Use of Technogenic Raw Materials in the Technology of Ceramic Materials

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Abstract. Studies have shown that burnt rocks and ash-and-slag materials, as corrective additives, improve the properties of poor-quality clay raw materials. The possibility of using this technogenic raw material in ceramics technology for the manufacture of ceramic products for various purposes is shown. The use of burnt rocks and ash-and-slag materials improves the sintering of the shard, intensifies the crystallization of mullite-like compounds, which has a positive effect on the physical and mechanical properties of ceramic products: strength and frost resistance increase, shrinkage deformations and water absorption decrease. The use of burnt rocks and ash-and-slag materials makes it possible to obtain refractory products on loam instead of refractory clays. The results of laboratory studies are confirmed by performed tests in the production of pilot batches of ceramic bricks and tiles, thin-walled ceramic products (roof tiles and artistic ceramics).

Keywords: Burnt rocks of mine dumps · Ash-and-slag · Dry ash (fly ash) · Aluminum slag · Chamotte-kaolin dust · Technogenic raw materials · Loam · Refractory clay · Ceramic mass · Ceramic products · Ceramic stones · Ceramic tiles · Refractory products · Physical and mechanical properties

1 Introduction

The ceramic industry is developing, creating and filling new niches in a changing environment. Pottery is the oldest of all man-made building materials. The ceramic art of each country reflects the era in which peoples live and create. Buildings made of ceramic materials are perceived as prestigious, the aesthetic appeal of which persists over time. Such products as wall bricks, ceramic tiles, facade and facing tiles, art and pottery ceramics, refractories, etc. are architecturally more expressive and durable in color, texture, shape. These are the most environmentally friendly and biologically inert materials in construction, with a calm radioactive background and do not contain any harmful impurities. The exceptional richness of the aesthetic possibilities of ceramics has ensured its wide use in almost all structural elements of buildings and structures, including roofing materials, external and internal cladding, in the chemical and metallurgical industry,

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namely acid-resistant and refractory materials, in electronics and radio engineering, in art and household products for various purposes, Ceramics does not afraid frost, does not absorb excess moisture, does not rot and is vapor permeable. Ceramic products have an almost unlimited service life.

Despite the increase in the production of prefabricated reinforced concrete products, plastic products, ceramic materials and products will be used on a par with wall, finishing, roofing materials, as well as special-purpose materials. Due to the fire resistance and high durability of bricks, the walls of buildings and structures made of it have advantages over walls made of wood, concrete, slag blocks and other materials.

The production of ceramic materials is one of the most material-intensive sectors of the national economy. In addition, in the technology of ceramics, an important point is a set of raw materials, the quality of which directly depends on the properties of the finished product [1]. Unfortunately, quality raw materials are irreparably depleted. Low-grade raw materials are increasingly used in ceramic technology. It is difficult to obtain products with the required characteristics from such raw materials without corrective additives. Industrial waste are used increasingly as a corrective additive.

The use of industrial waste in ceramics technology not only contributes to resource conservation, but with their help, the properties of the main raw material used are adjusted. For example, in the Rostov region (Russia), clayey raw materials for the production of ceramics are dominated by loams and low-dispersed clays, from which it is difficult to obtain ceramic products of increased grade and frost resistance. There are practically no refractory and high-melting clays for the manufacture of refractory products. The problem of improving the quality of clay raw materials for the production of ceramic products exists not only for the Rostov region, but also for other regions of the country. In this regard, the use of industrial waste in the technology of ceramic products is of particular relevance [2–4]. It is promising to use mine rocks and ash-and-slag waste as corrective additives to regulate the technological properties of low-grade clay raw materials in order to bring it to the required level [5–7]. There is a wide range of ceramic products on the building materials market. Products with high consumer properties at a relatively low cost can win the competition. The use of waste from the extraction and combustion of coal-mine rocks and ash-and-slag waste will contribute to solving these two problems: improving the quality and reducing the cost of producing ceramic products.

1.1 The Purpose of the Study

The paper studies the influence of additives of burnt rocks, ash-and-slag waste, aluminum slag, chamotte-kaolin dust on the technological and physico-mechanical properties of ceramic masses for construction ceramics, mainly clinker and facing bricks and ceramic stone, facing ceramic tiles, refractory products, roofing materials, artistic ceramic products.

2 Research Methods

To use ash-and-slag waste and burnt rocks of mine dumps in the technology of ceramic products, samples of technogenic and clay raw materials were taken. The sampling of technogenic raw materials was carried out in accordance with the instructions of generally accepted methods and the requirements of regulatory documents. The sampling principle of the mine and ash dump is based on the principle of point sampling. Averaged samples were compiled from point samples by thorough mixing. Samples for laboratory and analytical studies were taken by the averaged sample by the quartering method. Analytical and laboratory studies were carried out, a comprehensive assessment of the quality of the raw materials used was carried out. This approach consists in obtaining primary information on the chemical and material composition of raw materials. The research results make it possible to determine the main technological aspects of the manufacture of ceramic products for various purposes. Later, physical and mechanical and technological tests were carried out. Technological modes are checked and corrected in pilot-industrial conditions during the release of pilot batches of ceramic products. Rational combinations of laboratory research methods and production tests make it possible to develop optimal parameters for the technology for producing effective ceramic materials.

3 Results and Discussion

In this work, clay raw materials were used: loams of the Sukho-Chaltyrskoye and refractory clays of the Fedorovskoye deposits of the Rostov region (Russia). Burnt rocks of a mine dump, fly ash and ash-and-slag mixture, aluminum slag and chamotte-kaolin dust were selected as corrective additives. The results of the chemical analysis of clay raw materials are shown in Table 1.

The structure of the loam of the Sukho-Chaltyrskoye deposit is polydisperse and aggregate-granular, heterogeneous, some individual aggregates are cemented together; they can hardly be broken by hand in dry form. The texture of the clayey rock is disordered, namely loose and lumpy. The color of the loam varies from yellow to dark brown with white inclusions. Clay raw materials boil when treated with 10% hydrochloric acid solution.

Table 1 Chemical composition of clay raw materials, wt%

Sample	SiO_2	Al_2O_3	Fe_2O_3 total	CaO	MgO	SO_3 total	TiO_2	$K_2O + Na_2O$	p.p.p.[a]
Loam of Sukho-Chaltyrskoye	56.00	13.65	5.72	6.18	2.23	0.75	0.81	3.25	11.38
Clay of Fedorovskaya	59.37	27.76	1.54	0.77	0.63	0.12	0.83	1.23	7.12

[a] Loss on ignition

The main impurities of this clay raw material are quartz sand, carbonates, ferruginous compounds, feldspar grains, organic impurities, plant residues. Carbonate inclusions are mainly present in a finely dispersed state. The carbonate component is represented by organogenic calcite, found in clay in the form of finely dispersed uniformly distributed silty particles, loose smears and accumulations, in the form of dense stony inclusions. Loose smears and accumulations are destroyed during mechanical processing and turn into a uniformly distributed finely dispersed impurity, and therefore they do not significantly affect the properties of clay and the quality of the fired shard. The clayey part contains a hydromica component with an insignificant admixture of kaolinite and montmorillonite. The dusty fraction is represented mainly by silica, calcium carbonate and iron oxides, the sandy fraction is represented by quartz. According to the degree of plasticity, these loams belong to the group of medium plastic; according to their sensitivity to drying they belong to the group of highly sensitive clay raw materials. In terms of refractoriness, loam belongs to the group of low-melting raw materials; in terms of the degree of sintering, it belongs to the group of non-sintering clay raw materials. Refractoriness of loam corresponds to 1300 °C. In the temperature range of 900–1100 °C, fire shrinkage is 0.2–0.8%, total shrinkage is 10.8–11.0%, apparent density is 1.96–2.04 g/cm^3, water absorption is 13.7–14.9%, molding moisture is 23–26%. The molding ability of clay raw materials is satisfactory.

The Fedorovskoye deposit is represented by refractory highly dispersed, highly plastic (plasticity number $>$ 26) clays, predominantly gray, light and dark gray. According to the mineralogical composition, the clays are classified as kaolinite–hydromica with an admixture of montmorillonite. The mineral composition contains: kaolinite (38–48%), hydromica (20–23%), montmorillonite (8–14%), quartz (12–33%). The impurities include pyrite, siderite, opal, feldspar, plant residues. According to their granulometric composition, clays are included in the group of highly dispersed clay raw materials, with a high content of coloring oxides. Clay fire resistance is 1650 °C, sintering temperature is 1100–1150 °C, air shrinkage is 11–12%, molding moisture is 28–32%, molding ability is good.

As corrective additives to clay raw materials, the burned rocks of Petrovsky mine dumps, ash-and-slag materials of the Novocherkassk HDES, slag of the Belokalitvensky Metallurgical Combine (hereinafter the aluminum slag), chamoten-kaolin dust from kaolin firing at the Novocherkassk factory of ceramic products are used. All materials are technogenic raw materials in the Rostov region (Russia). The chemical composition of these products is given in Table 2.

Table 2 Chemical composition of corrective additives, weight%

Sample name	SiO_2	Al_2O_3	Fe_2O_3 total	CaO	MgO	SO_3 total	TiO_2	$K_2O + Na_2O$	p.p.p.
Burned rocks of the Petrovsky mine dumps	52.08	21.35	6.69	1.75	1.63	2.46	1.14	5.00	7.32
Fly ash of the Novocherkassk HDES	52.74	21.49	7.28	2.97	2.05	0.52	0.93	2.44	8.86
Ash-and-slag materials of the Novocherkassk HDES	51.52	21.31	6.03	3.07	1.97	0.79	0.67	2.61	11.89
Aluminum slag	14.96	25.84	7.37	3.13	24.49	4.70	0.32	1.46	17.10
Chamoten-kaolin dust	52.88	40.12	0.79	0.86	0.67	0.52	0.50	0.85	2.73

Aluminum slag is formed by melting the charge in melting furnaces of the foundry shop. Slags are removed from the surface of the molten metal, in the form of pieces and small brown particles with silver inclusions, stored in dumps. Refractory of aluminum slag corresponds to 1780 °C. Chamoten-kaolin dust is formed under Kaolin's firing on shamot at the Novocherkassk factory of ceramic products and is captured by electric filters.

Due to chemical composition, ash-and-slag materials and burned rocks of mine dumps belong to the semiacid raw materials, with a high content of coloring oxides. The genesis of their formation and properties are different.

Their composition and properties are influenced by the composition of carbon-containing rocks and mineral components of the fuel, the conditions of firing and combustion. The formation of burnt rocks occurs during a long (tens of years) self-ignition in dumps. Ash-and-slag materials are formed during the combustion of fine-grained coal in the furnaces of boilers. In the process of long-term (tens of years) self-ignition, burnt rocks are formed in the dumps.

Ash-and-slag waste is represented by dry ash (fly ash) and ash-and-slag mixture. Fly ash is captured by electric filters and shipped to cement trucks. The part of ash and fuel slag (ash-and-slag mixture) are sent to the dumps by a hydraulic ash-and-slag removal system. The ash-and-slag mixture contains, as a rule, up to 30% of fly ash.

In the mineral part of solid fuel, as well as in the initial mine rocks, clay minerals predominate. The most characteristic type of clay minerals in coal layer is kaolinite ($Al_2O_3{\cdot}2SiO_2{\cdot}2H_2O$). The features of the mineral and petrographic composition of burnt rocks and fly ash, accumulated in the Rostov region, are given in [8, 9]. The main groups of substances are present in ash fly and burnt rock: crystalline, amorphous and organic. The amorphous component of the ash is represented by a glass phase and an amorphized clay substance, the organic component is represented by semi-coking residues, colloidal carbon deposited on the surface of mineral particles.

Along with clay matter, sandstone, which are cemented grains of quartz, also undergo pyroprocesses. In the process of firing, quartz, having undergone a number of transformations, returns to the low-temperature modification of β-quartz, but already with a broken structural lattice. The iron impurities present under the influence of firing processes also undergo changes and pass into more active forms. Thus, in the composition of burnt rocks and ash-and-slag materials, active components appear in the form of metakaolinite, as well as oxides of SiO_2, Al_2O_3, Fe_2O_3, in which, under the influence of pyro-processes, the structure of the initial minerals was disturbed. The presence of these components is associated with the violation of the crystal lattice of clay minerals under thermal influences and the appearance of a certain energy potential in thermally altered products. The most active component of ash is vitrified substance and glass phase. The phase composition of burnt rocks has a significant difference, connected with the almost complete absence of a vitreous phase. Refractoriness of ash-and-slag materials and burnt rocks is within 1300–1380 °C.

Burned rocks and ash-and-slag materials in their composition contain approximately the same components that are introduced into ceramic masses with clay rocks. The polymRiverality of their composition makes it possible to use burnt rocks and ash-and-slag materials in the composition of ceramic masses for building and artistic ceramics, refractories as a structure-forming element, flux and lean additives. Ashes, having spherical particles, act as plasticizers, which improves the formability of the mixture. The quantity of carbonaceous impurities in this technogenic raw material should not exceed of 5%. The alumina content must be at least of 16.0–18.0%.

By changing the activity of burnt rocks and ash-and-slag materials by mechanical and chemical action, fractional composition, ratio of charge components and setting technological parameters, it is possible to control the properties of ceramic masses in accordance with the set goal.

One of the factors influencing the properties of a ceramic potsherd is the granulometric composition of the emaciated components. The influence of this indicator on the properties of ceramic masses: water absorption, strength in compression and bending are shown on diagrams (see Fig. 1). From the above test results, it follows that the minimum water absorption (2.95%) is achieved with a particle size distribution according to option II, that is with such a grain size composition, when the densest ceramic potsherd is formed. This ensures high strength values of the ceramic stone, namely the highest compressive strength (64.5 MPa), and bending strength (6.3 MPa).

Grain composition of non-plastic components of ceramic masses according to option II contains the following fractions: 2–3 mm^{-2}—3 wt%; 2–1 mm—40–45 wt%; 1–0.5 mm—30–35 wt%; <0.5 mm—20–25 wt%.

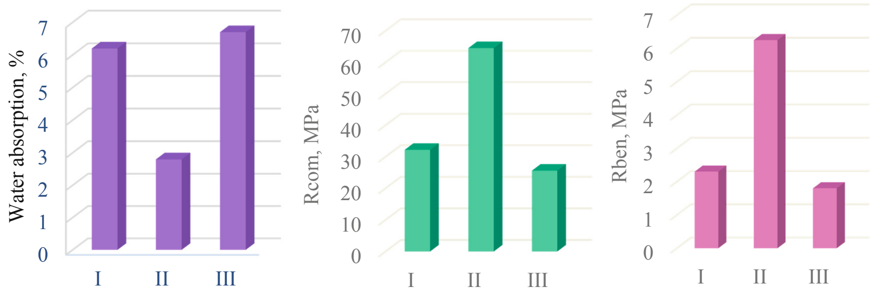

Fig. 1 Influence of the granulometric composition on the properties of ceramic masses I, II, III—variants of the granulometric composition of non-plastic components of the charge

An important factor affecting the properties of ceramic masses is the content of non-plastic materials in the raw material charge. In Fig. 2, using the example of burnt rocks, the effect of their content on the strength of the ceramic mass for various products is shown. From the data in the figure, it follows that for compositions with refractory Fedorov clay and Sukho-Chaltyrskoye loam, the content of burnt rocks ranges from 30 to 70%. For the manufacture of ordinary bricks on the loam of the Oktyabrskoye deposit, the grade strength is obtained, when the content of burnt rocks is from 20 to 40%.

The technology of ceramic products includes the following operations: preparation of initial components and preparation of a charge, molding of products, drying of raw materials, roasting, testing of physical and mechanical properties. The preparation of the components of the charge consisted in crushing, grinding and fractionation (selection of particle size distribution). The charge for ceramic facing bricks, stone and refractories was molded in a semi-dry way; the pressing compression was 45 MPa. To test the physical and mechanical properties of ceramic masses, laboratory samples (cubes, cylinders, tiles) were molded. Drying of the molded samples was carried out in a drying cabinet at a temperature not higher than 50 °C to a residual moisture content of 4–5%. Firing was carried out in a chamber muffle furnace with holding at a maximum temperature of 970–980 °C for 2 h. Firing mode was as follows: temperature rise from 20 to 850 °C with a rate of 3 °C per minute, from 850 °C to a maximum temperature with a rate of 1 °C per minute; cooling from maximum temperature to 20 °C for 16 h.

Facing tiles and artistic ceramics were manufactured using slip technology. Slip preparation of the charge ensures uniform distribution of all components during wet grinding in a ball mill for 15–16 h. From the slip in spray dryers, a press-powder was obtained for the manufacture of ceramic tiles.

Under factory conditions, when producing pilot batches of ceramic tiles, the optimum moisture content of the press powder was 7.5–8.0%. The pressing compression was 10–11 MPa. Drying of tiles was carried out in conveyor dryers with a roller conveyor. The maximum drying temperature was 270–280 °C, and the drying time was 21 min. The tiles were fired in a slotted roller furnace. The maximum firing temperature of the adobe was 920–980 °C, and glazed sample was 940–960 °C, with the firing duration of 21.4 min. In the factory, several compositions of ceramic masses were tested and 3600 m^2 of tiles in an experimental batch were manufactured.

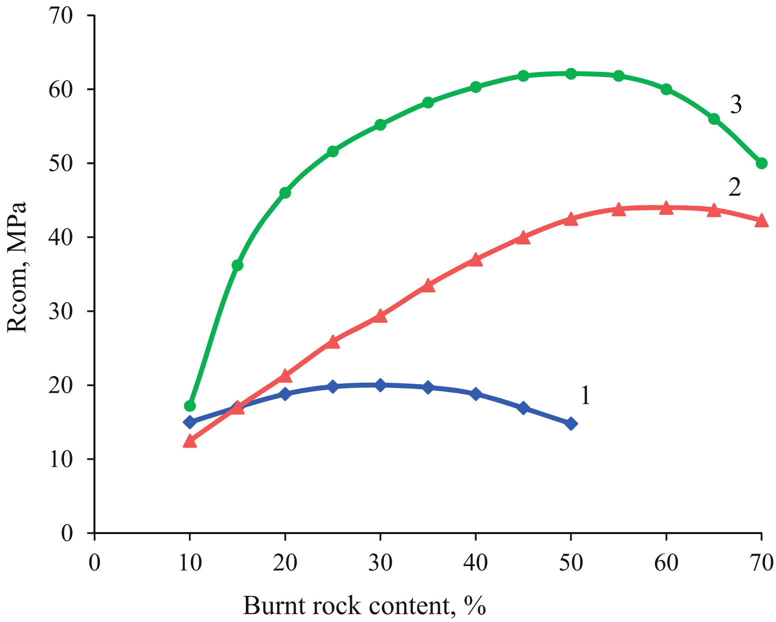

Fig. 2 Influence of the content of burnt rock on the strength of the ceramic mass: 1—brick; 2—refractories; 3—tiles

Tables 3, 4 and 5 show the compositions of raw mixtures and some physical and mechanical properties of ceramic products using technogenic raw materials.

Using the example of compositions of two components of ash and loam, taken in different ratios, the influence of the ash content on the shrinkage changes of ceramic masses was investigated. The research results are shown in Fig. 3. The ash content in the mixture was varied in the range from 0 to 90%, with a step of 5%. Determination of air and fire shrinkage was carried out on $50 \times 25 \times 10$ mm^3 slabs. With an increase in the ash content in the composition of the charge, its effectiveness increases: the shrinkage of ceramic masses decreases, with a 50% content and the coefficient of sensitivity to drying decreases approximately two times.

In production conditions of building materials at the factories in the Rostov region, pilot tests were carried out and pilot batches of facing and refractory bricks, ceramic tiles, tiles and artistic ceramics were manufactured. The preparation of masses for artistic ceramics using finely ground burnt rock was carried out using slip technology. A pilot batch of products was made by pouring the slip into plaster molds. Slip technological parameters: a specific gravity of 1.40–1.45 g/cm^3, a humidity of 30–45%, a fluidity of 33.5 s. Drying of products was carried out at a temperature of 80–100 °C to a residual moisture content of 1.0–1.5%. The firing temperature of adobe was 900–950 °C with an exposure at a maximum temperature during 1 h; glazed sample was subjected to 980–1060 °C with an exposure for 1.5 h. For glazing, both transparent colorless glazes and glazes with the addition of various pigments from the Voronezh plant (Russia) were

Table 3 Physical and mechanical properties of ceramic stones on technogenic raw materials

Composition, weight%				Strength, MPa		Water absorption, %
Loam	Chamotte-kaolin dust	Finely ground burnt rock	Crushed burnt rock	At compression	At bending	
65.0	–	–	35.0	30.2	5.3	7.5
60.0	–	–	40.0	29.6	4.9	7.7
55.0	15.0	–	30.0	33.5	4.5	7.3
50.0	20.0	30.0	–	67.8	10.1	6.0
40.0	20.0	40.0	–	61.3	9.2	6.4
30.0	33.0	17.0	–	53.0	8.8	6.9
35.0	–	25.0	40.0	44.3	7.7	8.2
45.0	–	30.0	25.0	48.0	8.5	8.8

Table 4 Influence of burnt rocks and ash-and-slag materials on the properties of ceramic tiles

Composition, weight%				Firing temperature, °C		Properties of facing tiles	
Clay of Fedorovskaya	Burnt rocks	Ash-and-slag mixture	Cullet	Adobe	Glazed	Shrinkage %	Water absorption, %
20.0	64.0	–	6.0	970	940	0.33	0.25
40.0	54.0	–	6.0	910	930	0.97	0.43
30.0	50.0	20.0	–	940	920	1.08	3.94
30.0	50.0	20.0	–	960	940	1.25	0.78
30.0	45.0	20.0	5.0	980	960	1.37	1.12
25.0	50.0	20.0	5.0	920	910	0.95	2.18
25.0	50.0	20.0	5.0	940	920	1.03	1.69

used. The goods can be decorated by painting and applying decorative coatings with ceramic paints, glazes, engobes, enamels, etc.

The results obtained showed that the use of ground rocks in the composition of ceramic masses improves the technological parameters of production and some physical and mechanical properties of the product. Ceramics with burnt rock are less sensitive to drying and firing than traditional ones; shrinkage of goods ranges from 3 to 5%. Deformations of the goods were not found, cracks, sagging, bubbles, bald patches, peeling and pricked glaze were absent. The products were waterproof.

Table 5 Physical and mechanical properties of refractory products based on technogenic raw materials

Composition, weight%						Fire resistance, °C	Strength, MPa	Porosity, %	Water absorption, %
Clay component		Burnt rock		Ash-and-slag mixture	Aluminum slag				
		Finely ground	Crushed						
Clay of Fedorovskaya	30	–	70	–	–	1580	32.4	25.8	16.8
Loam of Sukho-Chaltyrskoye	10	–	30	20	30	1670	38.7	25.0	14.0
Clay of Fedorovskaya	20	20	40	20	20	1730	45.2	25.0	14.0
Clay of Fedorovskaya	40	–	–	–	60	1680	40.8	25.0	14.0

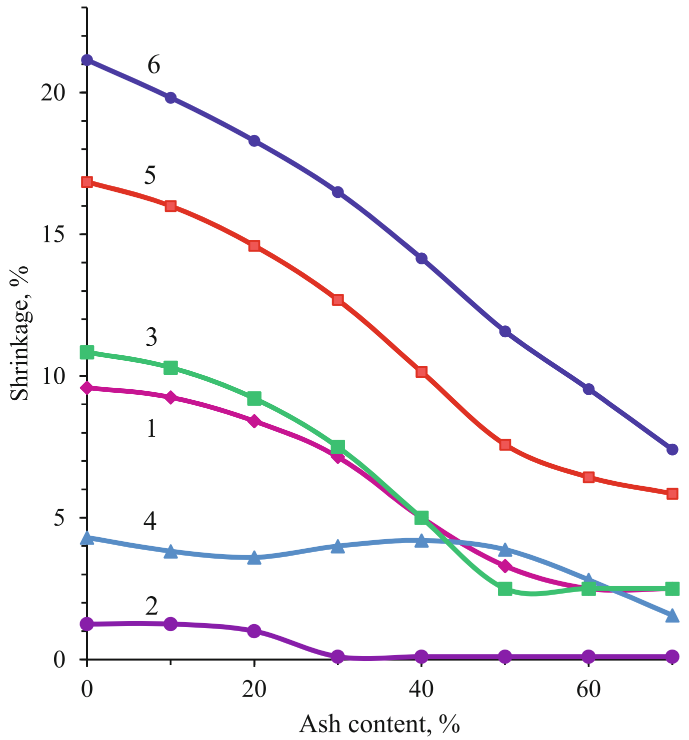

Fig. 3 Effect of ash content on the shrinkage properties of ceramic masses: 1—linear air shrinkage; 2—linear fire shrinkage; 3—total linear shrinkage; 4—volume air shrinkage; 5—volume fire shrinkage; 6—total volume shrinkage

In the factory, the compositions of ceramic masses were tested in the manufacture of grooved tape tiles. The manufacture of tiles with additions of ash-and-slag mixture was carried out using the technology of semi-dry pressing. To create a strong tile frame that works well for bending and compression, a fraction of less than 2 mm must be present in the grain composition of ash-and-slag mixture. Sukho-Chaltyrsky loam was used as a clay binder. The content of the ash-and-slag mixture changed from 15 to 35%. The molding moisture content of the mass was 11–12%. Air-dried tiles to a moisture content of 1.5–2.0% were fired in a tunnel furnace at a temperature of 980 °C. The compressive strength of the ceramic mass according to cubic specimens was 30–35 MPa. The tile has passed the tests for water resistance, destructive load and frost resistance. Frost resistance had grade F35. According to the results of testing the physical and mechanical properties, ceramic goods, manufactured in the factory, met the requirements of regulatory documents.

The raw material mixture for the manufacture of ceramic products is a multicomponent system consisting of a dispersed phase and a dispersion medium. It contains non-plastic finely dispersed fillers and granular fillers with a particle size from 0.001 to 2 mm. A clay component with a particle size of 0.001 mm is used as a binder. Such a system has an excess of surface free energy and is in a nonequilibrium state. Therefore, it strives for self-organization and spontaneous self-ordering. This is due to the excessive surface free energy in the dispersed system. From the standpoint of the polystructural theory, the aggregate and filler form a macrostructure, and the clay bond that unites them forms a microstructure [10, 11].

New physical and mechanical properties of a ceramic composite, as a dispersed system, is formed as a result of physicochemical interactions occurring between the original components of the raw mixture during molding, drying and firing. The presence of an amorphous substance and active components in burnt rocks and ash-and-slag materials contributes to the formation of a reinforcing frame in the system, in which individual grains are fastened together by the active components of the amorphous substance. The clay component cements the charge components into a single conglomerate. The packing density of the particles is provided by the polydisperse grain composition of the composition. In the process of drying in a dispersed system, first, in accordance with the principles of physicochemical mechanics [12], coagulation structures are formed, which, as moisture decreases and the contact area between particles increases, transform into condensation-crystallization structures, providing the initial strength of the raw material. The final formation of the structure and properties of the dispersed system occurs during firing.

Ceramic masses made from various raw materials have general regularities of physical and chemical transformations during their heat treatment [13–15]. The most important of them are: decomposition and transformation of raw materials minerals, chemical interaction of their components, phenomena occurring at the contact of grains in the presence of a liquid phase, dissolution of solid particles in a melt, and the formation of new crystalline compounds.

Ash-and-slag mixture and burnt rocks in the composition of the charge are fuel-containing and lean additives. They improve the particle size distribution and have a plasticizing effect, affect the formation of the structural framework of the charge, change the drying properties of the ceramic mass, and reduce the sensitivity to drying in clay raw materials. The presence of a glass phase in ash-and-slag mixtures and burnt rocks gives them the properties of flux.

Chamotte kaolin dust is also a lean additive and carrier of alumina. The selected composition of lean additives helps to reduce volumetric changes and the stability of the forming structure at all stages of the technological process. The joint introduction of two types of waste has the most beneficial effect on the properties of finished products. The content of iron oxides, the presence of a carbonaceous component, alkaline oxides intensify the sintering process of the shard and contribute to the formation of low-melting compounds and crystallization of new formations at an early stage of firing. The introduction of such complex additives intensifies the sintering process of raw mixtures due to the formation of low-melting eutectics, an increase in the glassy phase and the mobility of the silicate melt, its reactivity. As a result, the firing temperature decreases by 50–80 °C, and the mechanical strength and other characteristics of ceramic products increase.

In compositions for thin-walled ceramics (facing and metlakh tiles, artistic ceramics), cullet was used as flux. The use of cullet in mixtures with plastic clays improves the forming properties of the charge, and reduces the firing temperature. Clay and cullet form a liquid phase. Due to the involvement of low-melting minerals in phase transformations, the formation of a melt is enhanced. In this process, quartz and clay matter of the charge takes an active part. Intense melt formation is accompanied by an improvement in the liquid-phase sintering of ceramics and the formation of new crystalline phases that determine the properties of finished products.

The use of aluminum slags in combination with burnt rocks and ash-and-slag materials makes it possible to obtain products with a refractoriness of 1400–1700 °C, both with highly plastic refractory clays and low-melting loams.

The presence of reactive components in burnt rocks and ash-and-slag materials in combination with aluminum slags turns them into an active component in the composition of the raw charge into an active component participating in physicochemical transformations during the roasting process. The presence of aluminum slag as a corrective additive in the form of Al_2O_3 and its participation in the synthesis of new formations with active components of burnt rock and ash-and-slag materials gives the products with increased refractoriness. Low-melting clay of medium plasticity, such as loam, or highly plastic refractory clay, can be used as a binder. The fractional composition of non-plastic materials has a significant effect on the refractoriness and strength of products. Optimization of the fractional composition of waste and the achievement of the most-dense packing of the ceramic batch at the stage of semi-dry pressing, provides high physical and mechanical properties of the finished product.

It is effective to add finely ground ash and burnt rock fractions into the raw material mixture. Grinding of these wastes can be classified as a way of modifying them, improving the quality of substandard raw materials. By grinding, the crystal structure of quartz changes and the reactivity increases. At the joint firing of burnt rock, ash-and-slag material with clay, the sintering temperature of ceramics and the formation of new compounds, for example, mullite, anorthite, tridymite, hematite, and glass, decrease. Mullite presents in the composition of the original technogenic raw material also intensifies the formation of mullite-like compounds at lower ceramic sintering temperatures

(930–950 °C). The initial mullite acts as the center of the onset of crystallization of mullite-like compounds. The addition of chamotte-kaolin dust contributes to a more complete course of the mullitization process with an increase in the mullite phase in the melt. The presence of mullite, anorthite, wollastonite, tridymite significantly increases the strength and frost resistance of ceramic bricks with a low content of clay binder.

By adjusting the granulometric composition of non-plastic materials, it is possible to obtain refractory products using low-melting loams of medium plasticity instead of refractory clay. A special role belongs to the finely dispersed fraction. So, the finely ground fraction of the additive is evenly mixed with fine-dispersed clay and is an effective weaker. The binding and sintering part of the mass becomes clay, emaciated by one or another amount of dust-like fraction. If this finely dispersed fraction is sufficient, then the lean clay in drying and firing has moderate volumetric changes, which do not lead to a violation of the forming structure of the potsherd. With a decrease in the amount of a fine fraction, the degree of depletion of the binder clay decreases and the likelihood of the appearance of structural defects and disruption of its continuity increases.

The interaction of oxides of the main minerals in the systems under study begins even in the solid phase (up to 700 °C), continues in the melt, and ends with the strengthening of the structure because of intense crystallization (950–970 °C) of the compounds. Crystalline compounds are formed, namely mullite, anorthite, wollastonite and other minerals. The crystalline phase is the basis of ceramics and determines the values of mechanical strength, frost resistance, thermal resistance, water absorption and other basic properties. An increase in the strength of a potsherd of products at maximum firing temperatures within the range of 950–970 °C is explained both by the influence of newly formed compounds and by the action of the melt, which, due to the energy of surface tension, brings the particles of the mass closer and binds into a monolith. The structure of the ceramic potsherd is dense and homogeneous.

4 Conclusion

The obtained positive results of laboratory research and production tests confirm the possibility of using technogenic raw materials in the technology of ceramic products to adjust the properties of natural raw materials and regulate the characteristics of ceramic products. The possibility of using ash-and-slag materials and burnt rocks of mine dumps in the technology of ceramics and refractories is shown. The introduction of ash-and-slag materials and burnt mine rocks in different ratios into the charge makes it possible to regulate the properties of both raw materials and finished ceramic products. By selecting the optimal composition and technological modes of molding, drying and firing, it is possible to obtain a ceramic material with an optimal phase composition with high physical and mechanical properties and quality. In the result of the joint interaction of the charge components during firing, the required amount of minerals forms and a homogeneous structure of a ceramic potsherd of high strength and frost resistance forms with a low content of low-melting clay, such as a loam.

The main advantages of using burnt rocks and ash-and-slag waste in ceramics technology include the effect of reducing the sensitivity of raw materials to drying, expanding the sintering range, reducing the firing temperature, eliminating the formation of stresses in the material structure, the possibility of obtaining refractories, reducing shrinkage and water absorption, increasing the brand strength and frost resistance of finished products and decreasing rejects.

Large-scale use of technogenic raw materials will reduce the environmental burden on the environment, and will reduce the cost of maintaining waste dumps.

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