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CHARACTERISTICS OF MELTS FROM HIGH-TEMPERATURE TESTS OF LOWER QUARTENARY LOAMS AND TECHNOGENIC COAL ASH FROM BORALDAY TPP AS THE BASIS FOR THE PRODUCTION OF LIGHT CONCRETE FILLERS

Abstract. The study describes of the material composition, technological properties of light concrete fillers (aggregates) from Lower Quaternary loam and coal ash waste from TPP. Huge amount of ash (many hundreds of millions tons) has accumulated on the territory of Kazakhstan, which is a waste product of coal power industry. Organization of light concrete fillers production from waste would allow manufacturing various building structures on their basis.

Old and new ash burials from Boralday area contains up to 90% siliceous formations (mullite and quartz), which is characterized as a durable, fireproof and chemically stable substances. These natural formations are durableas part of the construction material. Due to the peculiarities of the mineral content of the formations under consideration, with negligible impurities of calcium and magnesium carbonates, they can be used directly as a filler of concrete. And with the additional firing of this ash, the lightness, heat and soundproofness of the concrete product will be added to the abovementioned qualities.

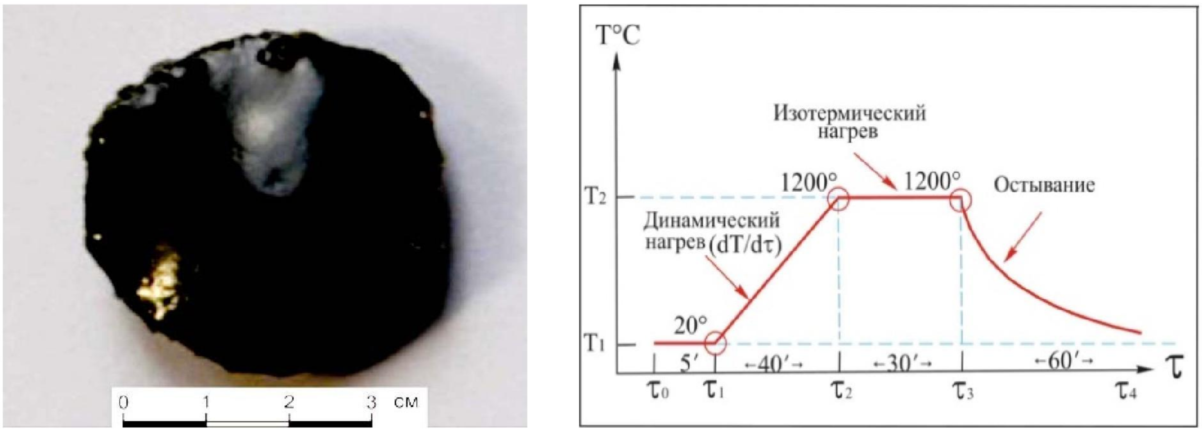
When calcining loam, some of its components (montmorillonite, muscovite, and chlorite) together with non-melted quartz particles form a homogeneous aggregate. Minerals such as calcite, dolomite and gypsum degenerated into calcium and magnesium oxides during dissociation, which eventually allowed to reduce the viscosity of the melt. The main aggregates of the melt (~ 50%) in the obtained firing product were powder granules of siliceous constituents of loam.

Thus, the product obtained at this stage of the study can already be used in the production of heat-resistant and mechanically strong flake aggregates of light concrete aggregates.
Keywords: keramzit, charge, loess-like loam, coal ash, thermal, X-ray phase and microprobe analyzes, melting of batch of high-temperature furnace.

Keramzit (expanded clay) has a reputation of a material with good insulating and strength properties. Keramzit is a porous rounded granule, which is obtained from raw materials by their firing and melting. A structure made of keramzit is durable and has a light weight and keramzit itself is a thermal insulator with excellent parameters. Traditionally, clays are used as a raw material for the production of expanded clay. Such Lower Quaternary loess like loams are widely developed in the foothills of the Zailisky Alatau, where their reserves are enormous.

On the territory of Kazakhstan, a huge amount of ash has accumulated (many hundreds of millions of tons) representing a waste of coal energy. The organization of industrial production of lightweight aggregates from such wastes would allow them to make various building structures on their basis. In this regard, the possibility of using as has a raw material for keramzit from industrial wastes of Boralday TPP was considered. For this, samples were selected and subsequently studied by laboratory methods [1, 2] in accordance with existing GOSTs [3, 4]. Subsequently, the samples were subjected to high-temperature tests in the chamber furnace LHT 04/16 (Nabertherm) with a dynamic temperature increase from 50 to

1200 °C and further to a temperature of 1300 °C. The temperature rise was controlled by the set time, after which the thermal installation automatically switched to the next heating mode at T° → constant. The process of the furnace thermal exposure to a sample was completed by free cooling of the system. The graphic scheme of high-temperature heating of samples in a chamber furnace is shown in figure 1 (Ungurtas vil.). On the y-axis, symbols T_1 and T_2 designate the initial temperature of the furnace and the temperature at which the heating regime changes,respectively. On the abscissa axis, ϑ_0, ϑ_1, ϑ_2, ϑ_3, and ϑ_4 time of thermal testing of stone material is shown. The work of the thermal installation is carried out according to the following scheme: 1) heating under conditions of dynamic temperature rise; 2) isothermal regime (thermal effect); 3) free cooling of the charge. After the test, the firing products were visually examined under a microscope. The evaluation was carried out for its suitability as a finished product or light concrete filler and for direct casting of heat-resistant, chemically stable, electrical insulating and heat-resistant products.



a b

Figure 1 – Photo illustration (a) of the product of firing (clay, the upper horizon, Ungurtas);
b – diagram of high-temperature heating of samples in a chamber furnace – 1200°C (5',40', 30')

The production requirements are based on the correspondence of the physical and chemical properties of each of the listed types of raw materials and is determined, first of all, by its elemental composition, structural features and accompanying mineral impurities. For this, melting of the initial material was carried out in various temperature regimes to select the optimal melting temperature of the charge [5, 6]. Another important requirement for the properties of raw materials is its thermochemical susceptibility to the firing process, which determines the homogenization of the resulting melt and the crystallization sequence of the substrate obtained [6-8].

Loams melt at a temperature of 1200° C and crystallization of the molten substrate proceeds during its cooling. The scheme of thermal effect on loam and ash is acceptable for the production of technical products with specified physical properties. As a result of loam heating in the indicated firing regime a firm to the touch product was obtained of a dark brown color with a light matte shade of the surface part of the ingot. At the same time, this substance retained all the three-dimensional outlines of the charge (dome shape) left on it during the preparation of the powder sample for a programmed thermal test. This characteristic of the new transformed substance was formed as a result of a combination of circumstances related to the thermal properties of the components of the test sample and were caused by the conditions of the combined heating of this object from 20 to 1200° C (figure 1).

When calcining the loam, minerals such as montmorillonite (6.7%), muscovite (7.2%) and chlorite (3.8%) allowed non-melted quartz particles to consolidate into a homogeneous aggregate. Whereas calcite, dolomite, and gypsum degenerated into calcium and magnesium oxides in the process of dissociation, which eventually reduced the viscosity of the melt. The main aggregates of the melt (~ 50%) in the obtained firing product were powder granules of siliceous constituents of loam. Thus, the product obtained at this stage of the study can already be used in the production of heat-resistant and mechanically strong flake aggregates of light concrete fillers.

The temperature-chronological scheme of the thermal test of the stone material shown in figure 1 further will be presented as follows: T°C ($\Delta\vartheta_1$, $\Delta\vartheta_2$, $\Delta\vartheta_3$). Based on the example of this sample, the first number means the upper temperature limit of the test and the values in parentheses correspond to the waiting time of the experiment, its dynamic heating, and the stage of isothermal calcination of the sample.

When calcining the loam in the mode indicated in figure 2, the material was obtained with appearance and physical properties very similar to the product of calcination of the previous sample. This fact is explained by the relationship between the composition of these rocks and the similarity of conditions for their calcination. These two samples contain almost the same set of minerals with close proportions of their quantity. In their compositions, the proportion of thermally active and thermally inert components is also observed. Direct confirmation of this is the proximity of the percentage content in these samples, both clay-carbonate and anhydrous siliceous formations. And finally, when calcining these samples, 12.3 and 11.9% of the mass are lost (in the form of H_2O, OH and CO_2 emissions), which indicates a proximity of the amount of thermally active mineral inclusions in them.

Figure 2 – Photo illustration of the product of firing clay loam (lower the horizon, the village of Ungurtas).
The temperature-temporal parameters of firing stone material in a high temperature heating to 1200°C (5', 40', 30')

The loess like loam north of the Boralday town repeats all the stages of the formation of the ceramic product that occurred during the firing of loam during the calcination at 1200 °C (5', 40', 30'). In all samples, as the burning temperature increased several stages of dehydration of clay inclusions and the processes of thermal dissociation of carbonate constituents of tested samples were observed. Dehydration of the system was provided by two types of hydrate emissions: removal of interlayer water (H2O) in the range from 60 to 215 °C and yield of hydroxyls (OH) from tetrahedral grids of clay minerals (220-830 °C). The dissociation of carbonate inclusions ($CaCO_3$ and CaMg $(CO_3)_2$) was studied by dynamically heating them on a thermal installation called derivatograph Q1500D.The thermal destruction of these impurities was carried out in the range of ~ 400-800 °C, in which the decomposition product (CO_2) indicated the degree of its belonging to dolomite and calcite and at the same time informed about quantitative content of these carbonates in the rock. Thus, the results of thermal analysis showed that the chemical decomposition of the thermally active components of the sample started at 40 °C is completely completed in the vicinity of 830 °C.As a result of this, in the substrate for calcination of clays, carbonates and gypsum in this temperature range centers are already formed in which the first points of melting are formed. These include melting of silicon-oxygen compounds, which are the products of thermochemical destruction of layered silicates. The process proceeds without significant participation of quartz, albite, and orthoclase present in the samples, since melting temperatures of these silicates are much higher than a sintering temperature of carbonate-argillaceous inclusions of the loams in question.

As results of a differential thermal analysis (DTA) showed, complete sintering of these objects with dynamic heating from 20 to 1000 °C did not occur, which is due to the high gradient dT°/dt = 10 deg/min, i.e. insufficient storage time of the charge in the high temperature range. In a special test of loam in the high-temperature installation, according to the scheme shown in Fig. 2 (1200 °C (5', 40', 30'), an alloy (from the carbonate-argillaceous part of the charge) was obtained, which unified in its mass unmelted chips of quartz, albite, and orthoclase (figure 3). The substance crystallized from such a melt has a number of advantages to construction products: it is environmentally friendly, durable, fire-resistant and chemically inert. Produced in this way product can be used as a casting material for the production of litter plates, facing coatings, and flake aggregates of concrete widely used in the construction of buildings and special structures. A combination of the three main factors is required in the production of such material: a certain composition of the raw materials, an upper limit of the calcination temperature, and holding time of the charge during its heating. All these factors were taken into account in our experiments in the process of selecting a test object as well as in selecting the temperature-chronological (T° and t') parameters for the dynamic and isothermal high-temperature (1200 °C) heating of the charge.

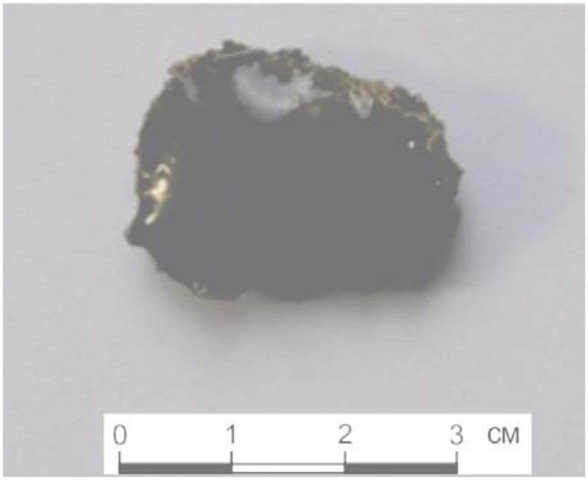


Figure 3 – 3hoto illustration of the product of firing clay loam (Boraldai); temperature-temporal parameters of firing stone material in a high temperature heating to 1200°C (5', 40', 30')

Loams north of Uzun-Agachvillage and the quarry of Boralday TPP have a polymineral composition of which 55% are not subjected to any phase transformations in the investigated temperature range and 45% decompose within 60-820 °C with a release into the atmosphere of 12.3% (of the sample mass) of volatile compounds: H_2O, OH and CO_2.Due to the low content of fine montmorillonite in the system (respectively 6.7, 4.6, and 6.2%), the probability of forming a large amount of refractory mullite, cristobalite (by roasting), is also low. But this is the only problem for low-temperature production (up to 1000 °C) of these clays, to obtain a material with qualities comparable to those of burnt bricks. With proper additions to these montmorillonite loams and a slight increase in the firing temperature, these formations will provide raw materials for the technology of manufacturing a fireproof, chemically inert, and mechanically strong concrete filler. In particular, these loams serve as a promising material for the production of expanded clay and thermal insulation materials. From a series of high-temperature tests performed with heating of these complexes, a group of products with qualities corresponding to the physical properties of expanded clay was identified. The choice of these qualities in crystallized melts was carried out taking into account the energy saving factors of furnace heating and the expression of the production cycle. The most acceptable calcination temperature of most samples was 1200 °C and time of isothermal roasting (without taking into account a preheating of the charge and its cooling) for different samples was 20-30 minutes.

The sample firing product (old storage ash, Boralday TPP) is presented as a hard, porous substance with a yellowish tinge of the surface on which dotted, sparsely populated dark specks of quartz and micro cracks with sizes from 2 to 4 mm are seen (figure 4). Heat treatment (20-1000°C) of the studied ash did not cause a significant reduction in the initial mass of the charge. The main stages of weight loss of the sample are in the temperature range of 20-800 °C, where the system loses up to 7.3% of its mass as a gaseous substance. Within these temperatures, the analytical balance of the derivatograph records all the steps of removing volatile components of the ash (in the form of moisture and carbon monoxide).

Figure 4 – Photo illustration (4) the product of annealing of the sample (the remains of an old storage pit Boraldai TPP); thermal-temporal parameters of firing stone material in a high temperature heating to 1200°C (5', 40', 30')

However, when the sample was heated in the range of 20-1200 °C, the weight loss was ~ 9%, i.e. in the range of 1000-1200 °C, the investigated charge loses another ~ 1.5% of its weight. This difference is due to the release of organic carbon monoxide (CO_{OR}) and carbonate CO_2 into the atmosphere. The reaction is due to thermal depressurization of microscopic silicon capsules included in the ash composition. Formation of these capsules and its contents was carried out even while burning fuel in the ovens of TPP. This way, in the process of combustion of coal, part of the organic and carbonate inclusions can appear in the spaces of these hermetic cells, whose shells at some point served as an obstacle for ingress of oxygen.

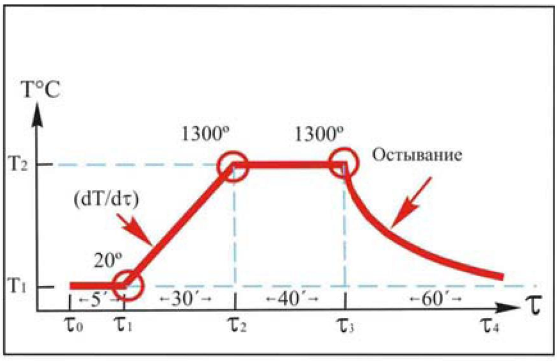
To determine the dependence of the change in the quality of the roasting product on changing the upper limit of the heating temperature from 1200 °C to 1300 °C, while maintaining the other earlier used heating parameters, this ash was tested at 1300 °C (5, 30', 40'), see figure 5.

Figure 5 – Photo illustration (5) of the product of calcination of ash of a new storage (Boraldai TPP); thermal-temporal parameters of firing stone material in a high temperature heat of 1300°C (5', 30', 40')

The coal ash of current dumps when heated at 1300 °C (5', 30', 40') forms a ceramic mass according to the external appearance of the previous firing of the ash obtained under the same temperature-chronological conditions of calcination. The sintered batch of the object under consideration is also presented in the form of a microporous formation, but with a few dark specks with diameters ranging from 0.5 to 2 mm. Most of the surface is dotted with micro-craters formed as a result of bursting of bubbles in the process of gas inclusions coming out of them. The resulting product does not contain cracks and is a consolidated mass with a more dim shade of the surface than was observed in the example of the abovementioned sample.

Based on results of X-ray tests, the mineral composition of the investigated charge mainly consists of mullite (68%) and quartz (22.4%) (figure 6). The new heating mode could not significantly change the ratio of these minerals and their aggregate state in the firing product. This is due to the insufficiency of the upper temperature limit (1300 °C) achieved in the experiment, which is below the melting point of mullite (1810-1530 °C) and quartz (1713-1728°C).The same should be attributed to the calcium and magnesium oxides obtained as a result of the decomposition present in the calcite and dolomite sample. However, CaO and MgO reduce viscosity of the liquid phase, the source of which can be one of the components of the studied ash, orthoclase. The feldspar is melted within (1130-1450 °C). Consequently, the development of ceramic formation in a system based on mullite and quartz as well as with the participation of calcium and magnesium oxides is performed as a result of melting of orthoclase, further crystallization of which ensures the consolidation of particles of the named minerals.

a



b

Figure 6 – (a) photo illustration the product of annealing of a sample of ash's old warehouse (Boraldai TPP); (b) – scheme for high-temperature ash heating in a chamber furnace - 1300 °C (5', 30', 40')

To reveal new qualities of expanded clay from old storage ash when changing the upper limit of the heating temperature from 1200 to 1300 °C a test was also conducted in the 1300 °C (5', 30', 40 ') mode, figure 6.Thermal treatment of this object in the new temperature range slightly increased its weight loss (~ 10%) and did not change the appearance of the sintered sample. Due to this, the resulting ceramic formation has the same hardness and micro porosity as the product made with the first firing process. Dark specks of crystalline origin are clearly traced on the surface of this formation. A distinctive feature of the new calcination product in relation to the external appearance of the compared material serves grayish-matt color of its surface. The yellowish-almond color of the formation was preceded by this color shade of the sintered charge at 1300 °C obtained in the heating mode of 1200 °C (5 ', 40', 30 ').

Thus, as a result of the given high-temperature modes of heating of the specified ash, highly porous materials with a special hardness, heat and noise insulating properties were obtained, characterized as chemically inert and fire-resistant substances. The procedure for obtaining materials with similar quality from the same ash in different heating regimes can later be used in large-scale production of construction products to find an acceptable technical and economic balance between the required quality of the products produced and the cost of energy resources for manufacturing them. Since this formation includes up to 50% of mullite ($Al_2(Al_{2.8}Si_{1.2})O_{9.6}$), 41% of quartz, and 9% of oxides (aluminum, calcium and iron) which do not have chemically active properties, environmental safety can be added to the abovementioned advantages of burnt material (figure 6). All these qualities of obtained products fully meet the technological requirements of light concrete fillers, which can be used in the construction of residential, administrative, and industrial buildings as well as for the construction of technical structures for various purposes.

The ashes of the old and new burials from the Boralday area contain up to 90% of siliceous formations (mullite and quartz) characterized as strong, fire-resistant, and chemically inert substances. As part of a building material, these natural formations are durable. Due to the peculiarities of the mineral content of the formations under consideration with negligible impurities of calcium and magnesium carbonates

(2.3 and 2.1%, respectively), they can be used directly as a concrete aggregate. And with the additional of firing of this ash, the lightness, heat, and sound proofness of the concrete product will be added to the abovementioned qualities.

The use of industrial waste from Boralday TPP as raw material for the production of expanded clay has a number of undeniable advantages over other types of natural material, namely the aggregate state of ash, low cost of energy, waste utilization, the solution of the environmental storage problem, and other benefits associated with the proximity of the heat-power center to a large metropolis. To obtain a test sample of quality expanded clay from said ash, isothermal heating of the charge at 1300 °C is required for 40 minutes (without taking into account the time of the furnace temperature rise and its cooling). Interest in this ash from the position of using it as raw material in the production of concrete filler is enormous in connection with the solution of environmental problems of recycling industrial waste and with an improvement of the quality of products and lowering of the cost of raw materials too.

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ЖЕҢІЛ БЕТОН ТОЛТЫРҒЫШТАР ӨНДІРІСТІҢ НЕГІЗІ РЕТІНДЕ ҚОЛДАНЫЛАТЫН ЖОҒАРЫ ТЕМПЕРАТУРАЛЫ СЫНАУЛАРДАН ӨТКЕН ТӨМЕНГІ ТӨРТТІК САЗДАҚТАРДЫҢ ЖӘНЕ БОРАЛДАЙ ЖЫЛУ ЭЛЕКТРОСТАНЦИЯНЫҢ ТЕХНОГЕНДІК КӨМІР КҮЛДЕРІНІҢ БАЛҚЫМАЛАРЫНЫҢ СИППАТАМАСЫ

Аннотация. Төменгі төрттік саздақтардан және жылулық электростансаның қалдықтардың көмір күлдерінен жасалған жеңіл бетон толтырғыштардың заттық құрамының, технологиялық қасиеттердің зерттеу мәселері қаралған. Қазақстан аймағында көмір энергетика қалдықтары түрінде көп мөлшері күлдер (жүздеген миллион тонна) қорланған. Өнеркәсіптік жеңіл бетон толтырғыш өндірісі ұйымдастыруы осы қалдықтар негізінде әртүрлі құрылыс құрылмалар дайындап шығаруға жағдай тұғызады.

Боралдай алаңындағы ескі және жаңа жерлеу күлдері 90% дейін кремний құрастырулар (муллит және кварц) жасайды және беріктік, отқатөзімділік, химиялық тұрақты зат ретінде сиппаталады. Құрылыс материалдары құрамында осы табиғи құрастырулар шыдаммерзімді болып саналады. Минералды мөлшері өзгешілігі себебінен қаралған құрастырулар өте аз кальций және магний карбонаттар түрінде зиянды қоспалар құрайды, оларды тікелей бетон толтырғыш ретінде колдануға болады. Қосымша күйдіру осы күлдің жоғарыда ескерілген қасиеттеріне тағы бірнеше қосылады – бетон бұйымдардың жеңілдігі, жылу және дыбыс жұтатын оқшаламасы.

Саздақты күйдіргенде құрамбөліктердің жартысы (монтмориллонит, мусковит және хлорит) балқылмаған кварц бөлшектерімен бірге біртектілік жентек құрайды. Кальцит, доломит, және гипс минералдары диссоциация арқылы магний және кальций окидтерге айналады, соңында балқыманын тұтқырлығын төмендетеді. Ең басты балқыманың толтырғышы (~50%) күйдіру арқылы алынған бұйымы кремнезем құраушы саздақтардың ұнтақтық түйіршіктері болған.

Осы зерттеу кезеңінде алынған бұйым өндірісте термиялық төзімді және механикалық берікті жеңіл бетон толтырғыш қабыршақты агрегат шығару үшін қолдану мүмкін.

Түйін сөздер: керамзит, шихта, лесс тарызды саздақтар, көмір күлі, термиялық, рентгенфаздық, микрозондық талдауы, жоғары температуралы пеште шихта балқытуы.

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ХАРАКТЕРИСТИКА РАСПЛАВОВ ВЫСОКОТЕМПЕРАТУРНЫХ ИСПЫТАНИЙ НИЖНЕЧЕТВЕРТИЧНЫХ СУГЛИНКОВ И ТЕХНОГЕННОЙ УГОЛЬНОЙ ЗОЛЫ БОРАЛДАЙСКОЙ ТЭЦ, КАК ОСНОВА ДЛЯ ПРОИЗВОДСТВА ЛЕГКИХ ЗАПОЛНИТЕЛЕЙ БЕТОНОВ

Аннотация. Рассматриваются вопросы изучения вещественного состава, технологических свойств легких заполнителей для бетонов из нижнечетвертичных суглинков и угольной золы – отходов ТЭЦ. На территории Казахстана накопилось огромное количество золы (многие сотни миллионов тонн), представляющие собой отходы угольной энергетики. Организация промышленного производства легких заполнителей из таких отходов позволила бы на их основе изготавливать различные строительные конструкции.

Золы старого и нового захоронения из площади Боралдай содержат в себе до 90% кремнистых образований (муллит и кварц), характеризующихся, как прочные, огнеупорные и химически устойчивые вещества. В составе строительного материала эти природные образования являются долговечными. В силу особенностей минерального содержания рассматриваемых образований с ничтожно малыми примесями в них карбонатов кальция и магния, они могут быть использованы непосредственно в качестве заполнителя бетона. А при дополнительном обжиге этой золы к вышеупомянутым качествам добавятся – легкость, тепло- и звуконепроницаемость бетонного изделия.

При обжиге суглинка, часть его компонентов (монтмориллонит, мусковит и хлорит), совместно с нерасплавившимися частицами кварца образуют однородный агрегат. Такие минералы, как кальцит, доломит и гипс, в процессе диссоциации, переродились в оксиды кальция и магния, что в итоге позволило снизить вязкость расплава. Главными заполнителями расплава (~50%) в полученном продукте обжига явились порошковые гранулы кремнеземистых составляющих суглинка.

Таким образом, полученный продукт на данном этапе исследования уже может быть использован при производстве термостойких и механически прочных чешуйчатых агрегатов легких заполнителей бетона.

Ключевые слова: керамзит, шихта, лессовидные суглинки, угольная зола, термический, рентгенофазовый и микрозондовый анализы, плавление шихты в высокотемпературной печи.