



ENERGY-EFFICIENT AND FIRE-RESISTANT LIGHT EXPANDED-CLAY GRANULATES FOR HEAT INSULATION VIA HEAT TREATMENT OF BENTONITE CLAYS WITH INDUSTRIAL WASTES

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ABSTRACT

The influence of brown coal and coal production waste on the bloating of bentonite clay was experimentally investigated for the purpose of optimizing the heat-insulation properties of fire-resistant expanded-clay granulates. The bloating coefficients and bulk densities of the expanded-clay granulate samples with additives showed clear dependence on firing temperature. Coal production waste and brown coal were both found to be suitable as intensifiers of beneficial bloating in bentonite clays of the Kyngrak-Keles deposit, Kazakhstan. In both cases, expanded-clay granulates with high heat-insulation effect and low bulk density was produced. X-ray diffractometry, electron microscopy, and differential thermal analysis helped reveal the bulk chemical and elemental compositions of the additives. This study establishes a quantitative compositional basis for heat-insulation granulate performance, opening up economical pathways to enhancing the energy efficiency of buildings and structures while increasing fire safety, environmental friendliness, and resistance to a range of climatic conditions.

Keywords: clay, energy-efficiency, fire-resistance, granulate, heat-insulation, waste.

INTRODUCTION

The problems of heat conservation and heat loss remain as relevant as ever in today's buildings and structures of industrial, residential, cultural and domestic purposes, including such structures as heating pipes. The main way to reduce energy consumption in the face of these problems is to increase the thermal resistance of the enclosing structures by using effective heat-insulation materials [1]. The importance of such approach to fuel and energy savings has been appreciated by the industrially developed countries of Europe and USA, where the volume of production of heat-insulation materials per capita is 5-7 times higher than in the Commonwealth of Independent States countries.

The production of heat-insulation materials makes up huge part of their cost. According to the Committee for State Energy Supervision Republic of Kazakhstan, energy losses occur primarily in connection with heating system. Up to 70% of heat losses in an ordinary building are estimated to occur at windows and doors, and up to 30% of heat losses occur through roofs and walls. As a result, during winter, heating in Kazakhstan requires four times more fuel per square meter than in Finland, which has similar weather conditions. According to experts, the energy-saving potential in the heat supply and heat consumption sector is at least 20%, or approximately 4.6 million tons of standard fuel per year [2-4].

For Kazakhstan, an improvement in the current situation is expected in the course of the implementation of "Key directions of the State program for accelerated industrial and innovative development of the Republic of Kazakhstan", which provides for the development of production of competitive, energy-saving building materials, products, and structures, as well as the expansion of its mineral resource base [5].

The State program of industrial and innovative development of the Republic of Kazakhstan for 2015-2020 sets out 100 concrete steps in solving the problems of increasing the overall share of domestic industrial goods in the building materials market. In the heat-insulation materials industry, successful implementation depends on further technological modernization of production and the related capability to produce a competitive product [6]. Nowadays, the domestic building materials industry has been able to satisfy only a portion of the Kazakhstan's construction industry demand, since, the significant share of the market is imported products. This import contribution prevents a shortage that would occur for almost all types of building materials [7].

In the nomenclature of heat-insulation materials, a special place is given to expanded clay, which is a light, porous material with a cellular structure. It is produced in the form of gravel [8], or less often in the form of chips, obtained by firing low-melting-point clay rocks that can bloat when they are quickly heated to a temperature of 1050°C-1300°C during a period of 25-45 min.

The shortage of building and heat-insulating materials of domestic production in the market allows scientifically substantiate completely new methods of obtaining expanded clay, as well as enlarge their range.

Scientists in Russia and Argentina are also engaged in scientific research in this area [9]. However, in comparison with the montmorillonite clay raw materials of South Kazakhstan, the clay raw materials used as the main components in expanded-clay pellet production in that research were of lower grade in terms of chemical and mineralogical composition. Indeed, montmorillonite clay



raw materials of South Kazakhstan are rich in basic oxides, which primarily lend high strength and porosity to the final product. Today in the USA, expanded-clay pellets are produced mainly from clay shale by the dry method and in Europe from clay and loam by the plastic method. Meanwhile, in Kazakhstan, the production of expandedclay pellets can be developed at a rapid pace due to the involvement of purely domestic natural montmorillonite clay raw materials. The bloating of these materials naturally yields a light, porous material with a fine cellular structure, a low bulk density, and significant strength and heat-shielding properties [10, 11].

Energy conservation in the construction industry is one of the most important components of energy saving, since the construction industry and the housing and utilities sectors take third place among Kazakhstan's economic sector in terms of the use of fuel and energy resources. Housing uses 85% of energy resources, building materials industry uses 11.4%, and construction uses 3.6%. One of the key areas of energy saving is to improve the thermal protection of buildings. For the cities of Kazakhstan, district heating is typical, a significant share of which currently uses suboptimal technology. Insufficient attention is paid to the reliability assessment of heat-insulation materials in enclosing structures. Furthermore, these materials are often not tuned to the climatic, material-technical, and economic conditions of certain regions of the country [12].

Modern requirements for energy conservation of enclosing structures dictate the use of high-tech materials and systems for effective thermal protection of buildings. However, the main types of insulants used in the Republic of Kazakhstan are mineral-cotton products, which constitute more than 60% of total volume of production and consumption. Another 8% consists of glass wool materials, while a full 20% consists of expanded polystyrene and other foamed plastics. The share of heatinsulation cellular concretes in the total volume of produced insulants does not exceed 3%; expanded perlite accounts for less than 0.3% [13].

An important means of reducing the cost of expanded-clay aggregates (ECA) is the use of high-quality raw materials of montmorillonite composition. Such materials exhibit high bloating coefficients, as determined by the physicochemical and pyroplastic properties of the clay raw materials. Among ECAs, the relevance of expanded-clay granulate use for heat-insulation purposes continues to rise [14]. In particular, expanded-clay granulate occupies a special place among bulk building materials. Quite often expanded-clay granulates are used as heat-insulation materials and porous aggregates for various grades of lightweight concrete. There are four main technological schemes for the preparation of raw granulates, and indeed four methods for the production of expanded-clay granulate: dry, plastic, powder-plastic, and wet [15].

The expanded-clay granulate obtained by any of the methods described above must be cooled after firing. It was found that the strength properties of the granulate depend on the cooling rate. If the expanded clay is cooled

too quickly, its grains may crack, or residual stresses will remain in them, which may appear in concrete. On the other hand, excessively slow cooling of expanded clay immediately after bloating may cause a decrease in its due to crushing of softened granulates. quality Furthermore, oxidative processes can play a role, with FeO reverting to Fe₂O₃, accompanied by destruction and loss of strength. Therefore, it is desirable to quickly cool the expanded-clay granulate to a temperature of 800°C-900°C immediately after bloating in order to fix the structure and prevent the oxidation of FeO. Then it is recommended to slowly cool the granulate to a temperature of 600°C-700°C over a period of 20 min in order to ensure the solidification of the glass phase without high thermal stresses. This cooling period also facilitates the formation of crystalline minerals, which increase the strength of the granulate. The use of this method provides relatively rapid cooling of expanded clay [16].

Singarwade *et al.* [17] used Alcofine 1203, which is a mineral additive and light expanded-clay aggregate (LECA), together with fly ash in various compositional ratios. Alcofine 1203 and fly ash improve the workability of fresh concrete, while the lightweight aggregate reduces the dead weight of the structure. In order to obtain the optimal percentage of substitute heat-insulation materials, they tested a variety of compositional ratios of various components, replacing the Alcofine 1203 with cement, as well as with large expanded-clay gravels.

Other research has considered the problems of thermal insulation [18-20], focusing on the development of gravity-flowing and energy-efficient foam concrete with lightweight aggregate (LAFC) for use as thermal insulation and as a structural material. Low-density concrete mixtures (for density values from 800to 1300 kg/m³) were prepared by reducing the volume of LECA from 49.4% to 20.1%. Ordinary portland cement was replaced with 5% and 10% silica fume (SF) to investigate the effects of SF on LAFC properties. The decrease in ECA volume produced increases in both compressive strength (from 6.5 to 24.30 MPa) and ultimate strength (from 0.52 to 1.63 MPa) of LAFC mixtures. LAFC mixture 800-0SF was the least dense and most porous; it exhibited a sorption coefficient of 70.63% and 2.56 $kgfm^{-2}min^{-0.5}$.

Non-bloating and slightly bloating clays can be used in various ways in the production of expanded-clay granulates. Basically, they increase the temperature range of clay bloating by altering the composition, localizing the liquid phase on granulate surfaces during firing, and creating specific firing conditions. LECAs constitute a widely used type of artificial lightweight aggregate. Since they are produced in a rotary kiln, they often exhibit a wide sorting curve. The micromechanics method with some simplifications was used to determine the elastic module of various sizes of such aggregates. As a rule, the smaller the particle size of the expanded clay, the higher the density. Two groups of quaternary LECAs were used each produced under the following identical conditions: particle density ranging from 480 to 1100 kg/m³ and granule size ranging from 4 to 14 mm [21, 22].

In order to avoid sticking of the material in the kiln, some authors have powdered the raw granules with various refractory additives. Such highly dispersed refractory particles are dissolved in the granule surface layer, thereby expanding the bloating interval by the surface viscosity. Quartz increasing sand. aluminosilicate rocks, petrochemical wastes, and hydrolysis wastes have been used as refractory powder additives [23]. Qualitative results have been obtained by introducing organic, alkaline, and iron-containing additives into the mixture, as well as complex materials such as organo-alkaline, organo-iron, and iron-alkaline materials. The organic additives create the necessary reducing conditions and it is advisable to introduce them into raw materials containing no more than 10% iron oxides [24-26].

Nevertheless, some researchers recommend heating in an oxidizing atmosphere, in order to ensure the diffusion of oxygen from the environment into the fired granule for complete conversion of carbon into CO₂ and intensification of the bloating process. In oxygen-poor conditions during the firing of high-carbonate raw materials with the addition of lignin (15%-35%), lignin particles located inside the granules undergo pyrogenetic decomposition according to the following reaction: C+H₂O \rightarrow CO+H₂; C+CO₂ \rightarrow 2CO. If the carbon monoxide does not encounter oxygen while diffusing from the decomposing particle, it begins to dissociate into CO₂ and C, i.e., soot carbon, whose deposition in the central part of the core sharply worsens the conditions for bloating [27]. At increased heating rates, the presence of solid carbon at the bloating stage, after the completion of the sintering processes, promotes the intensive reduction of large quantities of iron (III) oxide. This reduction leads to high pressure inside closed pores and increases the number of pores [27].

Girzhel *et al.* [28] showed that the use of an organo–iron–alkaline complex allows regulating the quality of the aggregate. By altering the ratio of iron and alkaline in the additive, it is possible to stabilize the bloating process of heterogeneous raw materials while increasing the homogeneity of the physical and technical properties of the expanded clay.

In clays suitable for the production of expandedclay granulates, the content of dust particles should not exceed 30%, carbonates of grain size exceeding 0.2 mm should not be present, and the content of organic inclusions should not be higher than 1%-2% [29]. Furthermore, when producing expanded clay from fuelcontaining industrial wastes, high-temperature treatment of raw materials is required to remove excess carbon. In order to preserve bloat ability in such mixtures, as well as in mixtures subjected to step-like or slow firing in doubledrum kilns, it is recommended to add sulfate slag to the clay raw material [30]. Such slag is a mixture of sodium, magnesium, calcium, soda sulfates, sodium chloride, and sodium sulfide. As an essentially alkaline additive, sulfate slag causes the formation of the quantity of melt required for bloating at lower firing temperatures while maintaining pyrogas-active properties regardless of the mode of preliminary heat treatment.

The need for production efficiency despite the lack of ideal raw materials raises the possibility of using industrial wastes, the chemical compositions of which do not always meet the requirements stated above for expanded-clay raw materials. In the context of the existing shortage of domestically produced building and heatinsulation materials, the present work considers the preparation of self-floated foam concrete from lightweight aggregate (LAFC) by mixing stable foam, ECA, and SF as the main raw materials. Formed LAFC mixtures are tested for mechanical, and heat-resistance properties. The implementation of the present work not only scientifically substantiates completely new methods of obtaining expanded clay but also expands the range of applications.

EXPERIMENTAL PART

This research used chemical, physical, and mechanical methods of analysis, as well as technical and operational test methods. The scanning electron microscopy (SEM) studies and X-ray energy-dispersive microanalysis of raw materials of obtained samples of products were carried out at the Testing Regional Laboratory of Engineering Profile "Structural and biochemical materials" of M. Auezov SOUTH KAZAKHSTAN UNIVERSITY (SKU) on JEOL universal scanning (raster) electron microscope (SEM) manufactured by JEOL (Japan).

Scanning electron microscopes JSM-6490LV, JCM-6000, and JSM-5610LV with a maximum magnifying power of 300000×. The physicochemical analyzes of raw materials were carried out in a specialized laboratory of physicochemical methods of analysis "Sapa". Technical and operational test methods were carried out in a special laboratory "Comprehensive laboratory of modern test methods" of M. Auezov SKU.

The Turkistan region of Kazakhstan is one of the richest regions in the world in terms of expanded-clay raw materials, hosting large and very promising deposits of bentonite and bentonite-like clays such as the Keles and Kyngrak-Keles deposits. The Kyngrak-Keles deposit is located in Saryagash district of Turkistan region and confined to the northern slope of the Kyngrak dome-shaped double-plunging anticline. The productive stratum is represented by dark green bentonite clays. At the base of these clays 15.7-m-thick, poorly cemented sandstone of the same origin and time of occurrence, capping a series of red upper Paleogene to Neogene clays [31, 32].

The results of chemical analysis (Supplementary Table-1) show that the silicon, aluminum, and iron oxide content in Kyngrak-Keles bentonite clays fully meet the requirements of GOST 9759-83 for expanded-clay raw materials.



Table-1. Chemical composition of bentonite clays of the Kyngrak-Keles deposit.

Oxides	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃
%	52-63	10-15	4-6	0,4-2,3	2,7-3,5	0,28-1,6

The studied Kyngrak-Keles deposit bentonite clays were sampled and then ground in an ML-1rball mill, passing through a vibration stand with a 1-mm sieve at the bottom, after which they were dried in a drying oven at a temperature of 30°C. The studied clay, prepared in advance and weighed for further experiments, was then mixed with coal production waste as an additive in an automatic paddle mixer (Russia) mixer in a dry state, gradually moistening with water until a pasty consistency was obtained. Thus moistened, the mass was left to rest for 4 h, after which it was mixed again. A pressed tablet was formed from the prepared mass by the method of filling, using a PGM-100MG4A hydraulic press PGM-100MG4A "Stroypribor," Manufacturer Chelyabinsk. Russia

hydraulic press, followed by drying the already pressed tablets at a temperature of 100° C- 140° C.

An important characteristic of clay raw materials is fire and air shrinkage; such shrinkage causes a decrease in the linear dimensions and volume of the clay sample during its drying. For the studied clay, the value of linear air shrinkage under conditions of slow natural drying was 10.8%, and under conditions of rigid artificial drying -7.8%. Fire shrinkage during sample firing at a temperature of 950°C was 5.5%. In order to establish the mineralogical composition of the clays, X-ray phase analysis of the studied clays (Figure-1) was carried out using an X-ray diffractometer (Advance Bruker AXS, Germany).



Figure-1. X-ray image of absolute intensity of Kyngrak-Keles bentonite clays.

According to the X-ray analysis, the mineralogical composition of Kyngrak-Keles bentonite clays is primarily montmorillonite (3.356 Å), quartz (4.270 and 1.821 Å), and illite (2.463 Å).

For a deeper investigation of the studied clays' material composition and the mineralogical and structural features of the constituent mineral phases, electron microscopic analysis was carried out. This analysis included SEM with X-ray energy-dispersive microanalysis using an REM SCANNIING (BITMAP) ELECTRON MICROSCOPE JSM-6490LV scanning electron microscope with a maximum magnifying power of $300000\times$, the following elements were recorded: Si, O, Fe, K, Mg, and Ca (Figure-2). The SEM photograph of the sample shows both aggregates (10-15 µm in size) and individual cloud-like particles.



Figure-2. Electron micrograph and energy-dispersive spectrum of the studied clay.



Figure-2 shows the characteristic presence of FeO in the studied clays. As a result of reduction processes, FeO takes on an acidic state, actively reacting with aluminum and silicon oxides and forming a number of eutectics and solutions of complex composition while exerting a strong fluxing effect. The wetting ability of FeO compared to other iron oxide phases promotes the formation of a system with optimal softening parameters, at which bloating occurs intensively and completely. Further electron microscopy and X-ray energy-dispersive microanalysis (Figure-3) was carried out on JEOL JCM-6000 and JSM-5610LV SEMs at magnifications of 100 to 1000 times. The morphological structural features of the bulk of the studied Kyngrak-Keles deposit bentonite clays were found to be composed of microaggregates of a complex structure. These microaggregates consisted of sheet-like associations, forming isometric and slightly elongated ultramicro aggregates, in which basal planes of neighboring clay particles were in contact.



Figure-3. a) Scanning Electron Microscopy (JCM-6000) and b) SEM (JSM-5610LV) photographs of the structure and morphological features of the studied finely dispersed colloidal dark green Kyngrak-Keles deposit bentonite clays.

At bloating temperatures, Kyngrak-Keles bentonite clays consisted of a crystalline phase composed mainly of Si, Al, and O. The prevalence of this phase decreases by 50%-70% during the first part of the bloating process and another 1%-10% during the last parts observed through a microscope, and is by morphology (old picture 3)

A liquid phase consisted of low-melting-point components and some Si, Al, and O. The Si-Al-O content reached 90% or more of the total melt by the end of the bloating process. A gaseous phase also occurred, varying in composition and quantity.

Differential thermal studies of Kyngrak-Keles deposit bentonite clays show (Figure-4) characteristic signs of changes in properties. Two endo-effects were observed. The first, fixed at a temperature of 100°C-180°C, was accompanied by a loss of weight and was associated with a release of free and adsorbed water. A small, mild endothermic effect in the 200°C-900°C range was associated with removal of the main part of the chemically bound (constitutional) water of various minerals: montmorillonite, hydromica, hydrochlorite, kaolinite, mica, and gypsum. This removal precluded a clear endo-effect that would have accompanied their decomposition. The dissociation of various carbonates with the release of carbon dioxide, generally ceased in the same temperature range. In the range of 200°C-600°C, the volatile components of organic impurities were released, and at 700°C and above, sulfur dioxide was released from gypsum, and sulfides oxidized.



Figure-4. Differential thermal analysis of the studied clays.

Meanwhile, under the influence of reducing conditions, the interactions of minerals both with each other and with organic impurities were significantly accelerated with the release of the gaseous phase. Dehydration during firing was accompanied by a gradual destruction of crystal lattices: kaolinite at 400°C-650°C, montmorillonite at 300°C-900°C, and hydromicas at 900°C-1050°C. At this point, complete destruction of the crystal lattices of clay minerals occurred, and they became amorphous with the release of residues of constitutional water. This amorphization increased their reactivity and produced numerous micropores, which along with the pores formed as a result of physical contact between the smallest elementary particles and their complexes, these amorphization pores determined the total porosity of the material in the period preceding bloating.

Redox processes in the range of 300°C-1050°C have a significant effect on phase transformations. The presence of organic impurities, iron oxides, and constitutional water in clay raw materials creates favorable conditions for the development of reversible reactions with alternating oxidation and reduction of iron oxides, oxidation of carbon and hydrogen, and reduction of their combustion products. At the same time, reducing reactions begin to prevail as the temperature rises, accompanied by the accumulation of iron oxide, which does not disappear until the end of firing. The process of oxidation of previously reduced iron begins only when the rate of water vapor release from dehydrating minerals decreases so much that it ceases to interfere with the diffusion of oxygen into the sample.

This experimental investigation established that during the firing of expanded clay, all clay minerals and fluxing agents passed into the melt, forming pore walls, where at 950°C-1050°C a glass phase appeared thanks to the participation of iron oxide and other fluxing agents along local areas of a weakly porous mass. At 1050°C-1200°C, the overwhelming majority of expanded-clay raw materials softened due to the formation of an increasing number of low-melting-point eutectics thanks to the participation of fluxing agents, especially iron oxide and alkalis. The melt assimilated other finely dispersed components, and the mass passed into a pyroplastic state, characterized by a demonstrated homogeneity of the melt and nearly optimal viscosity for bloating.

In the course of heat treatment, gaseous products were released from a homogeneous mineral mixture off studied clays'. When a homogeneous mineral mixture of the studied clays was heated, a chemical interaction occurred in the areas of contact between solid-phase minerals. Here as a result of further interaction of components due to melting of the most low-melting eutectics and compounds as temperature increased, a liquid phase appeared, the quantity of which continuously increased due to the appearance at higher temperatures of additional eutectics and the interaction of an already formed liquid phase with crystalline components. Given a sufficient quantity of the liquid phase, the studied clay mass began to decrease in viscosity and plastically deform as the temperature rose.

These experimental studies have established that when bubbles of the gaseous phase with a certain pressure elasticity appear, the clay mass has a certain optimal viscosity for a time sufficient to complete the pore formation process. As other studies have shown, the number and size of pores, as well as the total porosity of the material, change significantly during the firing process under the influence of shrinkage deformation and structural element rearrangement. These changes are mainly due to the mineralogical composition and the

degree of dispersion of the original clay raw material. The finer the clay, the more of the low-temperature gaseous phase is released from the mineralogical components, and thus the greater the microporosity of the material.

Once the ignition temperature of organic impurities is reached, their oxidation and combustion occur with the release of carbon dioxide, carbon, and hydrocarbons, some of which, like water vapor, are consumed in redox processes. During this period fundamentally important processes are the material carbonization under reducing conditions inside individual granules according to the following reaction: $C + CO_2 \leftrightarrow 2CO$.

As a result of heat treatment of clays at a rate that varies during the firing of expanded clay from 15-30 to 50-100°C/min, various reactions are somewhat shifted to the region of higher temperatures: decomposition, dissociation, and interaction of the components of the mass with the release of gaseous products. These reactions provide the gas phase resources needed for bloating of the material, which occurs in the range of 1050°C-1200°C, with the precise temperature determined by the characteristic value of the given clay raw material. As the material is heated to 900°C-1000°C, the pore size distribution continues to change, but the total porosity continuously increases before sharply decreasing during sintering. This decrease in total porosity is mainly due to the formation of larger pores with an increasing number of tiny ones. Clay minerals such as montmorillonite (20%), micas, and hydromicas present in the studied bentonite clays are also sources of gas formation.

The authors next studied the influence of brown coal and coal production wastes on the bloating of

Kyngrak-Keles bentonite clays. For laboratory experiments, brown coal from the Karazhyra deposit was studied, the characteristics of which are shown in Supplementary Table-2.

Table-2. Coal characteristi	cs of	the	Karazhy	ra
deposit, in	%.			

Indicators	Value
Total moisture	14
Analytical moisture	5,9
Ash content	18
Volatile matter release	47
Total sulfur	0,44
Carbon	74,29
Hydrogen	5,39
Nitrogen	1,27
Oxygen	18,33
Phosphorus	0,04

After grinding and sieving through a No. 1 sieve, the coal was mixed with clay powder, and the charge was moistened to a moisture content of 30%. Masses were prepared with coal fractions of 1%, 3%, and 5%. The test results for expanded-clay granulates fired at temperatures of 1080° C to 1160° C are shown in Supplementary Table 3 and in Figures 5 and 6.

ïring temperature, ⁰ C	Swelling coefficient	Bulk weight, g/cm ³	Water absorption,%	Fotal (true) porosity, volume,%	Open (apparent) porosity, volume,%	Closed porosity, volume,%			
I			1%	coal					
1080	1.5	0.994	6.1	61.0	6.1	54.9			
1100	1,6	0,937	6,4	63.3	6,0	57.3			
1120	1,8	0,838	6,6	67,2	5,5	61,7			
1140	2,3	0,660	6,1	74,2	4,0	70,2			
1160	2,6	0,596	6,2	76,6	3,7	72,9			
	3% coal								
1080	1,7	0,896	10,5	64,9	9,3	55,6			
1100	1,8	0,833	9,9	67,4	8,3	59,1			
1120	2,1	0,698	10,5	72,6	7,3	65,3			
1140	2,4	0,630	12,5	75,3	7,8	67,5			
1160	2,6	0,586	12,3	77,0	7,1	69,9			
5% coal									
1080	1,5	0,950	10,2	62,8	9,8	53,0			
1100	1,6	0,817	10,5	68,0	8,6	59,4			
1120	2,0	0,717	11,3	71,9	8,3	63,6			
1140	2,3	0,652	13,8	74,4	9,1	65,3			
1160	2,3	0,613	14,0	75,2	8,8	66,4			

Table-3. Physical and mechanical parameters of ceramic granulates based on the studied bentonite clays of the Kyngrak-Keles deposit with the addition of coal.

The data in the table and figures indicate that the addition of coal contributes to the intensification of clay bloating. Bloating coefficients during firing of coal-containing samples at temperatures between 1080 and 1160° C were in the range of 1.5-2.6. At the same

temperatures, bloating coefficients of clay without additives did not exceed 1.5. The bulk density of granules with the addition of coal varied from 0.6 to 1 g/cm³, compared to 1.0-1.1 g/cm³ for granules from clay without additives.



Figure-5. Change in the bloating coefficient of the obtained expanded-clay granulate based on the studied Kyngrak-Keles deposit bentonite clays with the addition of coal, depending on the firing temperature.



Figure-6. Change in the bulk density of the obtained expanded-clay granulate based on the studied Kyngrak-Keles deposit bentonite clays with the addition of coal, depending on the firing temperature.

Trends were close to rectilinear for both the bloating coefficient and the bulk density over the temperature range 1080° C- 1140° C. For 5% coal addition, a noticeable reversal of the curve was observed at 1140° C, above which the bloating intensity decreased. The optimal bulk density of expanded-clay granulate can be obtained by firing at 1140° C or higher. The bulk density of granules

from the mass containing 1% coal was noticeably inferior to those of the masses containing 3% and 5% coal.

Turning now to coal production wastes as additives, five samples were studied in the compositional range of 1%-10% coal production waste. The results, shown in Supplementary Table-4 and Figures 7 and 8, indicate that coal production wastes can serve as useful bloating additives for Kyngrak-Keles bentonite clays.

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T Firing temperature, ⁰ C	Swelling coefficient	Bulk weight, g/cm ³	Water absorption,%	Total (true) porosity, volume,%	Open (apparent) porosity, volume,%	Closed porosity, volume,%		
			1% of coal m	ining waste				
1080	0,8	1,81	6,4	21,1	21,6	9,5		
1100	0,9	1,68	7,1	34,2	12,0	22,2		
1120	1,0	1,55	6,4	39,3	9,7	29,6		
1140	1,2	1,30	6,6	49,1	8,7	40,4		
1160	1,5	1,11	3,4	56,4	3,9	52,5		
1180	1,7	1,03	4,5	59,6	4,8	54,8		
1200	1,8	0,99	5,1	61,2	5,2	56,0		
3% of coal mining waste								
1080	1,0	1,54	7,1	40,0	11,0	29,0		
1100	1,0	1,52	6,6	40,4	7,6	32,8		
1120	1,0	1,43	6,3	44,0	8,7	35,3		
1140	1,3	1,17	4,4	54,2	5,1	49,1		
1160	1,5	0,98	5,6	61,6	5,5	56,1		
1180	1,9	0,81	6,3	68,3	5,2	63,1		
1200	2,0	0,75	6,0	70,6	5,0	65,6		
			5% of coal mi	ining waste				
1080	0,8	1,59	6,2	37,7	9,9	27,8		
1100	1,0	1,36	5,9	46,7	8,0	38,7		
1120	1,1	1,19	7,2	53,4	9,0	44,4		
1140	1,2	1,15	5,8	55,0	6,7	48,3		
1160	1,4	0,97	5,9	62,0	5,5	56,5		
1180	1,4	0,93	5,7	63,6	5,5	58,1		
1200	1,4	0,92	5,8	64,0	5,6	58,4		
			7% of coal m	ining waste				
1080	0,9	1,64	6,2	35,7	10,2	25,5		
1100	1,1	1,31	7,4	48,7	9,8	38,9		
1120	1,2	1,17	7,5	54,2	8,9	45,3		
1140	1,4	1,02	7,8	60,0	8,1	51,9		
1160	1,4	1,01	7,4	60,4	7,7	52,7		
1180	1,7	0,84	6,8	67,1	5,8	61,3		
1200	1,7	0,83	9,1	67,5	5,5	62,0		
10% of coal mining waste								
1080	1,0	1,36	6,3	46,7	8,7	38,0		
1100	1,1	1,25	6,1	51,0	8,1	42,9		
1120	1,2	1,11	6,4	56,5	7,2	49,3		
1140	1,2	1,14	6,6	55,3	7,6	47,7		
1160	1,4	0,99	5,9	61,2	5,8	55,4		
1180	1,5	0,93	6,0	63,6	6,7	56,9		
1200	17	0.85	64	66 7	55	61.2		

Table-4. Physical and mechanical parameters of ceramic granules based on the studied bentonite clays of the Kyngrak-Keles deposit with the addition of coal mining waste.



Figure-7. Change in the bloating coefficient of the obtained expanded-clay granulate based on the studied Kyngrak-Keles deposit bentonite clays with the addition of coal production wastes, depending on the firing temperature.



Figure-8. Change in the bulk density of the obtained expanded-clay granulate based on the studied Kyngrak-Keles deposit bentonite clays with the addition of coal production wastes, depending on the firing temperature.

The swelling coefficient of the studied clay with the addition of 1% and 3% of coal mining waste during firing from 1080°C to 1200°C varies from 1.8 to 2.0; simultaneously, with the addition of 5% at the same firing temperatures, the swelling coefficient decreases from 2.0 to 1.4. The bulk density of granules from clay with the addition of coal mining waste varies from 0.99 to 0.75 g/cm³, and from clay without the additive - from 1.665 to 1.053 g/cm³.A further increase in the additive from 7% to 10% has practically no effect on the swelling and bulk density of clays.

RESULTS AND DISCUSSIONS

This investigation's results can be generalized to give the following explanation of these additives' effects on the bloating of Kyngrak-Keles deposit bentonite clays. The inorganic part of each additive is refractory, thus acts as a mass softener. The resulting pores facilitate the release of gaseous products. Therefore, as the additive content increases, the total porosity of sample increases. Only a determinate amount of gas released from each granule remains in its pores and, at elevated temperatures of 1180°C-1200°C, promotes bloating of the samples.

If the rate of temperature rise is increased, the surface of the sample heats up faster. Thus a sufficient amount of the liquid phase forms quickly at the surface, and the pores become clogged. The gases generated within expand when heated and bloat the pellet. This process does not take place simultaneously over the entire volume but rather moves gradually from the surface to the center. This diachroneity contributes to the increased bloating of the sample.

CONCLUSIONS

For the studied clay, the linear air shrinkage value under conditions of slow natural drying is 10.8%, and with a rigid mode of artificial drying 7.8%. During firing of the samples at a temperature of 950°C, fire shrinkage is 5.5%. The bloating of clays can be successfully increased by using coal production waste as a softener.

During heat treatment, clay minerals and fluxing agents pass into the melt, forming pore walls along with the occurrence of a glass phase. At this point the raw material softens at the maximum temperature of 600°C-700°Cdue to the increasing formation of low-melting eutectics with the participation of fluxing agents and the assimilation of the melt of other finely dispersed



components. Afterward, the mass passes into a pyroplastic state, characterized by a demonstrated homogeneity of the melt and an optimal viscosity for bloating to a high porosity.

In the process of heat treatment, the number and size of pores are significantly modified, as is the total porosity of the material. The shrinkage deformations and rearrangements of structural elements that bring about these modifications are mainly determined by mineralogical composition and by the degree of dispersion of the initial clay raw material. Finer clays release higher volumes of low-temperature gaseous phases from their mineralogical components, yielding materials of higher microporosity.

REFERENCES

- [1] 2015. Catalog of industrial and innovative projects of the Ministry for Investment and Development of the Republic of Kazakhstan. Astana City; 2015. p. 60.
- [2] Onatsky SP. 1971. Expandedclay production. 2nd ed. Moscow: Moscow Publishing House of Literature on Construction. p. 310.
- [3] Construction bulletin [Internet]. Experts estimate the energy-saving potential in the Republic of Kazakhstan at about 4.6 million tons of fuel equivalent per year. [cited 01 December 2014] Available from: https://www.inform.kz/ru/potencialenergosberezheniya-v-rk-eksperty-ocenivayutprimerno-v-4-6-mln-tonn-uslovnogo-topliva-vgod_a2732191.
- [4] [cited 01 December 2014] Available from: https://www.inform.kz/ru/potencialenergosberezheniya-v-rk-eksperty-ocenivayutprimerno-v-4-6-mln-tonn-uslovnogo-topliva-vgod_a2732191.
- [5] 2010. State program of forced industrial and innovative development of the Republic of Kazakhstan for 2010–2014. Astana. p. 95.
- [6] 2014. State program of industrial and innovative development of the Republic of Kazakhstan for 2015-2019, approved by the Decree of the President of the Republic of Kazakhstan on 1 August 2014. No. 874. Astana. p. 60.
- [7] Kocherov YN, Zhakipbayev BY, Kaldybayev AB. 2014. Raw materials base of South Kazakhstan for obtaining high-strength heat insulation expandedclay pellets. Sci. World. 8: 51-53.

- [8] Makulbekova GO, Kambarova NA, Sultanmurat KS, Kocherov YN. 2018. To the question of the use of the south-Kazakhstan light-floating clays of colloidal composition montmorillonite and for obtaining heat-insulating and fire-safety ceramsite In: Proceedings of V International granules. Conference "Industrial Technologies and Engineering" ICITE-2018, Volume I. M. Shymkent, Kazakhstan: Auezov South Kazakhstan State University. pp. 229-232.
- [9] Volzone C, Garrido LB. 2012. High temperature structural modifications of intercalated montmorillonite clay mineral with OH-Al polymers. Proc. Mat. Sci. 1: 164-171.
- [10] Bishimbayev VK. 2009. Mineral and raw material and technological base of South Kazakhstan cluster of building and silicate materials. Almaty. p. 266.
- [11]Kocherov YN, Zhakipbayev BY, Kaldybayev AB. 2014. On the issue of using South Kazakhstan lowmelting clays of montmorillonite composition for obtaining expanded-clay pellets. Sci. World. 1: 38-39.
- [12] Agency on statistics of the Republic of Kazakhstan [Internet]. [cited 26 January 2021] Available from: http://www.stat.kz.
- [13] Marketing research of expandedclay market [Internet]. [cited 10 January 2021] Available from: http://www.research-techart.ru.
- [14] Zhakipbayev BY, Kulmakhanova AS, Sarsenbayev NB, Tagybayev AB. 2016. On the issue of studying Kyngrak-Keles bentonite clays in order to obtain from them energy-efficient lightweight expanded-clay gravel for thermal insulation purposes. Collection of scientific papers of international scientific-practical conference of theoretical and applied developments of young scientists Modern scientific and practical solutions and approaches, 2016." Scientific Publishing House Infinity. pp. 255-262.
- [15] Rabukhin AI, Savelyev VG. 2008. Physical chemistry of refractory compounds of non-metallic and silicate compounds. Vol. 1, Moscow: Infra-M; p. 303 Available from: https://www.ozon.ru/context/detail/id/2203467/?code =OZONF3CL13.
- [16] [cited 02 July 2016] Available from: https://search.rsl.ru/ru/record/01002449268.

- [17] Zhakipbayev BY, Minaidarov SA, Kulmakhanova AS, Kocherov YN, Kolesnikov AS. 2017. Technology of obtaining heat insulation expanded-clay granulates based on bentonite clays of South Kazakhstan region. Bull. KazNRTU. 359-363.
- [18] Singarwade H, Kulkarni P, Wagh S, Bhagat A, Tadas S. 2021. Experimental evaluation of hybrid concrete using expanded clay aggregate/alccofine1203/fly ash at normal and accelerated curing. Mater. Today Proc. 43: 1110-1116.
- [19] Ahmad MR, Chen B, Shah SFA. 2019. Investigate the influence of expanded clay aggregate and silica fume on the properties of lightweight concrete. Constr. Build. Mater. 220: 253-266.
- [20] Nahhab AH, Ketab AK. 2020. Physical and mechanical performance of cement-based renders with different contents of fly ash, expanded cork granules and expanded clay. Constr. Build. Mater. 233: 117922.
- [21] Ingrao C, Selvaggi R, Valenti F, Matarazzo A, Pecorino B, Arcidiacono C. 2019. Life cycle assessments of expanded clay granulate production using different fuels. Resour. Conserv. Recycl. 141: 398-409.
- [22] Ardakani A, Yazdani M. 2014. The relation between particle density and static elastic moduli of lightweight expanded clay aggregates. Appl. Clay Sci. 93-94: 28-34.
- [23] Shulman D. 1999. Lightweight, low water content expanded shale, clay and slate cementitious compositions and methods of their production and use. Cem. Conc. Compos. 21: 242.
- [24] Makulbekova GO, Kocherov YN, Ramatullayeva LI, Kenzhaliyeva GD. 2020. Influence of accelerated firing process on the porosity of Kyngrak-Keles bentonite clays. In: International scientific-pratical conference "Science and Education-2020. Nur-Sultan. pp. 121-123.
- [25] Makulbekova GO, Kocherov YN, Pivovarov AA, Kenzhaliyeva GD, Mamitova AD. 2020. Study of the process of joint heat treatment of bentonite clays and ash from thermal power plants of Kyngrak-Keles deposit in order to obtain heat-insulation and fire-safe expanded-clay granules. Bull. Kaz NRTU. 4: 511-516.

- [26] Galpern EJ. 1995. Application of coal-containing waste in production of brick and expanded clay aggregate. Coal Sci. Technol. 24: 1633-1635.
- [27] Makulbekova GO, Kocherov YN, Kenzhaliyeva GD, Mamitova AD, Begimbetova AS. 2020. Influence of lignite on the porosity of Kyngrak-Keles bentonite clays. Bull. Kaz NRTU. 5: 325-330.
- [28] Zhou Y, Zhang R, Huang J, et al. 2020. Influence of alkaline solution injection for wettability and permeability of coal with CO₂ injection. Energy. 202: 117799.
- [29] Girzhel AM, Galpera EI, Rogovoy MI. 1984. Increasing the bloating of heat-treated mine rocks by introducing iron and alkali-containing additives. Build. Mater. 3: 24-25.
- [30] Lukanicheva TP, Shcherbakova NP. 1980. Factors that determine the amount of free calcium oxide in expanded clay. Constr. Arch. 9: 80-83.
- [31] Ahmad MR, Chen B. 2019. Experimental research on the performance of lightweight concrete containing foam and expanded clay aggregate. Compos. BEng. 171: 46-60.
- [32] Kulinich VV, Uzhkenov BS, Bayakunova SY, Antonenko AA, Kabbo MD. 2000. Deposits of mining raw materials in Almaty, Kazakhstan, Kazakhstan: Directory. Almaty. p. 233.