Periodica Polytechnica Civil Engineering, 67(3), pp. 706-715, 2023

Sintering and Crystallization Intensifiers for Production of Ceramic Paving Blocks by Vibropressing Technology

Sarsenbek Montaev¹, Berik Omarov^{2*}, Raimberdi Ristavletov², Karzhaubay Dosov¹, Nurgul Montayeva¹, Kanat Dosaliev¹

² Department of Construction and Building Materials, Faculty of Architecture, Construction and Transport, Mukhtar Auezov South Kazakhstan University, Tauke Khan Avenue 5, 160012 Shymkent, Kazakhstan

* Corresponding author, e-mail: omrbe@mail.ru

Received: 09 January 2023, Accepted: 18 March 2023, Published online: 28 March 2023

Abstract

The article presents the results of research on application of sintering and crystallization initiators based on a composition of blastfurnace granulated slag and glass wastes in the ceramic masses for production of ceramic paving blocks by vibro-pressing. The leading role of sintering and crystallization initiators in assuring the strong and dense structure of ceramic pieces was updated. The main laws of changes in physical and mechanical properties of ceramic paving stone samples depending on the amount of sintering and crystallization initiators in the burning temperature range 950–1000 °C have been established. It was determined that the availability of finely dispersed glass powder (fraction less than 0.1 mm) as a component of crystallization sintering initiators contributes to early emergence of liquid phase in the ceramic mass, as softening temperature of glass powder begins already at 720–750 °C. According to the results of X-ray phase and electron microscopic analysis it was determined that crystallization of low-temperature form of ß-wollastonite (CaSiO₃) is observed in the samples burnt at the temperature range of 950–1000 °C. It was proved that the availability of ß-wollastonite in the ceramic mass serves as a reinforcing component. It has been established that high strength values are achieved in those compositions where ß-wollastonite crystallization in the burning products is the highest. As a result of scientific and experimental work the feasibility of producing the ceramic paving stones by vibropressing containing sintering and crystallization initiators that meet the requirements of quality, aesthetics, environmental friendliness, resource- and energy-saving was proved.

Keywords

ceramic paving blocks, sintering and crystallization initiators, vibropressing, wollastonite, glass waste, granulated blast furnace slag

1 Introduction

With a development of Kazakhstan's construction industry, research in the technology of production of ceramic materials and products is becoming more and more relevant. Priority tasks in this area are to provide industrial and civil construction with high-quality, environmentally friendly materials, introduction of resource- and energysaving technologies, reducing production costs, as well as expanding the raw material base [1]. A limited number of domestic deposits of high-quality ceramic raw materials, no modern technological additives and mineralizers, no domestic high-performance equipment, shortage of new technological solutions at the stage of forming, drying, and burning hold back intensive development of the industry [1, 2]. Low-grade clay loams with high iron oxide content, carbonate inclusions and sulfate compounds, as well as highquality refractory clays with low and medium iron oxide content are used as the main clay raw materials in the production of ceramic materials and products [3].

Three methods of forming are mainly used in the production of building ceramics: casting, plastic, and semi-dry forming. The main requirement for all methods of forming is a homogeneity of the product, which determines the behavior of formed products during drying, burning and physical and chemical properties of an end product.

Application of vibropressing method in the production of ceramic paving blocks provides high density from mixtures with relatively low water content, simplifies the

¹ Department of Construction and Building Materials, Industrial-Technological Institute, Zhangir Khan West Kazakhstan Agrarian Technical University, Zhangir Khan Street 51, 090009 Uralsk, Kazakhstan

forming process, increases the mobility of technology from simplicity of installation, setting up, operation and possibility to produce products of different shapes and configurations in one technological line. Currently, however, all these advantages of vibrocompression are only used in the production of concrete paving blocks. Research on application of vibropressing method for the production of ceramic paving blocks based on readily available clay will expand the base of domestic materials used in urban landscaping, characterized by durability, chemical stability, environmental friendliness and aesthetics [4, 5].

Therefore, the actual problem at the present time is to develop an effective technology for the production of ceramic paving blocks based on readily available clay components using a vibrocompression method [5, 6]. Burning is one of the main stages in the technology of ceramic products, at which a final formation of the phase composition structure takes place in the sintering process [7–11]. Literature analysis shows that the burning temperature for obtaining high-quality ceramic material based on refractory clay raw materials ranges between 1000 to 1150 °C. Only at such high temperatures is sintering intensification of the ceramic matrix and formation of the structure and phase composition, stabilization of ceramic pieces color is achieved.

Despite a variety of material chemical compositions in the technology of ceramic production, the common technological operation is the sintering of materials at temperatures below the materials' melting point. Sintering is defined not only as a physical and chemical process, but also as a technological operation [12, 13] in which mechanical and chemically bound water is removed; organic substances are burned out; thermal decomposition of crystalline compounds. The following stages involve solid-phase chemical reactions (mutual dissolution of components to form new phases, melting of individual components, polymorphic transformations, concentration of internal stresses, etc.) [14]. Sintering processes are particularly influenced by the following technological factors: mechanical, thermal and chemical. The mechanical parameters that accelerate sintering include material grinding (grinding fineness values are determined by economic considerations [15]) and material compaction before sintering (pressing). Sintering temperature (determined by material properties and requirements for a given porosity) and temperature rise rate (determined by need for even heating of burning material and obtaining material without defects) primarily affect the speed of sintering and achievement of sintered state of the material [16].

Chemical activation of sintering is reduced to inclusion of additives, both forming and not forming liquid phase. In order to obtain high quality products, functional additives are added to the ceramic mass [17-25]. Additives forming the liquid phase, selected under two conditions: the liquid phase must be well-wetting and have the lowest possible viscosity, the additive is included in such an amount that the total content of a liquid phase at sintering temperature would be below 10% [26]. Additives that do not form a liquid phase with a basic material are divided into three groups: activating the sintering process and simultaneously accelerating recrystallization (TiO₂ in Al₂O₃; LiO₂ in MgO; CaO in TiO₂, etc.); activating sintering but slowing the recrystallization process (MgO or BeO in Al₂O₂); slowing the sintering process and slowing grain growth (CaO, CoO, Cd₂O₃ in Al₂O₃) [27]. Usually, additives have an effect on sintering at low concentrations. It should be kept in mind that additives forming solid solutions accelerate sintering and additives forming chemical compounds slow it down.

The effect of additives depends on concentration. Optimal concentration of additives must be within solubility and not exceed the concentration that leads to the formation of side crystalline phases (for silicates and oxides of the system MgO-Al₂O₃-SiO₂ optimal proportion of additive is in the range 0.05–1.0%) [28–30]. Increasing the concentration of additives leads to the formation of new crystalline phases in the intergranular space, representing oxides of additives or products of their interaction with a basic oxide.

The quantity of additives also affects recrystallization (significantly soluble additives increase oxide recrystallization during sintering, and low-soluble additives (<1 %) either have little effect on recrystallization or obstruct it) [31]. A mechanism of microadditives action is a simultaneous interaction of additives with basic substance on the contact surface and diffusion of cationic additive inside grains and microcrystals. The additives can also play the role of a kind of lubricant that facilitates the sliding of macroparticles. Practically using activating additives, even in small quantities, can significantly reduce the sintering temperature and modify the structure of ceramic pieces [31-35]. Many existing enterprises for production of ceramic products are focused on operating the technological equipment based only on clay raw materials, regardless of obvious advantages of various activating additives in the composition of ceramic masses, which ensure energy saving and quality of the finished product. Therefore, these enterprises do not have the technical ability to use small activating additives, which allow for energy and resource saving.

To address this problem, it is necessary not only to develop new effective compositions of sintering and crystallization intensifiers that promote creation of a crystalline framework structure and increase interaction activity of mixture components subject to lower sintering temperature, but also to issue practical recommendations on their implementation in specific production.

Objective of the work: Development of sintering and crystallization intensifiers and their use in the composition of ceramic mass for production of ceramic paving blocks by vibrocompression method.

2 Research methodology, initial materials

At the initial stage, studies were conducted to study the physical and mechanical properties and chemical and mineralogical characteristics of selected raw materials. The method of scanning electron microscopy (REM) of JSM-6390LV with energy dispersion microanalysis was used to determine the local elemental composition of rock samples, method of mass spectrometry with inductively coupled plasma ICP-MS Agilent 7500cx was used to determine the chemical elemental composition. To determine the mineralogical composition the X'Pert PRO MPD X-ray diffractometry method was used. X-ray phase analysis (XRF) of samples was carried out with a special apparatus DRON-3.

As the raw materials under study were selected loam and bentonite clay deposits of Turkistan oblast. At the initial state, the loam was light brown in color and was characterized by an unoriented texture and silty structure. The rock contains calcium carbonates both as large (up to 3 to 5 mm) inclusions and in a very thin state (pelitamorphic carbonates). Bentonite clay was gray-green in color with an admixture of yellow, red and brown colors and was characterized by having 2 types of texture: oriented and entangled with a coarse-dispersed structure. Results of chemical analysis are presented in Table 1.

By the content of basic oxides $(Al_2O_3 \text{ and } Fe_2O_3 \text{ per cal$ $cined substance})$ in accordance with State Standard 9169-75 [36], the rocks studied can be classified as those belonging to the acid (loam) and semi-acid (bentonite clay) groups with high content of coloring oxides, specifically Fe₂O₃. Based on X-ray diffraction and microscopic analyses, the clay part of loam is monomineral, consisting of kaolinite, and bentonite clay is represented mainly by montmorillonite and kaolinite. Hydromica is present in smaller quantities in the loam. In the nonclayey part of loam the free quartz, calcite CaCO₃, feldspar (microcline KAlSi₃O₈, albite NaAlSi₃O₈), specular stone (Figs. 1, 2 and Tables 2, 3) were identified.

Areometric method was used to determine the clay granulometric size composition (State Standard 12536-2014 [37]). The data are presented in Table 3.

Based on the research results, it was found that the granulometric composition of clays are like each other by significant content of dust fraction, while they differ in the clay component and sand fraction. It should be noted that bentonite clay contains more than half of clay and less sand than loam.

When determining coarse-grained inclusions, both clay materials were crushed to a lump size of at most 10 mm and dissolved in water for a day. After that, the residue on sieve No. 05 was determined. The index of sandiness was evaluated by the residue on sieve No. 0063. The results are shown in Table 4. Formational moisture content of clays was determined by organoleptic method with subsequent determination of moisture content by weight method. The forming moisture was 15.94 % and 31.58 % for the studied clays loam and bentonite. Plasticity was determined for both clays by the balancing cone method on State Standard 21216-2014 [38]. The data characterizing the plastic properties of clays are given in Table 5.

In accordance with classification by the number of plasticity, adopted for clay raw materials, clay loam belongs to the low plasticity raw materials, and bentonite clay - to the medium plasticity.

To obtain sintering and crystallization intensifiers, the granulated blast furnace slag of JSC "Arcelor Mittal Temirtau" and glass waste in the form of glass scrap and glass powder of "Steklo-Service" LLP are of particular interest. Blast furnace granulated slag is a loose gray material. Sharp cooling of melted slag in the process of granulation causes mainly its glassy structure. The glass phase content in them is 65–97% (Table 6).

| Table 1 Chemical composition of loam and bentonite deposits of Turkistan oblast | | | | | | | | | | | |
|---|---------------------------------|--------------------|--------------------------------|------------------|------|------|-------------------|------------------|--------|-------|--|
| Raw material | Mass fraction of a component, % | | | | | | | | | | |
| | SiO ₂ | Al ₂ O3 | Fe ₂ O ₃ | TiO ₂ | CaO | MgO | Na ₂ O | K ₂ O | SO_3 | 1.o.i | |
| Clay loam | 53.0 | 11.0 | 4.2 | 0.68 | 10.8 | 2.72 | 1.366 | 3.48 | 0.23 | 12.0 | |
| Bentonite | 54.2 | 14.5 | 8.0 | 0.9 | 2.62 | 2.16 | 0.86 | 3.28 | 3.61 | 9.4 | |



80 µm



(a)



Spectrum 4 0 0.5 1 1.5 2 2.5 3 Full scale 1489 imp. Cursor:3.117 (28 imp.) 3.5 7.5 keV 5.5 4.5 5 6 3.5 6.5 0 0.5 1 1.5 2 2.5 3 Full scale 1489 imp. Cursor: 3.117 (32 imp.)

(b)

Fig. 1 Results of loam studies by scanning electron microscopy with INCA Energy microanalysis system: (a) microstructure of loam, (b) spectra of points under study



Electronic image 1



Fig. 2 Results of loam studies by scanning electron microscopy with INCA Energy microanalysis system: (a) microstructure of loam, (b) spectra of points under study

Chemical composition of blast furnace granulated slag of JSC "Arcelor Mittal Temirtau", mass %: 40.62 SiO₂; 16.24 Al₂O₃; 0.19–0.52 Fe₂O₃, 42.11 CaO; 0.43 FeO; 5.33-10.39 MgO; 1.66 SO₃; 0.36-1.5 Na₂O; 0.42-1.32 K₂O; 0.62-0.88 TiO₂; 0.92 loss on ignition.

Sharp cooling of melted slag in the granulation process causes mainly its glassy structure. The glass phase content in them is 65–97%.

X-ray phase analysis of heat-treated slag within temperature range of 950-1000 °C shows the existence of wollastonite in it (d/n = 3.85; 3.50; 3.30; 2.96; 2.706; 2.55; 2.34; 2.18; 2.02; 1.82; 10^{-10} m), melilite (d/n = 3.06; 2.86; 2.47; 2.30; 1.98; 1.88; 10^{-10} m) and cuspidine (d/n = 3.30; $3.06; 2.55; 2.30 \times 10^{-10} \text{ m}$).

As a result of "Steklo-Service" LLP activity, which is one of the largest centers of industrial glass processing in Kazakhstan [39], fine dispersed glass powder and glass scrap is formed, which is a waste of this enterprise. Annual generation of this waste is more than 2.500-3.000 tons. Currently there are more than 30 thousand tons in the

Table 2 Chemical elemental analysis of loam, %

| G (| | | | | | Element | | | | | | T (1 |
|----------|-------|------|------|------|-------|---------|------|------|------|------|-------|-------|
| Spectrum | 0 | Na | Mg | Al | Si | S | K | Ca | Cr | Mn | Fe | Total |
| 1 | 22.25 | 0.70 | 1.20 | 3.50 | 10.38 | 0.00 | 0.76 | 1.93 | 0.67 | 0.53 | 58.08 | 100.0 |
| 3 | 60.09 | 0.27 | 0.49 | 2.23 | 33.20 | 0.17 | 0.56 | 1.56 | - | - | 1.43 | 100.0 |
| 4 | 57.95 | 0.45 | 0.35 | 1.54 | 36.64 | 0.08 | 0.44 | 1.51 | - | - | 1.03 | 100.0 |
| 5 | 56.92 | 0.69 | 1.41 | 4.83 | 24.78 | 0.25 | 1.31 | 6.32 | - | - | 3.50 | 100.0 |
| Max | 60.09 | 0.70 | 1.41 | 4.83 | 36.64 | 0.25 | 1.31 | 6.32 | 0.67 | 0.53 | 58.08 | |
| Min | 22.25 | 0.27 | 0.35 | 1.54 | 10.38 | 0.00 | 0.44 | 1.51 | 0.67 | 0.53 | 1.03 | |

| Table 3 Granulometric | composition | of clay loam and | bentonite clay |
|-----------------------|-------------|------------------|----------------|
|-----------------------|-------------|------------------|----------------|

| Fraction, mm | < 0.005 | 0.005-0.01 | 0.01-0.05 | 0.05-0.1 | 0.1 - 0.2 | 0.2-0.5 | 0.5–1 | 1–2 | 2-5 | >5 |
|----------------|---------|------------|-----------|----------|-----------|---------|-------|------|------|----|
| Clay loam | | | | | | | | | | |
| Content, % | 17.79 | 16.68 | 61.71 | 2.90 | 0.68 | 0.13 | 0.05 | 0.05 | 0.02 | 0 |
| Bentonite clay | | | | | | | | | | |
| Content, % | 36.06 | 25.13 | 31.14 | 4.06 | 0.41 | 0.64 | 1.02 | 0.55 | 1.00 | 0 |

| Table 4 Coarse- | grained inc | lusions and | sandiness of | f clay rocks |
|-----------------|-------------|-------------|--------------|--------------|
| | 0 | | | 2 |

| None of the mean out | Cont | tent, % |
|---------------------------|-----------|----------------|
| Name of the property | Clay loam | Bentonite clay |
| Coarse grained inclusions | 0.4 | 2.4 |
| Sandiness | 7.8 | 3.4 |
| | | |

| Table 5 Plasticity indicators of clay loam and bentonite | | | | | | | | |
|--|----------------------------|------|-------------|-------------------|------------|--------|--|--|
| Name of the raw material | Absolute hus state of b | Nui | Number of | | | | | |
| | Lower fluidity limit | | Lir plas | nit of sticity | plasticity | | | |
| Clay loam | 23.85 | | 19.22 | | 4.63 | | | |
| Bentonite clay | 61.06 | | 40.02 | | 21.04 | | | |
| Table 6 Granulometric composition of blast furnace granulated slag | | | | | | | | |
| Diameter of sieve holes, mm | 2.5 | 1.25 | 0.63 | 0.315 | 0.14 | > 0.14 | | |

dumps. Chemical composition of glass waste of "Steklo-Service" LLP, mass %: 71.8–72.4 SiO₂; 1.8–2.2 Al₂O₃; 0.2 Fe₂O₃; 6.4–6.7 CaO; 3.8–4.2 MgO; 14.5–14.9 Na₂O; 0.5– 1.5 K₂O; 0.5 SO₂.

14-17 35-37 26-30 14-17

2-5

2-4

Residue on sieve, %

Based on the results of X-ray diffraction analysis (XRD), it was found that the glass waste of "Steklo-Service" LLP is X-ray amorphous, indicating the lack of crystalline phases. As a result of the study, it was determined that the temperature of beginning of softening is 720-750 °C.

To achieve this goal, sintering and crystallization initiators were first separately prepared for further addition to the basic ceramic mass. Preparation of sintering and crystallization initiator was carried out according to the following technological sequence: blast furnace granulated slag and glass wastes were weighed using electronic scales with a relation of 1:1. Then, the components were loaded into a laboratory ball mill and co-milled to a specific surface of 2000–2500 cm²/g. Obtained sintering and crystallization initiator powders were used as mini additives in the basic ceramic mass.

Four compositions of ceramic masses were prepared for production of ceramic paving blocks. Ceramic compositions were prepared by mixing dry powders of clay loam, bentonite, and sintering and crystallization initiators in the proportions shown in Table 7.

To prepare ceramic masses, clay loam and bentonite were first dried in a drying box at 70–80 °C to a residual moisture of 5–7% and dosed using electronic scales according to Table 7 and grinded together in a laboratory ball mill until they passed completely through a 1.0 mm sieve. Sintering and crystallization initiators in the range of 5–15% weight of clay powders were added separately to the clay powders

| Table 7 Studied compositions of ceramic masses | | | | | | | | |
|--|------------------|-----------|--|--|--|--|--|--|
| | Mass fraction, % | | | | | | | |
| Composition numbers | Clay loam | Bentonite | Sintering and crystallization initiators | | | | | |
| 1 | 85 | 5 | 5 | | | | | |
| 2 | 70 | 10 | 7 | | | | | |
| 3 | 55 | 15 | 10 | | | | | |
| 4 | 45 | 20 | 15 | | | | | |
| Control composition without additive | 80 | 20 | - | | | | | |

and thoroughly mixed in a laboratory stirrer until a homogeneous mixture was obtained. Then water was added to 10–12% of the dry mixture and stirred again until a homogeneous mixture was obtained. The moistened ceramic mass was cured in a drying cabinet for 48 hours to saturate the mixture completely. After curing time and ceramic masses were formed the samples of cylinders with dimensions of 50 × 50 mm by vibrocompression. Formed samples were dried in a drying box at t = 70-80 °C to constant weight. Dried samples were burned in a laboratory electric furnace SNOL 58/350 at 950–1000 °C. The rate of temperature rise was 150 °C/hour. Burnt samples were cooled in the shutdown furnace to room temperature (Fig. 3).

After the thermal-treated samples were tested to determine the physical and mechanical properties. The physical and mechanical properties tested were the drying sensitivity coefficient by Chizhsky's method [40], compressive and flexural strength, average density, water absorption, and frost resistance.

Duration of period of freshly formed sample obliteration by radiant heat flux until crack formation in it (sample of size $55 \times 55 \times 10$ mm) was taken as the criterion of sensitivity to drying. Irradiation period before cracking was determined as the arithmetic mean of test results from three specimens and evaluated the sensitivity to drying of ceramic mass: highly sensitive is less than 100



Fig. 3 A general view of ceramic samples formed by vibrocompression and containing sintering and crystallization initiators (950–1000 °C)

seconds, medium sensitive 101–108 seconds, low sensitive is more than 180 seconds. Using this method, highly sensitive ceramic masses, when exposed to irradiation, more quickly the first cracks appear in them.

3 Results and discussion

With medium-sensitive and low-sensitive ceramic masses, the first cracks appear in longer irradiations. Therefore, the more ceramic masses are highly sensitive to drying, the faster the first cracks appear when they are thermally irradiated. The results of scientific and experimental work are presented in Table 8.

As the results of obtained scientific-experimental works show, that with an increase of sintering and crystallization initiator content the drying properties of the ceramic mass improves. Specifically, the ceramic mass using sintering and crystallization initiators transfer the mixture under study from the category of highly sensitive to the category of medium sensitive. A further increase in sintering and crystallization initiators up to 15% puts the ceramic mass in the category of low-sensitivity mixtures. The indicated effect is apparently explained by a more complete wedging of highly sensitive to drying dispersed particles of bentonite loam by more finely dispersed particles of sintering and crystallization initiators. As a result, finely grinded particles of sintering and crystallization initiators promote easy transfer of moisture from the ceramic mass without defects and drying cracks.

As a result of analysis of physical and mechanical properties of thermal treated samples in the temperature range 950-1000 °C allowed to establish the main patterns of their changes depending on additions of sintering and crystallization initiators. As the number of sintering and crystallization initiators increases, the average density and compressive and flexural strength of the samples increase.

At a burning temperature of 1000 °C the extent of increase in the indicators of these properties increases. So, an increase in average density increases from 1.87 to 2.26 g/cm³ and compressive strength from 22.7 MPa to 44.3 MPa.

| 1 1 | | | - | | |
|--------------------------------|--|--|--|---|--|
| sensitivity Average den | sity, Streng | gth, MPa | Water absorption, | Frost resistance, cycles | |
| ent, seconds g/cm ³ | At compression | At bending. | % | | |
| 165 1.87–1.92 | 2 27.7–29.6 | 2.4 | 8.4–9.5 | 95 | |
| 175 1.92–2.03 | 3 32.2–33.4 | 3.5 | 7.3-8.2 | 100 | |
| 182 2.17–2.19 | 38.2–39.3 | 4.8 | 6.4–7.3 | 115 | |
| 185 2.24–2.2 | 6 42.4–44.3 | 6.6 | 4.5-5.4 | 120 | |
| 110 1.58 | 18.5 | 2.2 | 17.5 | 40 | |
| | sensitivity Average den g/cm ³ 165 1.87–1.92 175 1.92–2.02 182 2.17–2.19 185 2. 24–2.2 110 1.58 | sensitivity Average density, g/cm ³ Strenge At compression 165 1.87–1.92 27.7–29.6 175 1.92–2.03 32.2–33.4 182 2.17–2.19 38.2–39.3 185 2. 24–2.26 42.4–44.3 110 1.58 18.5 | Average density, gent, seconds Average density, g/cm ³ Strength, MPa 165 1.87–1.92 27.7–29.6 2.4 175 1.92–2.03 32.2–33.4 3.5 182 2.17–2.19 38.2–39.3 4.8 185 2. 24–2.26 42.4–44.3 6.6 110 1.58 18.5 2.2 | sensitivity ent, seconds Average density, g/cm ³ Strength, MPa Water absorption, % 165 1.87–1.92 27.7–29.6 2.4 8.4–9.5 175 1.92–2.03 32.2–33.4 3.5 7.3–8.2 182 2.17–2.19 38.2–39.3 4.8 6.4–7.3 185 2.24–2.26 42.4–44.3 6.6 4.5–5.4 110 1.58 18.5 2.2 17.5 | |

Comparative analysis shows that the increase in strength of samples at a burning temperature of 1000 °C with an increase in the number of additives of sintering and crystallization initiators to 15% is almost 1.5 times. Apparently, a finely dispersed powder of sintering and crystallization initiators intensifies the sintering process in the composition with clay minerals under influence of high temperature. Thanks to the increased specific surface area of sintering and crystallization initiators probably increases the reactivity in a raw mixture by increasing the number of contacts between particles, contributing to improve the physical and mechanical properties of samples not only at the burning stages but also at the stages of forming and drying.

Studies in the change of physical-mechanical properties and the structure of ceramics show that the greatest homogeneity, density and strength has the samples containing sintering and crystallization initiators in the amount of 7.0% to 15.0% and burnt in the burning temperature range 950–1000 °C. The front surface of ceramic specimens formed by vibrocompression and burnt in the temperature interval 950–1000 °C is particularly smooth without defects, and the surface of specimens in the fracture has a high sintered homogeneity (Fig. 4).

This fact proves that it is the addition of sintering and crystallization initiators that promote liquid-phase sintering and crystallization, which leads to densification and hardening of ceramic piece structure.

It should also be noted that the existence of fine dispersed glass powder (fraction less than 0.1 mm) as part of sintering initiators of crystallization promotes early emergence of the liquid phase in the ceramic mass, as the softening temperature of glass powder already begins at 720–750 °C. On the X-ray radiograph (Fig. 5) there is a sharp increase in reflexes - wallastonite with a significant decrease in the reflex of quartz. And the absolute increase in the main lines of wollastonite is 2.97×10^{-10} m.



Fig. 4 Dense macrostructure of samples burnt in the temperature range 950–1000 °C. (a) photo of the front surface of a ceramic sample, (b) photo of a ceramic sample surface in the fracture

Wollastonite is a natural calcium silicate with chemical formula $CaSiO_3$. Natural wollastonite is characterized by a needle-like structure of crystals, which form needle-shaped grains when split. Due to the needle shape of wollastonite grains, it is mainly used as a micro reinforcing filler. Therefore, wollastonite in a ceramic mass plays the role of a reinforcing component.

Indeed, it should be noted that high strength values are achieved in those compositions where the greatest crystallization of b-wollastonite in the burning products.

In the samples (Fig. 6) burnt in the temperature range 950-1000 °C, needle-shaped crystallized minerals of low-temperature form of β -wollastonite are observed.



Fig. 5 X-ray diagram of burnt ceramic samples in the temperature range 950–1000 °C



100 µm Electronic image 1



Fig. 6 Microstructure of the clay loam-loam granulated slag-glass powder ceramic composition (enlargement x2000) (a) microstructure, (b) spectra of points under study

To a greater extent, β -wollastonite minerals are observed in samples of compositions where the quantity of sintering and crystallization initiators is 7–15%.

The facts of improving of forming and final properties of the samples are also confirmed by changes of water absorption parameters. Analysis of changes in the water absorption indicators shows that with an increase in the quantity of sintering and crystallization initiators, there is a significant decrease in their indicators. Thus, a decrease in the water absorption of burnt samples at a burning temperature of 1000 °C ranges from 9.5% to 5.4%.

Fig. 7 shows fragments of the burning process of natural samples of ceramic paving blocks using sintering and crystallization initiators.

Determination of the basic laws of changes in physical and mechanical properties of samples obtained by vibro-pressing depending on content of sintering and crystallization initiators allowed to evaluate the effectiveness of their use in producing ceramic paving blocks with high performance properties.

4 Conclusions

By results of research on using sintering and crystallization initiators based on composition of blast-furnace granulated slag and glass waste in the composition of ceramic mass for production of ceramic paving blocks by vibrocompression:



Fig. 7 Fragments of the burning process of natural samples of ceramic paving blocks using sintering and crystallization initiators;a) burning process, b) finished samples

References

 Lygina, T. Z., Kornilov, A. B., Senatorov, P. P. "Sostoyaniye proizvodstva stenovykh keramicheskikh materialov v Rossiyskoy Federatsii" (State of production of wall ceramic materials in the Russian Federation), Stroitel'nyye materialy), Construction Materials, 4, pp. 10–11, 2009. (in Russian)

- Scientific and experimental work on creation of sintering and crystallization initiators using blast-furnace granulated slag of JSC "Arcelor Mittal Temirtau" and glass waste of "Steklo servis" LLP for production of ceramic paving block by vibrocompression was carried out.
- 2. The main laws of changes in physical and mechanical properties of ceramic paving block samples depending on the quantity of sintering initiators and additive crystallization in the burning temperature range 950–1000 °C have been established.
- 3. It was determined that the existence of fine glass powder (fraction less than 0.1 mm) in the composition of sintering initiators contributes to early emergence of liquid phase in the ceramic mass, as temperature of glass powder softening begins already at the temperature of 720–750 °C.
- 4. It was determined that increasing the quantity of sintering and crystallization initiators 15% transfer the ceramic mass into the category of low-sensitivity mixtures. This allows, performs drying of formed samples at an accelerated rate without drying cracks.
- 5. By results of the X-ray phase and electron microscopic analysis it is established that in the samples burnt at a temperature in the range of 950–1000 °C crystallization of the low-temperature form of β-wollastonite is observed (CaSiO₃).
- 6. It is proved that the availability of β-wollastonite in the composition of ceramic mass plays the role of a reinforcing component. Indeed, it should be noted that high strength values are achieved in those compositions where β-wollastonite crystallization is the highest in the burning products.
- 7. As a result of the scientific and experimental work the feasibility of production of ceramic paving blocks by vibrocompression containing sintering and crystallization initiators that meet the requirements of quality, aesthetics, environmental friendliness, resource-and energy-saving is proved.
- [2] Cabrera-Covarrubias, F. G., Gómez-Soberón, J. M., Almaral-Sánchez, J. L., Corral-Higuera, R., Gómez-Soberón, M. C. "Implementation of Interaction Diagram of the Properties in Fresh for Mortars with Ceramic Aggregates", Periodica Polytechnica Civil Engineering, 61(2), pp. 335–340, 2017. https://doi.org/10.3311/PPci.9651

[3] Dondi, M., Raimondo, M., Zanelli, C. "Clays and bodies for ceramic tiles: Reappraisal and technological classification", Applied Clay Science, 96, pp. 91–109, 2014.

https://doi.org/10.1016/j.clay.2014.01.013

- [4] Montayev, S. A., Adilova, N. B., Omarov, B. A., Ristavletov, R. A., Shakeshev, B. T. "Study of clay raw materials of Turkestan region for the production of ceramic paving stones", Bulletin of Kazakh Leading Academy of Architecture and Construction, 1(83), pp. 170–180, 2022. (in Russian)
 - https://doi.org/10.51488/1680-080X/2022.1-13
- [5] Montaev, S. A., Zharylgapov, S. M., Montaeva, N. S., Shakeshev, B. T. "Research of possibility of producing ceramic paving stones by vibrocompression with the purpose of using them in the improvement of urban areas", IOP Conference Series: Materials Science and Engineering, 775, 012118, 2020. https://doi.org/10.1088/1757-899X/775/1/012118
- [6] Dzhumaniyazov, Z. B., Babayev, Z. K., Sharipov, D. S. H. "Dorozhnaya keramicheskaya bruschatka na osnove mestnykh lossovidnykh porod modifitsirovannyy stekloboyem" (Road ceramic paving blocks on the basis of local loess-like rocks modified with glass-block), Universum: Tekhnicheskiye Nauki, 1(82), 2021. [online] Available at: https://7universum.com/ru/tech/ archive/item/11197 [Accessed: 24 January 2021]. (in Russian)
- [7] Pavlov, V. F. "Fiziko-khimicheskiye osnovy obzhiga izdeliy stroitel'noy keramiki" (Physico-chemical bases of burning products of building ceramics), Stroyizdat, 1976. (in Russian)
- [8] Terjék, A., Józsa, Z. "Analysis of Surface Properties Determining Slip Resistance of Ceramic Tiles", Periodica Polytechnica Civil Engineering, 59(3), pp. 393–404, 2015. https://doi.org/10.3311/PPci.7796
- [9] Mosin, Yu.M., Pershikov, S. A. "Trekhmernaya model' protsessa diffuzionnogo spekaniya keramiki" (Three-dimensional model of diffusion sintering of ceramics), Neorganicheskiye Materialy (Inorganic Materials), 36(10), pp. 12771280, 2000. (in Russian)
- [10] Pershikov, S. A., Vitko, T. L. "Izucheniye kinetiki spekaniya poroshkov stekla razlichnoy dispersnosti" (Studying the kinetics of sintering of glass powders of various dispersion), Advances in Chemistry and Chemical Technology: Collection of Scientific Papers, 16(3), pp. 91–92, 2022. (in Russian)
- [11] Dovzhenko, I. G. "Intensification of agglomeration of ceramic brick with application of the waste of aluminium manufacture", Fundamental Research, 12(2), pp. 341–344, 2011.
- [12] Gur'yeva, V. A. "Osobennosti protsessa spekaniya keramicheskikh mass, soderzhashchikh silikaty magniya" (Features of the sintering process of ceramic masses containing magnesium silicates), Glass and Ceramics, 11, pp. 26–28, 2008 (in Russian)
- [13] Budnikov, P. P., Ginstling, A. M. "Reaktsii v smesyakh tverdykh veshchestv" (Reactions in mixtures of solids), Stroyizdat, 1971. (in Russian)
- [14] Pivinskiy, Y. E. "Teoreticheskiye aspekty tekhnologii keramiki i ogneuporov. Izbrannyye trudy. Tom 1" (Theoretical aspects of technology of ceramics and refractories. Selected Works. Vol. 1.), Stroyizdat, 2003. (in Russian) ISBN 5-87897-101-1
- [15] Gorokhova, E. V. "Materialovedeniye i tekhnologiya keramiki" (Materials science and technology of ceramics: manual), The Highest School, 2009. (in Russian) ISBN 978-985-06-1706-4

- [16] Pogrebenkov, V. M. "Tekhnologiya tonkoy i stroitel'noy keramiki" (Technology of fine and building ceramics), Tomsk Polytechnic University, Study Guide, 2005. (in Russian)
- [17] Belyakov, A. V., Pershikov, S. A., Sukhozhak A. N. "The roleof carbon on production of transparent corundum ceramics based on alkoxy powder technology", Glass and Ceramics, 9, pp. 18–22, 1999. (in Russian)
- [18] Sagin, J., Adenova, D., Tolepbayeva, A., Poryadin, V. "Underground water resources in Kazakhstan", International Journal of Environmental Studies, 74(3), pp. 386–398, 2017 https://doi.org/10.1080/00207233.2017.1288059
- [19] Hasanah, N., Tristi, J., Rahayu, D. "Atenolol imprinted polymer with butanol as a porogenic solvent: using two polymerization methods", Rasayan Journal of Chemistry, 13(3), pp. 1313–1320, 2020. https://doi.org/10.31788/RJC.2020.1335765
- [20] Belyakov, A. V., Sukhozhak, A. N., Pershikov, S. A., Kuznetsov, A. I., Rastorguev, Yu. I., Goncharik, M. M., Pavlov, E.V. "Method of preparing aluminium oxide powder to manufacture transparent ceramic products", D.I. Mendeleev Russian University of Chemical Technology, Russia, RU2117631C1, 1998.
- [21] Gur'yeva, V. A. "Otsenka svoystv keramicheskikh izdeliy na osnove tekhnogennogo syr'ya, soderzhashchego silikaty magniya" (Evaluation of the properties of ceramic products based on manmade raw materials containing magnesium silicates), Stroitel'nyye Materialy (Building Materials), 12 (648), pp. 46–48, 2008.
- [22] Wang, C., Liu, J., Du, H., Guo, A. "Effect of fly ash cenospheres on the microstructure and properties of silica-based composites", Ceramics International, 38(5), pp. 4395–4400, 2012. https://doi.org/10.1016/j.ceramint.2012.01.044
- [23] Deepthi, M. V., Sharma, M., Sailaja, R. R. N., Anantha, P., Sampathkumaran, P., Seetharamu, S. "Mechanical and thermal characteristics of high density polyethylene-fly ash Cenospheres composites", Materials & Design, 31(4), pp. 2051–2060, 2010. https://doi.org/10.1016/j.matdes.2009.10.014
- [24] Kulkarni, M. B., Bambole, V. A., Mahanwar, P. A. "Effect of particle size of fly ash cenospheres on the properties of acrylonitrile butadiene styrene-filled composites", Journal of Thermoplastic Composite Materials, 27(2), pp. 251–267, 2014. https://doi.org/10.1177/0892705712443253
- [25] Thaarrini, J., Ramasamy, V. "Properties of Foundry Sand, Ground Granulated Blast Furnace Slag and Bottom Ash Based Geopolymers under Ambient Conditions", Periodica Polytechnica Civil Engineering, 60(2), pp. 159–168, 2016. https://doi.org/10.3311/PPci.8014
- [26] Ayrapetov, G. A., Bezrodnyy, O. K., Zholobov, A. L., Zhukov, A. V. "Stroitel'nyye materialy" (Construction materials), Phoenix, 2007. ISBN 5-222-05904-9 (in Russian)
- [27] Shishakina, O. A., Palamarchuk, A. A. "Application smooth in the production of ceramic materials", International Journal of Applied and Fundamental Research, 11, pp. 105–109, 2019 (in Russian)
- [28] Strelov, K. K., Kashcheyev, I. D. "Teoreticheskiye osnovy tekhnologii ogneupornykh materialov" (Theoretical bases of technology of refractory materials), Metallurgiya, 1996. (in Russian) ISBN 5-229-01212-9

- [29] Vakalova, T. V. "Aktivatsiya protsessov sinteza i spekaniya kompozitsiy na osnove oksidov v sisteme «mullit–kordiyerit»" (Activation of the processes of synthesis and sintering of compositions based on oxides in the "mullite - cordierite" system), Izvestiya Vuzov. Physics, 56 (7/2), pp. 189–194, 2013. (in Russian)
- [30] Vakalova, T. V., KHabas, T. A., Pogrebenkov, V. M., Biryukova, A. A. "Activation of process synthesis and sintering of mullitecordierite compositions based on natural raw materials", International Journal of Applied and Fundamental Research, 5-3, pp. 379–384, 2015. (in Russian)
- [31] Sandulyak, A. V., Sandulyak, A. A., Ershov, D. V., Sandulyak D. A., Ershova V. A. "Magnetic separation of raw materials for glass and ceramic production: problems of ferruginous impurity control (review)", Glass and Ceramics, 69, pp. 208–213, 2012. https://doi.org/10.1007/s10717-012-9448-7
- [32] Khabas, T. A., Vereshchagin, V. I., Vakalova, T. V., Kirchanov, A. A., Kulikovskaya, N. A., Kozhevnikova, N. G. "Low-Temperature Synthesis of the Cordierite Phase in Ceramic Mixtures of Natural Raw Materials", Refractories and Industrial Ceramics, 44, pp. 181–185, 2003. https://doi.org/10.1023/A:1026360403004
- [33] Bakunov, V. S., Lukin, E. S. "Characteristics of high-density technical ceramics technology. Structure regulation during sintering", Glass and Ceramics, 65, pp. 231–235, 2008. https://doi.org/10.1007/s10717-008-9054-x

- [34] Lotov, V. A. "Correlation Between Changes in Linear Dimensions and Volumetric Phase Composition of Ceramics in Sintering", Glass and Ceramics, 62, pp. 21–24, 2005. https://doi.org/10.1007/s10717-005-0023-3
- [35] Dokandari, P. A., Topal, A. "Effects of Warm Mix Asphalt Additives on Aging Characteristics of Bituminous Mixtures", Periodica Polytechnica Civil Engineering, 59(4), pp. 475–486, 2015. https://doi.org/10.3311/PPci.7364
- [36] State Standard (GOST) "9169-75 Clay raw materials for the ceramic industry. Classification", Standartinform, Moscow, Russia, 2001. (in Russian)
- [37] State Standard (GOST) "12536-2014 Soils. Methods for laboratory determination of granulometric (grain) and microaggregate composition", Standartinform, Moscow, Russia, 2019. (in Russian)
- [38] State Standard (GOST) "21216-2014 Clay material. Test Methods", Standartinform, Moscow, Russia, 2015. (in Russian)
- [39] Montayev, S. A., Montayeva, A. S., Adilova, N. B., Shinguzhiyeva, A. B., Montayeva N. S., Taskaliyev, A. T. "Prospects of Creating the Technology of Composite Adsorbent for Water Purification Based on the Composition of Siliceous and Clay Rocks of Kazakhstan", International Journal of Mechanical Engineering and Technology, 9(1), pp. 805–813, 2018.
- [40] Zhigulina, A. Yu., Montaev, S. A., Zharylgapov, S. M. "Physicalmechanical Properties and Structure of Wall Ceramics with Composite Additives Modifications", Procedia Engineering, 111, pp. 896–901, 2015 https://doi.org/10.1016/j.proces.2015.07.165

https://doi.org/10.1016/j.proeng.2015.07.165