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Wall Ceramics Products Based on Opoka and Coal Slurry

V.D. Kotlyar*, K.A. Lapunova, G.A. Kozlov

Rostov State University of Civil Engineering, Socialisticheskaya St. 162, 344022, Rostov-on-Don, Russia.

Abstract

The article shows high prospects of high-performance wall ceramics products with average density less than 700-800 kg / m^3 and thermal conductivity less than 0.15–0.20 W/(m · °C) manufacturing with minimum costs. There is a brief description of siliceous opal-cristobalite rocks - opoka and by-products of coal processing - dehydrated coal slurries being valuable man-caused raw material. The results of studies on the production of ceramic stones of high efficiency compression molding based on clay and clay-carbonate opoka with the addition of coal slurry are shown. The main technological factors and regularities affecting the properties of products are defined. The results of research on the impact of the amount of coal slurry on the strength, density and water absorption of products taking into account the firing temperature are given. The phase-logical and mineralogical transformations occurring during firing were examined. The recommended process scheme for the production of highly efficient ceramic stones is given. The feasibility study for the products manufacturing of this type on the basis of opoka and coal slurry is given

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Keywords: ceramic stones; opoka; coal slurries; density; strength; compression molding.

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1. Introductory

The successful development of building industry is inextricably linked with the production of building ceramics products, the production nomenclature of which is expanding continuously. A special place among the products of wall ceramics is occupied by large sized high-performance products with an average density less than 700-800 kg/m^3 and thermal conductivity less than 0.15–0.20 W/(m · °C). If in western Europe their share in the total volume of wall ceramics is 60-70%, in Russia it's only 10-15%. That is why, the actual practical task is a significant increase

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* Corresponding author. Tel.: +7-928-904-7225; fax:+7-863-201-9057.
E-mail address: diatomit_kvd@mail.ru

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in the production of high-performance products of wall ceramics and the successful solution of this problem is impossible without large-scale research.

The most important measures that increase the efficiency of production of wall ceramics products are: reduction in the density and thermal conductivity of products by increasing the porosity of a crock and the emptiness of products; improvement of physical and mechanical properties; reduction of production costs and speeding of the technological process. One of the limiting factors in this case is the raw material base. Many plants for various reasons have difficulty precisely with raw materials. Qualitative clay raw material is used for the production of fine ceramics and facing bricks and its cost is high enough.

Factories have to use raw materials having unsatisfactory properties, containing harmful sulfur impurities and carbonate inclusions. That is why, the expansion of the raw material base with the use of new non-traditional raw materials is a topical scientific and technical challenge for the wall ceramics industry. As one of the perspective ways of solving this problem is the use of siliceous opal-cristobalite rocks - opoka with a wide spread in many regions of Russia and foreign countries.

The second important point is the maximum reduction in the cost of products, which in enlarged form consists of the cost of plant construction and production costs. In this respect, a more promising technology is compression molding of wall ceramics products. Its main advantage compared with the extrusion process are as follows:

- unit capital costs for the construction of the enterprise is substantially lower;
- technological cycle of production is reduced to 1.5-2;
- technical weaponry of plants, the level of mechanization and automation of the manufacturing and transportation processes of raw materials and semi-finished products are increased;
- unit fuel consumption is reduced, since the drying of molded products is replaced with the insignificant adobe brick drying;
- the cost of production is reduced by 20-35%, mainly due to the reduction of labor costs and reducing fuel consumption.

In addition, a significant source of firing cost reduction , and accordingly, the unit cost can be the use of by-products of coal benefication- coal slurries. Moreover, their use as a mix ingredient allows to reduce the density of a crock and thermal conductivity of products, at the same time, as experience has shown, achievement of the density of at least 800 kg / m^3 and a thermal conductivity less than 0.20 W/(m · °C) is most favorably in a combined way - due to the formation of the porous structure of the crock and the emptiness of the products.

2. Topicality and scholarly importance of the issue

Many researchers have been studied the issue of production of large-scale perforated cellular products of wall ceramics [1-3]. Interest in siliceous opal-cristobalite rocks - opoka as in ceramic raw material is relatively recent [4-11]. Conducted by us and other researchers studies have shown high promise of using this type of raw material for the production of various types of wall ceramics. However, the issues of obtaining large-scale products with burnable fuel-carrying additives, issues of phase transformations during firing, the formation of structure and properties of the products were not touched upon.

The use of waste coal and coal benefication in the production of wall ceramics has been known for a long time [12-15]. The main role carried by coal slurry is reduction of fuel consumption on firing and decrease in the average density of the products. However, experiments on their use together with opoka have been barely performed. The issues of the formation of properties of the products and firing, phase and mineralogical transformations during firing and peculiarities of technology have not been studied. Taking in consideration the above, topicality of studies of production of large-scale wall ceramics products based on the opoka and coal slurry raise no doubt.

3. Statement of the problem

The aim of the research is developing of the scientific and technological foundations of the production of high-performance wall ceramics products based on siliceous opal-cristobalite rocks - opoka and waste coal - coal slurry. Tasks of the research, the results of which are performed in this article are as follows:

- to determine technological parameters of the production of high-performance wall ceramics products based on the opoka and coal slurry;
- to examine properties of the resulting products;
- to study phase transformations occurring during the firing and patterns of the formation of crock structure.

4. Theoretical part

Opoka is light microcellular rocks composed mainly of microparticulates opal silica. There are always clay minerals in one amount or another in opoka, mainly from the group of hydro micas and montmorillonite, in carbonate kinds of opoka. The color varies from yellow to dark gray. The average density is about 1200-1600 kg/m^3 and porosity of 40-60%. In general, the chemical and mineralogical composition of the opoka is very diverse. Usually they deposite on the surface being relief-forming rock. The fields are characterized by high capacity of the rock and consistency of the mineral composition.

A more rational thing for opoka, due to its stonelike structure and low plasticity, is a compression method of products manufacturing. Density of the crock based on opoka is 1.3–1.6 g/cm^3. The possibility of manufacturing of wall ceramics products based on opoka was proved in our previous studies [4–8].

Coal slurry is a large-tonnage, fine-grained waste in the solid part of which there is a significant amount of coal. In recent years, the amount of coal slurry increased dramatically, not least due to an increase in ash content of produced coal, fines content, etc. [15,16]. At present, only Rostov region has accumulated tens of millions of tons of coal slurry, which can become a compound fuel-carrying and pore-forming component in raw masses of brick factories. Their use allows to reduce gas consumption in the firing and cost of products.

Coal slurries in dehydrated form are dark gray, almost black powder with fraction composition 0–1 mm with fraction content less than 0.5 mm on average 60-80% (Fig. 1).

Fig. 1. A micrograph of coal sludge

In regard of chemical composition in a qualitative sense coal slurries are similar to clay rocks. However, the quantification of basic oxides content can change due to fluctuations of the coal component. Table 1 shows the averaged data on the chemical composition of Eastern Donbass coal slurry with and without carbon component with an ash content of about 50%. The amount of coal itself in the slurries may be from 20 to 55%, the calorific value - 2000 to 4200 kcal/kg.

Table 1. The average chemical composition of coal slurry

LOI	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	K_2O	Na_2O
49,98	29,38	10,71	3,49	1,11	0,80	1,01	1,94	0,55
2,0-4,0	54,2-60,6	17,7-21,9	5,6-8,2	1,2-4,0	0,9-2,0	1,2-2,8	3,2-4,4	1,0-2,0

The predominant coal sludge components in addition to the coal component are claystone-like clays, argillites and clay shales. There are grains of siltstones, sandstones, feldspar as impurities. Fine particles of calcite may occur in a small number. Clay in the waste material has polymineral composition with the predominance of hydrous micas and kaolinite. Figure 2 shows coal slurries X-ray of "Obukhov" factory that is typical of the Eastern Donbass.

Sharp peaks 998, 500, 256 pm indicate the presence of hydrous micas of illite type. According to the peaks kaolinite is diagnosed (710; 355; 233 pm), as well as minerals from the chlorite group of chamosite type, tyuringit etc. (1400, 710; 469; 353; 348; 200 pm). Presence of minerals of the amphibole group - prenit - is diagnosed (348; 281 pm). Peaks 307, 460 pm and others indicate the presence of pirofillits. Its composition - $Al_2O_3 \cdot 4SiO_2 \cdot H_2O$; Al_2O_3 - 28,3%, SiO_2 - 66,7%, H_2O - 5,0% almost always shows perfect formula. Its crystal structure contains three-layer pack, consisting of 2 layers of SiO_4-tetrahedra connected by the layer of octahedra $[Al(O, OH)_6]$ and during weathering it cnahges into kaolin. A small peak of 318-320 pm indicates the presence of feldspars. Quartz is clearly diagnosed by high intensity peak 334 pm and other minor peaks (1,813; 4.24; 2.45; 2.28). The presence of montmorillonite in waste coal is quite rare. The coal component was marked by broad halo at angles 10-30^0 2Θ.

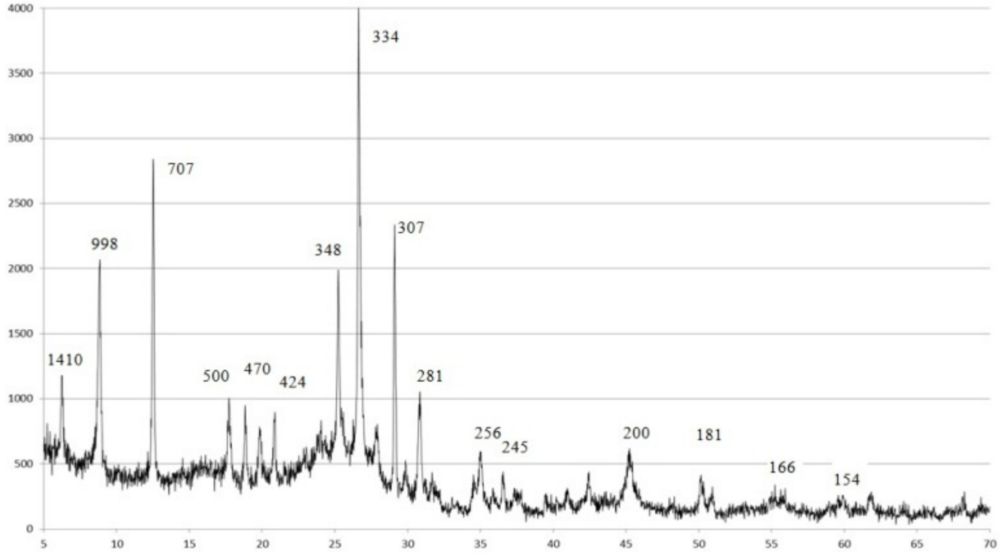

Fig. 2. Coal sludge radiograph

Taking into consideration the fact that the mass fraction of K_2O in mica and hydrous micas is about 10%, the content of given minerals in coal sludge is about 20%. The size of silicon module (Al_2O_3/SiO_2) equal to 0.36 indicates hydromicaceous-kaolinitic association of clay minerals taking into account the presence of chlorites, pyrophyllite and other minerals. In general terms, the value of silicon module for clays varies from 0.25 to 0.38. Montmorillonite has the lowest one, kaolinite - the highest. According to this indicator, one can determine the approximate amount of clay minerals.

It is necessary for one to know the processes taking place during firing for the maximum efficiency of coal slurry using in the production of wall ceramics. This will allow to predict the number of input sludge, firing modes, the flow of gaseous fuel, etc. As an example, we provide the description the transformations taking place during firing of sludge of "Obukhov" being typical for the Rostov region. A large number of coal component levels the effects associated with the presence of clay minerals. A large number of coal component eliminates the effects associated with the presence of clay minerals. Large exo-effect associated with the oxidation of anthracite evolves. Its peak is reached at a temperature of its inflammation 600-660 °C together with a large weight loss. Prior to this, beginning with 250 °C temperature one can observe a slight weight loss associated with the oxidation of dissipated organics, and beginning with 500 °C temperature and with the release of the bound water from the crystal lattice - clay minerals. However, associated with the moisture loss of clay minerals, is overlaped with a large exo-effect of anthracite oxidation. A small step in the region of 500 °C in the DTA curve indicates this.

Thermograms of the pointed out mineral component of coal slurries are characterized by the removal of water at 120-160 °C temperatures; by smooth exothermic effect caused by the oxidation of the remaining organic substances; by endoenergic effect at the temperatures of 570-575 °C, associated with polymorphic transformations of quartz as well as endoenergic effect associated with the loss of crystal water of such minerals as kaolinite, illite, pyrophyllite, mica, chlorite. One can also observe small exothermic effects at temperatures of 960-1000 °C. This is determined by the presence of kaolinite and pyrophyllite. These minerals lose crystalline hydrates at the temperatures ranging from 550 to 800 °C, and thereafter formed metakaolinite representing a close association of silica and alumina, changes from crystal structure to the amorphous state at 980-1000 °C, that is reflected by exothermic effect of amorphisation. These findings stand together with the results obtained by other researchers [17-19].

5. Results of experimental studies

The amount of fuel introduced into the raw mix can reach 80-90% of the amount of fuel needed for products firing. Gas in fact is used only to support the firing and its flow rate can be reduced to 20-40 m3 per 1,000 pieces of a conventional brick. However, to obtain high-quality products with using coal slurries it is necessary to maintain an oxidizing atmosphere during the entire firing cycle in the furnace for complete carbon burnout and to provide the adjustment of a firing mode in each zone of the furnace.

The use of opoka with coal slurry has the following positive aspects. In clay masses, due to their low gas permeability, the problem when entering the coal slurry is incomplete burning of the coal component. This entails a reduction in physical and technical characteristics of the products, increase of the duration of the firing process and the inability to make full usage of coal slurries for gas savings. High porosity of the opoka and high gas permeability promotes the burning of the coal component. Maximum rate of carbon burning is in the range 900-950 °C, i.e., below optimum temperature necessary for products burning. It contributes to substantial gas savings. In addition, coal slurries improve compressibility of press powders based of the opoka. They work as a plasticizer. In the process of its entering the compacts strength increase, the ratio of compression and press powder humidity is reduced, internal and external friction during compaction is reduced, the service life of the press tooling increases, the uniformity of the products firing is achieved and their resistance to frost increases. We have conducted laboratory-technological researches with variety of opoka deposits and coal slurries of many washing plants. As an example we give the results of experiments and set dependencies for opoka of Zhuravsky deposit and coal slurries of "Obukhov" washing plant. Opoka of Zhuravsky deposit of Rostov region is carbon-bearing and medium-alumina according to lithologic and technological type. Its composition is shown in table 2.

Table 2. The chemical composition of the opoka of Zhuravsky deposit

LOI	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	K_2O	Na_2O
8,28	66,18	10,54	2,97	8,55	0,95	0,30	1,42	0,62

During the laboratory-technological researches opoka was preliminarily pulverized in a dry form before passing through a sieve of 1.25 mm, with the fraction content of less than 0.315 mm about 50%. Then, raw mixes were made in a predetermined ratio. Thereafter the samples were pressed at a pressure of 20 MPa. Calculations have shown that the maximum content of coal sludge in the raw mix should not exceed 20-25%. Figures 3 and 4 show dependencies of the influence of coal slurries quantity in raw masses on the density and strength of the samples.

Experiments have shown that close to the optimum ones for the given raw materials firing temperature is 1000-1030 °C, taking into account full carbon burnout and main properties of the products. As can be seen from the results of the researches, mean density of the samples naturally declines during increase in the coal slurries' content in raw masses. More considerable density decline occurs at a small content of the sludge, and with an increase of its content the process slows down. This occurs due to the intensification of baking and active interaction of the components of coal sludge and opal silica of opoka. It can be seen on the graphs by gradual flattening of the density curves. As seen, density of the products of less than 800 kg/m^3 is achieved at a sludge content of 15-25% and a product porosity of 35-45%. Density of the products naturally declines with an increase of the sludge content. Nevertheless, the samples density is high enough for the production of hollow products with M100-150 strength marks, that is quite acceptable for supporting and enclosing structures. The microporosity of opoka provides a complete carbon burnout and a good products exterior. The crock structure as well as the porosity of the products predetermine their low thermal conductivity - less than 0.20 W/(m · °C). Further significant decline in thermal conductivity of the products can be achieved by filling the voids with insulating materials - foam concrete, mineral wool, etc.

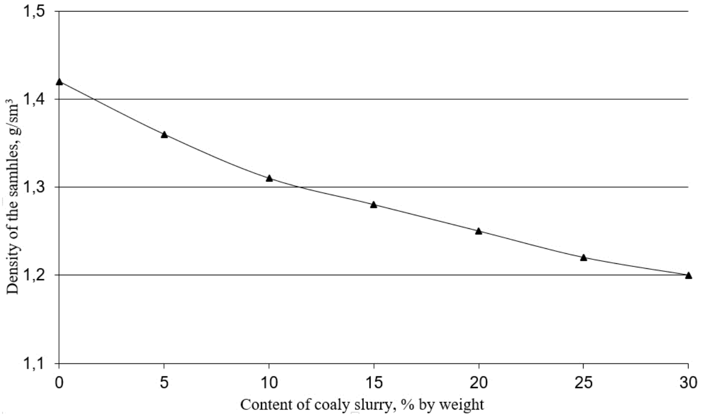

Fig. 3. Influence of coal slurries' content upon mean density of the samples

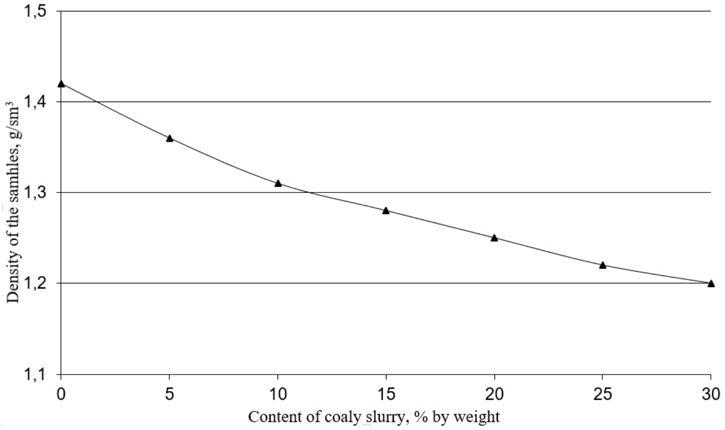

Fig. 4. Influence of coal slurries' content upon density of the samples

Technology of production of ceramic stones of compression molding on the basis of opoka and coal slurry has its own peculiarities associated with many technological highlights. The question of the shape and size of voids requires careful examination taking into account technological process of products formation, their physical and mechanical properties, thermal conductivity, etc. In light of technology, the round or square cavities with smooth corners uniformly arranged round the product area, with a total porosity of 25-45% are optimum [20,21].

Changes in coal slurries and ceramic masses occurring during the firing were studied with the help of X-ray diffraction. Figures 5-7 show X-ray patterns of coal sludge of Obukhovskaya washing plant fired at different temperatures.

The total intensity of the diffraction peaks declines at the firing temperature 900 °C, which means a total amorphization of crystalline phases. Mica, hydromica (999, 502 pm) and amphibole (348; 281 pm) partially retain their crystal lattice. A significant reduction in quartz peaks' intensity points out at its amorphization and quantity reduction connected with the change into the melt. It occurs due to a high content of alkalies and iron. Introduced peak of 251 nm indicates the appearance of hematite. Burnout of coal component is confirmed by the absence of a broad halo at angles 10-30^o 2Θ. The intensity of quartz peaks declines. There are clearer peaks characteristic of the hematite (269, 182 pm) and feldspars (318-320 pm).

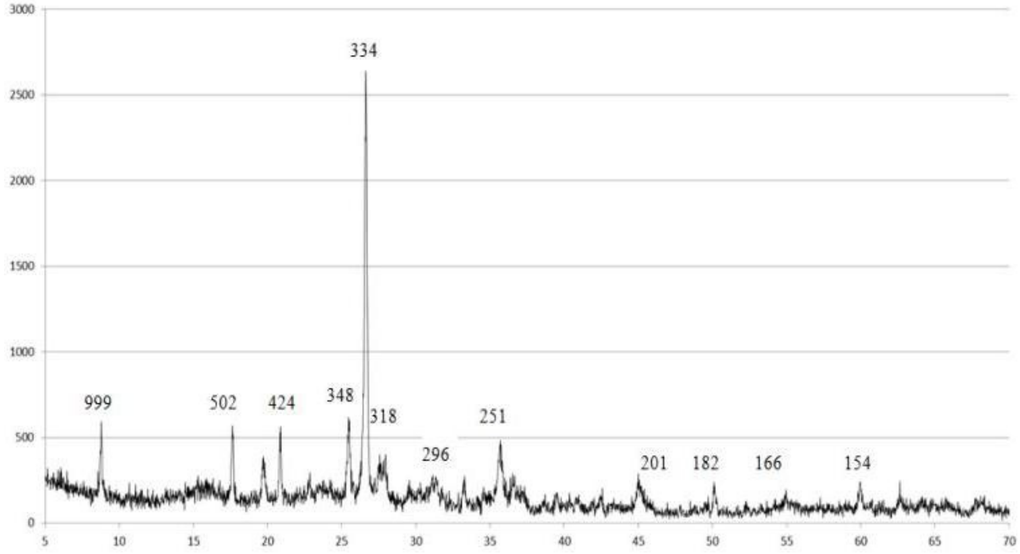

Fig. 5. Radiographs of coal slurry fired at 900 °C

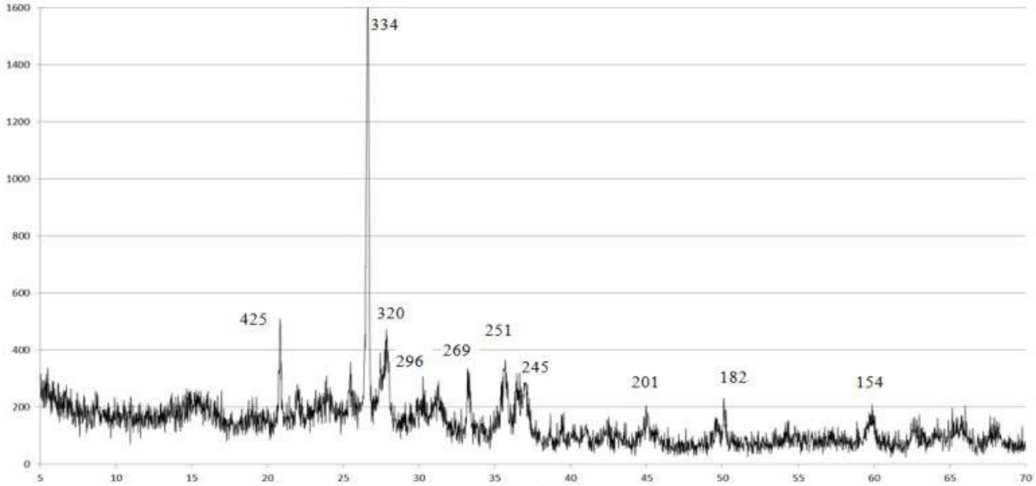

Fig. 6. Radiographs of coal slurry fired at 1000 °C

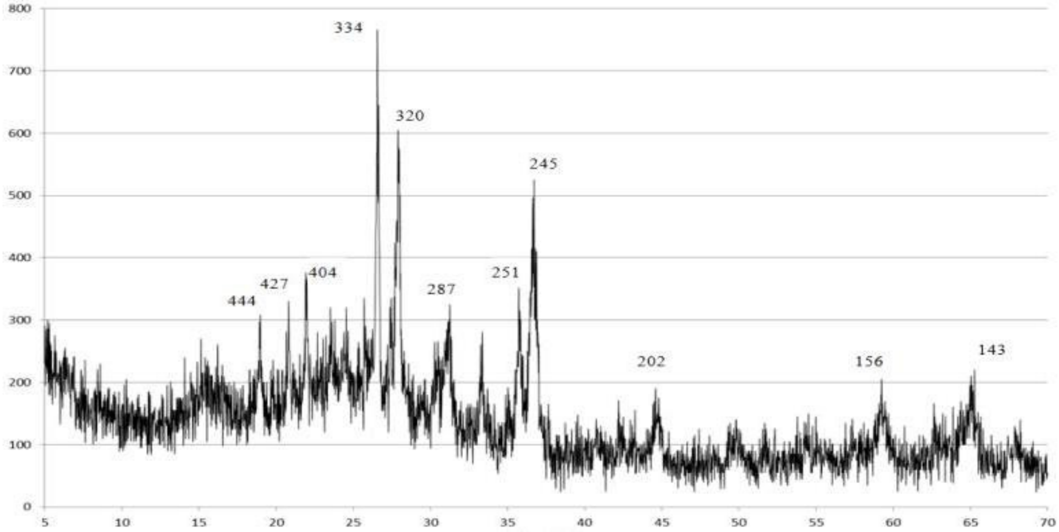

Fig. 7. Radiographs of coal slurry fired at 1100 °C

We can observe fuzzy peaks typical for alumino-silicates (kyanite, sillimanite - 296, 250), spinels. The intensity quartz peaks is naturally lower at the firing temperature 1100 °C comparing with the firing temperature of 1000 °C. Feldspars' peaks become clearer. Peaks of hematite save their intensity. Typical for cristobalite peak (404 pm) appears. The peak of 245 pm increases, that can be caused by the crystallization of fayalite ($FeO \cdot SiO_2$). There are also peaks characteristic of ferruginous varieties of silicates and aluminosilicates of calcium and magnesium (okermanit, gehlenite, melillite - 245, 285-287 pm).

The results of theoretical studies are confirmed by practical data, consisting in the fact that more dramatic increase in the strength of the samples occurs in raw mixtures containing coal sludge at firing temperatures ranging between 1000-1060 °C. The necessary condition here is a complete carbon burnout. For example, Figure 8 shows a graph of the dependency of strength of the ceramic samples from the firing temperature on the basis of clay opoka of Kamenolomenskiy deposit at coal slurries content 15% by weight. Density decline at 1100 °C firing temperature occurs due to burnout of the samples.

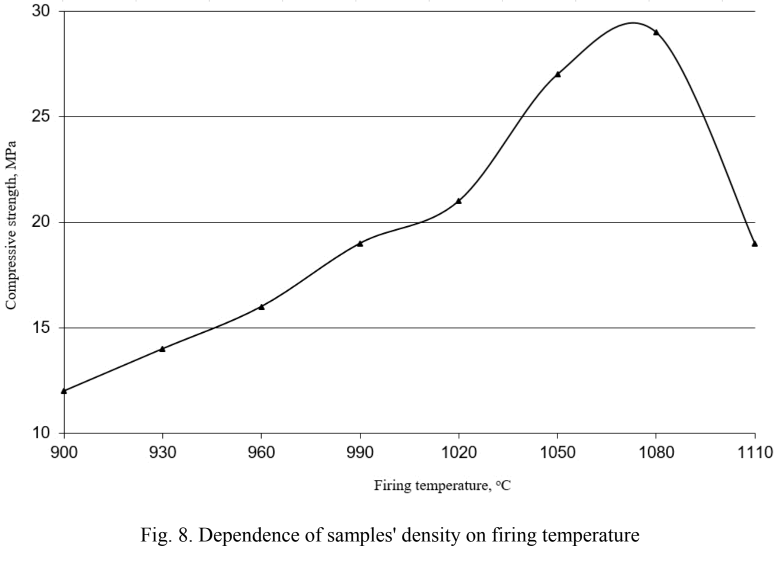

Fig. 8. Dependence of samples' density on firing temperature

6. Conclusion

Thus, as a result of the research, the technical and economic feasibility of producing wall ceramics products with lower density and thermal conductivity on the basis of opoka and coal slurry by compression molding technology with a minimum gas flow rate in the firing is shown. The studied transformations allow to optimize the firing mode for achieving maximum energy-saving effect. Implementing measures for the production of ceramic blocks, based on opoka and coal slurry at new and upgraded plants in light of undertaken studies will allow to obtain products of high efficiency at minimum cost.

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