cellular concrete recommended by the majority of regulatory documents. The greatest effect is achieved by using high-calcium ash.

All the previous decisions on the development of technologies of non-autoclaved aerated concrete based on high-calcium ash TPP on coal were sent to the maximum of their introduction to the raw mixture. This resulted in unnecessarily complex and energy-intensive technologies (permanent change dosages and technological modes in accordance with fluctuations in the properties of ash, mandatory steaming, and some decisions grind components or drying products). All this did not allow to widely implement the proposed technology, especially in small enterprises. Therefore, it required the development of non-autoclave gas concrete technology based on high-calcium ash TPP gives the material with consistently high construction and technical properties on technology that does not require steaming, grind and other complex for small productions process stages.

Changes in the thermal regimes of processing materials containing ash can also ensure the formation of a porous structure. The replacement of cement with ashes makes it possible to also get foam concrete. But to achieve the necessary physical properties of this product, you need to adjust the composition of the initial mixture. This of course required additional research.

In our earlier studies [5, 6], we changed the structure of the material using thermal modes of processing the raw mix and selecting its rational composition. And thus it was possible to get a new porous material that can serve as thermal insulation.

## Problem statement

The purpose of this work is to study the possibility of replacing cement with the ash of the Burshtyn TPP in technologies for producing concrete products, foam concrete and the production of porous insulation material.

We set the goal of our research to find a rational composition of the raw mix for the production of efficient concrete, foam concrete and porous materials with the maximum possible replacement of cement with ash.

The main indicator of porous insulation is thermal conductivity. Therefore, this paper also aims to develop a method for evaluating this indicator for new porous materials.

## Research results. Influence of ash components on structure formation processes

Due to the content in the study ash of basic oxides ($SiO_2$, $Al_2O_3$, $Fe_2O_3$, CaO, MgO, $K_2O$) it can be attributed to the high-calcium mineral resources, which typically use a raw mixture before thermal swelling in the production of TPM. A result we get a solid porous materials [9-12].

The use of ash in pure form in building materials compounded by the negative impact of calcium oxide, which is present in free form in a state of burnout.

Hydration of CaO particles, often covered with a vitreous shell leading to cracking and fracture of hardened material. Neutralize the negative impact of CaO, perhaps in different ways: physical, chemical, and by sharing with cement. The positive effect of in the latter case will occur both due to dilution effect and deterrent effect of destructive phenomena solid cement stone. In our work we use both methods. Since calcium oxide in the ash BTPP not much, each of the methods may be appropriate. The most widely, to eliminate the destructive effects of ash are hardening additive calcium chloride or other chlorides. In our technology for the production of porous concrete to intensify the gassing requires the presence of alkali NaOH, which can be synthesized as a result exchange reactions (alkali in our technology can be added to the raw material mixture as a separate component).

It is possible also to its gradual formation of ash elements BTPP, which would control chemical transformations in the raw mixture in step swelling. New dual compound promote rapid formation of a mixture of plasticity and its early hardening. These properties can be the basis of the controlled process of forming a given structure, which is the aim of this study.

Therefore in the interaction these chemical elements, accelerated hydration CaO and accelerated the process of formation hydrates mixture.

When interacting with lime in the presence of aluminum phases of Portland cement clinker and ash, the reaction to form the hydro-sulfo aluminate and hydro-chlor- aluminate of calcium:

$$\begin{aligned} &\mathrm{nCaO + Ca_3(AlO_3)_2 + 2nNaCl + (m+1)H_2O \rightarrow} \\ &\mathrm{\rightarrow 3Ca_3(AlO_3)_2 \cdot nCaCl_2 \cdot mH_2O + 2nNaOH} \end{aligned} \tag{1}$$

$$\begin{aligned} &\mathrm{nCaO + Ca_3(AlO_3)_2 + 2Na_2SO_4 + (m+1)H_2O \rightarrow} \\ &\mathrm{\rightarrow 3Ca_3(AlO_3)_2 \cdot nCaSO_4 \cdot mH_2O + 2nNaOH} \end{aligned} \tag{2}$$

It will accelerate the hydration of CaO and ash released alkaline solution NaOH.

As a result exchange reactions that occur between sodium sulphate and cement hydration products formed additional quantity of gypsum and alkali NaOH (reaction (2)). Then NaOH easy carbonization by carbon dioxide that enters the solution from the air by the reaction:

$$\mathrm{2NaOH + H_2CO_3 \rightarrow Na_2CO_3 + 2H_2O} \tag{3}$$

Sodium carbonate is primarily interacts with gypsum, as it is most soluble product of cement hydration and under the influence of NaOH, it significantly increased solubility:

$$\mathrm{CaSO_4 \cdot 2H_2O + Na_2CO_3 \rightarrow CaCO_3 + Na_2SO_4 + aq.} \tag{4}$$

Is well soluble sodium sulfate again reacts with calcium oxide to form gypsum and alkali (2). Reactions Eq. (2) and Eq. (3) intermediate and Eq. (4) main.

Because of the fact that Burshtyn ash contains up to 61% aluminosilicate glass phase in the ash-cement compositions will be similar to the reaction between with sodium sulfate. This is certainly a positive moment, since in theory we have the ability to influence the kinetic parameters of swelling. Also, carbonated shrinkage that occurs during the use of products will partly compensate for their expansion deformation due to quenching of free lime.

In the DTA curves hydrated mixture based on fly ash, Portland cement, silicate recorded four endothermic effects, accompanied by a decrease in weight (Fig. 2).

All endo-effects, as the differential – thermal analysis associated with weight loss in a wide temperature range. Significant endo-effect occurs at temperatures 50-250°C extremes of from 115°C to 123°C and is associated with the removal of adsorbed water with helium-like hydration products, such as calcium hydrosilicates type CSH (I), as well as water of crystallization of hydro- sulfo-aluminate of calcium AFt – phase.

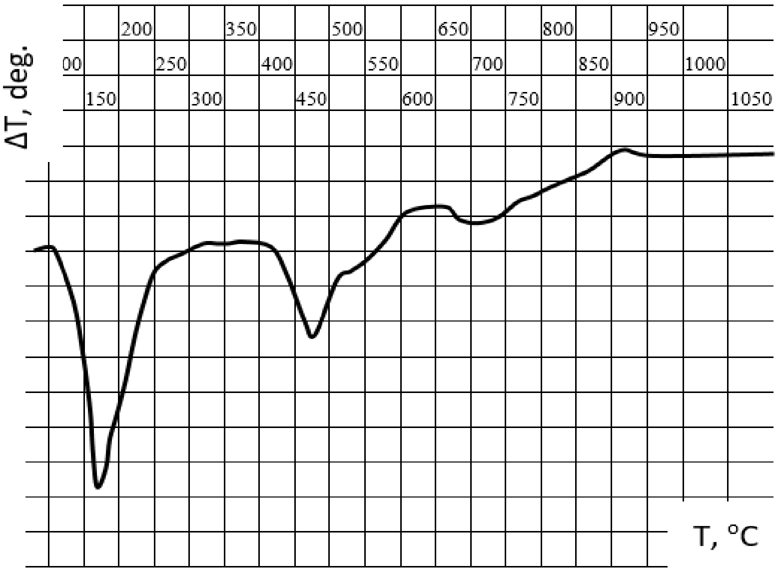

***FIGURE 2.*** *DTA raw mix with the addition of 70 wt. parts of BTPP ash and 5 wt. parts of Portland cement M100 and 15 wt. parts sand pieces*

A clear endothermic effect is observed in the temperature range 370-420°C and describes the process of dehydration of calcium hydroxide scheme:

$$Ca(OH)_2 \rightarrow CaO + H_2O \tag{5}$$

The small endo-effects at 652°C and 780°C associated with the processes of decomposition hydrosilicates calcium (CSH (II)) and calcination calcite. At temperatures of about 930°C, small exo-effect is caused by crystallization tobermo-barito-like gel in wollastonite.

Since the swelling and the formation of structural strength aerated concrete array depend significantly on water-solid ratio (WSR), the first stage searched the optimal amount of water for mixing in ash-cement gas concrete compositions.

For the purpose of determine the effect of water-solid ratio on swelling aerated concrete, aerated concrete mixtures were manufactured with WSR in the range of 0.2 to 0.6. In this case, aerated concrete mixture made based on cement and sand or based on cement and ash Burshtyn TPP (in the ratio from 100 x 0 to 30 x 70) using chemical additives.

The mixture was prepared as follows: samples of ash and sand mixed with water at a temperature of 20-30°C, added cement and stirred for 2 minutes. Further, in each test was injected the same number of aluminum suspension of the calculation of obtaining the average density of aerated concrete 700 kg/m$^3$, stirred for a further 1 minute and poured in volumetric capacity, which was swelling the mixture at an ambient temperature of 20°C. After the complete swelling mixture controlled its height as a percentage of the height of the fill. Then found the perfect amount of water and chemical additives to the maximum height of swelling. The results are presented in Table 1.

Researches have shown that the studied range with increasing WSR height of expanded cement-sand aerated concrete increases. For ash-cement aerated concrete is the optimum ratio for WSR, which is 0.5. With the use of chemical additives NaCl and $Na_2SO_4$ amount of water does not change except for warehouses in which these additives are used in small amounts (0.5%). In our studies, we varied the amount of NaCl and $Na_2SO_4$ from 0% to 5%. Table 1 shows the optimal ratios of these additives. The number of repetitions of all measurements – 6. Decrease WSR in this case is probably due to "dilution" mixture through peptization effect of fine particles that can get aerated concrete with uniform porosity with less water. But the additives do not affect the process of swelling as a dry ash (it prolonged storage) by chemical reactions, these compounds are formed, and adding or increasing their number does not change the quantitative results of this process (as seen also from Table 1).

The use of Burshtyn ash instead of sand can increase the height of the swelling by 70% and the use of chemical additives – an additional 3% to 7% due to the intensification of processes of gas emission as a result of the gradual formation of NaOH in exchange reactions, which activates processes gassing.

***TABLE 1.** Effect of PTS on percentage swelling of concrete (%)*

| Mix | WSR | | | | |
|---|---|---|---|---|---|
| | 0.2 | 0.3 | 0.4 | 0.5 | 0.6 |
| Cement + Sand | 120 | 195 | 220 | 225 | 225 |
| Cement + Ash | 200 | 280 | 350 | 370 | 360 |
| Cement + Ash + $Na_2SO_4$, 1% | 200 | 290 | 350 | 376 | 370 |
| Cement + Ash + $Na_2SO_4$, 2% | 205 | 290 | 355 | 380 | 380 |
| Cement + Ash + NaCl, 1% | 210 | 295 | 370 | 385 | 380 |
| Cement + Ash + NaCl, 2% | 205 | 295 | 370 | 390 | 370 |

The use of chemical additives can reduce the terms of hardening concrete mass as they provide fast water binding and accumulation of solid phase with maximum density filling space frame. In our opinion this is achieved through additional intensive synthesis and AFt AFm phases associated increased amount of $H_2O$, with a high growth rate and ensure the quick formation of structural strength.

Increasing the WSR, more than 0.5 leads to the separation of the initial mixture to form large cavities with a diameter of 2 cm. This is usually due to swelling induction processes and prehension gas. In addition, the increase in WSR promoted extension of swelling and prehension of gas mass since it was accompanied by a decrease in the limiting stress and shear under plastic strength of porous concrete. The introduction of additional quantities of water reduces the strength of concrete, increase their deformation and final moisture content of the material.

The main properties of gas-concrete mixtures directly dependent on the rheology-ash cement and cement-sand aerated concrete. Under the influence of physical and chemical processes occurring in the interaction of cement, coal ash BTPP and water, rheological properties of such mixtures vary. Changes viscosity and maximum stress displacement increases strength plastic systems. The degree of change rheological characteristics depend on the type of raw mixture aerated, water-solid ratio and additives used. From the velocity structure formation gas concrete mixtures depends time of stay in array form. Therefore, the study of rheological characteristics of such systems is an urgent task.

For determination of strength of aerated concrete have been selected compositions with the largest percentage of swelling (Table. 1). The results are presented in Figure 3. Slow structure formation, apparently a slow set of structural strength and increase shrinkage, has a classic cement-sand aerated concrete. It is characterized by slow growth strength, which is to end grasp cement (4 hours) 0.8 Pa, and in 10 hours – a total of 1.8 Pa, while for subsequent technological processes an array of aerated concrete should be 2.50-3.0 Pa.

For ash-cement aerated concrete typical slow rate of recruitment strength, even after 10 hours you can perform various operations that provides technology for manufacturing gas concrete structures. It should be noted that after 1 day strength of cement-ash aerated concrete is higher on average 50-70%.

## Thermophysical characteristics of porous thermal insulation materials

Thermophysical characteristics of porous thermal insulation materials (PTM) are generally determined by the structure, size, type and shape of pores, as well as by their mutual arrangement in the material [1, 2]. Thermal conductivity is one of the most important among these characteristics. Thermal conductivity in porous material is caused by different physical processes and can be reduced to three types: conduction, convection and radiation. Literature sources imply that thermal conductivity dependence is represented as an exponential function [3-5]. These dependencies fail to have a sufficiently clear and pronounced nature and do not allow developing an analytical expression to describe this function, especially at high values of material density.

In our experiments, the thermal conductivity coefficient was determined in the dry and sorption humidity states, not exceeding 20%.

The thermal conductivity of porous thermal insulation materials was studied using an IT - λ - 400 device. Cylindrical test specimens, 5 mm thick and 15 mm in diameter, were placed in the device and heated to 800°C. Within this temperature range, the material thermal conductivity was determined according to the standard procedure described in the device operating instructions.

The observed data were processed using the designed experiment approach. Thermal conductivity is considered as the target function ($Y$, W/(m·K)). The experiment was conducted according to the program of the central composite rotatable second-order design by Box-Hunter [5]. The design nucleus is represented by half-replicated experiment $2^{5-1}$ ($1 = X_1X_2X_3X_4X_5$). The factors, studied in the previous series of experiments, are considered as controllable ones. The selected factors comply with controllability requirements, mutual independence and unambiguity; variable factors shall meet these criteria during experiment design process. 16 experiments were conducted at basic levels and supplemented by another 10 experiments at star points (in our case, the axial distance value is 2) and six experiments at the plan centre. The basic levels, intervals of factor variation and research area boundaries were selected according to results of previous experiments and based on a priori information (Table 2).

*TABLE 2. Basic levels and intervals of factor variation and research area boundaries*

| **Factor** | **Code** | **Value** | | | | | **Variability interval** |
|---|---|---|---|---|---|---|---|
| | | **-2** | **-1** | **0** | **+1** | **+2** | **Δ** |
| Content of Burshtyn TPP ash, weight fraction | $X_1$ | 0 | 30 | 60 | 90 | 120 | 30 |
| Clay content, weight fraction | $X_2$ | 0 | 20 | 40 | 60 | 80 | 20 |
| Water content, weight fraction | $X_3$ | 10 | 30 | 50 | 70 | 90 | 20 |
| Processing temperature, °C | $X_4$ | 100 | 150 | 300 | 450 | 600 | 150 |
| Content of $Na_2SO_4$, weight fraction | $X_5$ | 0 | 3 | 6 | 9 | 12 | 3 |

The response function is approximated by a second-order polynomial:

$$Y = b_0 + \sum_{1<i<k} b_i X_i + \sum_{1<i<k} b_i X_i^2 \sum_{1<i,l<k} b_{i,l} X_i X_l \qquad (6)$$

where $k$ is the number of independent variables.

The observed data processing and analysis of regression model were performed using “Experiment design” module of Statgraphics 5.0 Plus statistical program. The significance of model coefficients was determined using P-level and shown on a standardized Pareto chart. The vertical line in Figure 3 corresponds to 95% of the statistical significance of coefficients.

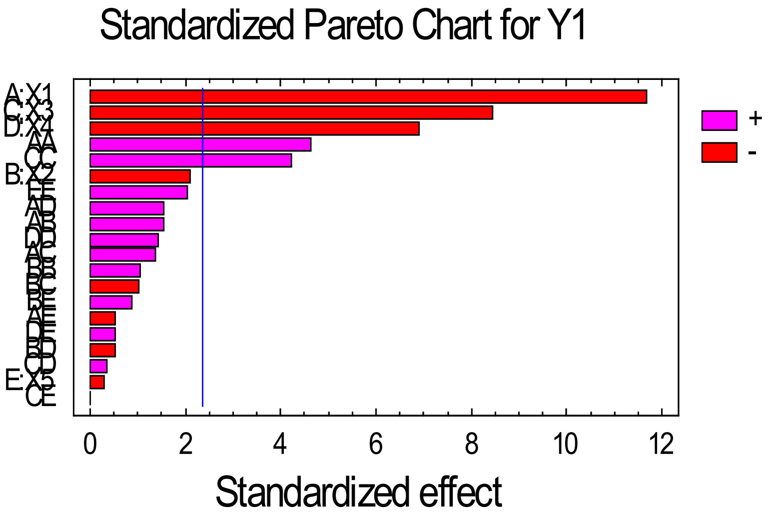

***FIGURE 3.*** *Significance of model coefficients (Pareto chart)*

According to data in Figure 3, the coefficients for linear terms of the regression equation for ash, water and temperature contents are considered as statistically significant. In this case, the coefficients for pair-wise interactions are statistically insignificant and may be neglected for this model calculation.

Regression equations, considering significance of coefficients are as follows:

$$\begin{gathered} Y1 = 0.978724 - 0.00966389 \cdot X_1 - 0.00824062 \cdot X_3 - 0.000705556 \cdot X_4 + \\ + 0.0000322917 \cdot X_1^2 + 0.0000664062 \cdot X_3^2 \end{gathered} \tag{7}$$

The model adequacy to the analysed process is confirmed by a high value (about 100%) of determination coefficient $R_2$ = 99.44%, and low value of standard error of estimate SE = 0.1598.

Figure 4 shows the comparison of observed and predicted data.

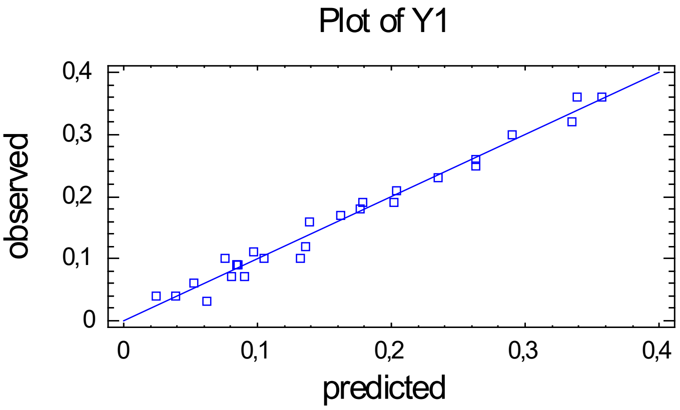

***FIGURE 4.*** *Comparison of observed and predicted model data*

As can be seen in many cases, the difference between these data is negligible. Most of the experimental points are located near the straight line.

In Figures 5 and 6 the surfaces of pair-wise factors effect on thermal conductivity of Burshtyn TPP ash-based PTM.

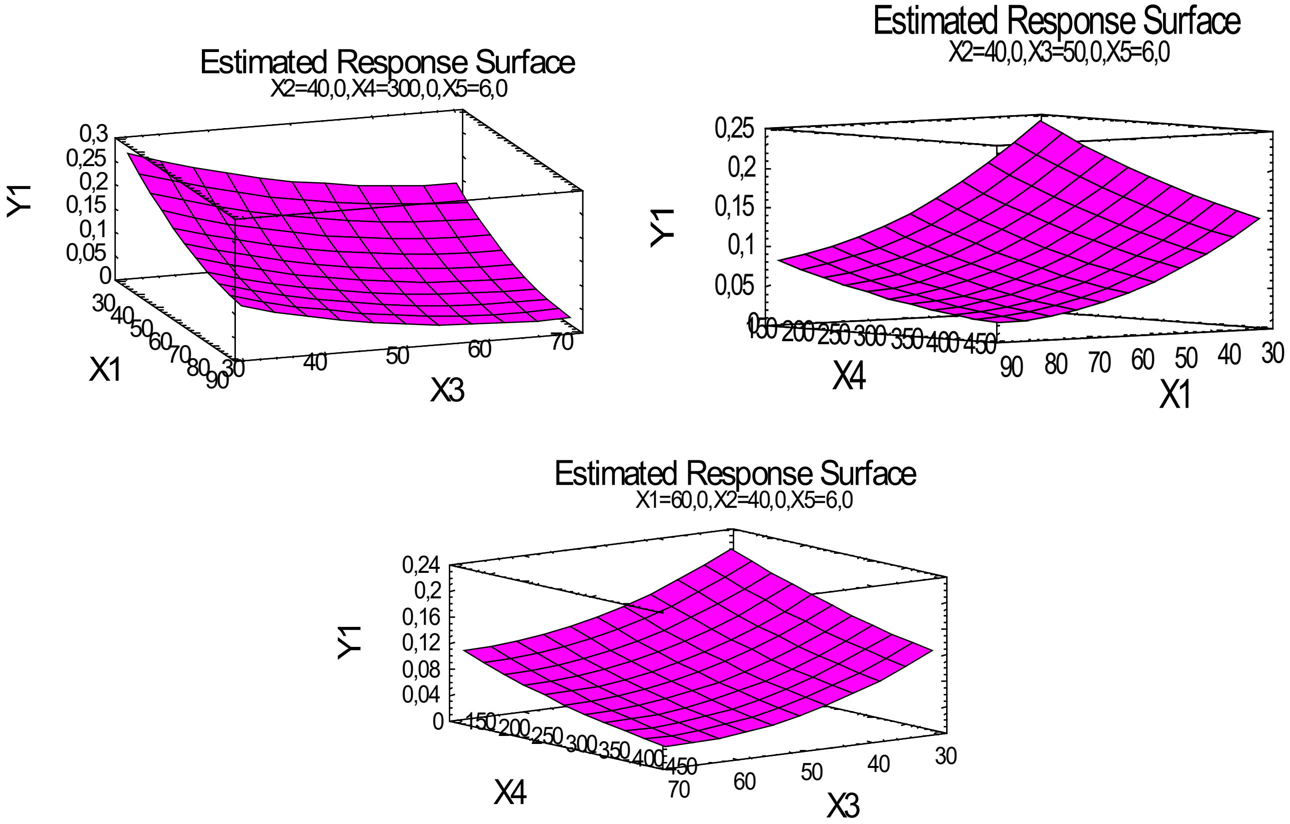

***FIGURE 5.*** *Surfaces of pair-wise factors effect on PTM thermal conductivity*

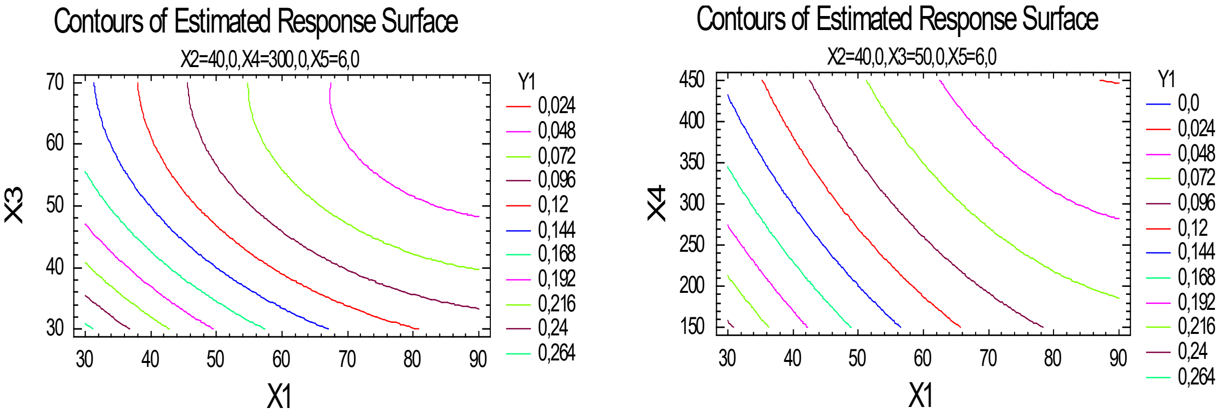

***FIGURE 6.*** *Surfaces of pair-wise factors effect on PTM thermal conductivity*

## Conclusions

As it is obvious from three-dimensional cross sections of hypersurface $Y_1$ ($X_i$) and contour curves of these surfaces, thermal conductivity of porous thermal insulation materials increases as the weight fraction of Burshtyn TPP ash ($X_1$) and water content ($X_3$), as well as swelling temperature ($X_4$) decrease. It goes in line with our understanding of the effect of specified factors on thermal conductivity.

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