INCREASE OF CRACKING RESISTANCE OF CERAMIC MASSES OF LOW-PLASTIC CLAY

The object of research is the physical and chemical processes of forming the structure and properties of ceramic masses based on local low-melting clay raw materials of the Kyiv region of Ukraine by adjusting the chemical and mineralogical composition and technological regimes.

Building ceramic materials are durable, ecological and natural. They provide increased comfort of buildings due to the creation of a favorable temperature and humidity climate of the premises. When using low-melting raw materials in production, there is a need to develop ways and methods to improve the quality of building ceramics. The efficiency of the manufacture of ceramic products largely depends on the processes that occur during drying. This is of crucial importance and affects the quality of finished products and accounts for 10–12 % of the total cost of finished products.

Polymineral clay compositions with the addition of natural mineral raw materials are mainly used for the production of construction materials. For effective use of these materials, it is necessary to study their technological properties. Therefore, the question of researching masses based on low-melting clays with high sensitivity to drying, and the use of zeolite-containing mineral rock as an admixture is relevant. This will allow expanding the nomenclature of building ceramics products. Modern physico-chemical and physico-technological methods of research of raw materials and masses based on them during drying were used to solve the task of obtaining ceramic material from local raw materials with the use of a non-deficient natural additive of zeolite-containing rock as an admixture. The conducted studies indicate that the addition of zeolite-containing rock can be used to improve the drying properties of ceramic masses based on low-melting clays. Adding admixture of zeolite-containing rock also increased the compressive strength of finished products, which ensures defect-free transportation of products to other technological operations.

Keywords: ceramic materials, clay raw materials, zeolite, drying, mechanical strength, siliceous materials, building ceramics.

1. Introduction

In modern conditions, the question arises about the need to increase the production of ecologically clean, competitive and inexpensive ceramic materials. This can be achieved by finding new technological solutions using modern approaches to assessing the potential of initial raw materials [1, 2]. It is known about the reduction of stocks of high-quality clay raw materials and the reduction of depreciating materials used in the production of building ceramics. Therefore, it is relevant to research the ways and methods of creating high-quality ceramics from local low-melting raw materials, with high sensitivity to drying, and the use of zeolite-containing mineral rock as a reducing admixture.

The quality of finished ceramic products is determined by the processes that take place during drying and firing. Most of the cracks and deformation of products occur during drying. Defects that are formed during heat treatment occur during the shrinkage period, when a solid structure is formed in one part of the product, and the other part continues to change in size. As a result, stresses, warping, and cracks occur. Drying properties reflect the changes that occur in the ceramic mass during its drying. These include air shrinkage, sensitivity to drying, and water-conducting properties of clay.

The paper [3] studied the behavior of three different clays with regard to drying performance. Ceramic formulations were subjected to forced drying cycles lasting 180 min, changing the temperature from 30 to 90 °C and the air speed from 1.5 to 4.0 m/s. Retraction turned out to be a determining factor for the probability of cracking. Samples obtained at 10 % retraction in the dry zone showed losses of >25 %.

Expanded clay contributes to the drying process of a ceramic product, minimizing losses. With a sensitivity coefficient (k-factor) of 1.6, losses in the drying process amount to >25.
Clay with ductile properties and low content of coarser particles is more susceptible to drying out \((k\text{-factor}=3.5)\) and is prone to cracking in the ceramic shard during rapid drying cycles. When adding up to 33 % of this clay, losses amounted to more than 50 %, with the addition of up to 16 %, the loss was 25 %. On the contrary, argillite and sandy clay showed a low sensitivity to drying \((k\text{-factor}<1.2)\), minimizing losses in the ceramic process \((<4 \%)\).

The drying sensitivity coefficient proved to be a highly effective parameter for research and showed the relationship between clay properties, drying conditions and losses, but the effect of additives and other drying factors on the initial product was not considered in the paper.

The authors of the study [4] identified the main reasons for the appearance of cracks during the drying of ceramic bricks. According to the study, the grain size distribution and volumes of X-ray amorphous submicron and nanoparticle brick clays do not affect the sensitivity to the dry state of extruded and formed raw ceramic tile products. A strong correlation was found between the amount of X-ray amorphous nanoparticles in the raw material and the bending strength of the sintered ceramic rods. The greater the content of submicron and nanoparticles in clay minerals, the greater the flexural strength of the manufactured sintered ceramics.

The appearance of cracks during drying is caused by incorrect forming pressure, residual stresses inside the extruded and pressed body, and incorrect heating rate during drying, and not by the fine-grained structure, but the optimal drying mode of the studied clay was not selected in the work.

Research [5] considered the influence of drying parameters on the properties of the obtained ceramic samples, namely: use a higher air flow rate. This avoids the risk of condensation in the tunnel dryer for green brick drying; however, the higher air flow speeds up the drying rate, thus causing damage. The optimal values of the mass flow of hot and outside air and the optimal temperature of the pipe are considered. Four different temperatures \((-5, 10, 20 \text{ and } 30 \, ^\circ\text{C})\) and three different relative humidities \((40, 60 \text{ and } 80 \, \% )\) were chosen for the outdoor air. The optimal operating parameters and the required temperature of the stack to avoid condensation were calculated for various cases, but the addition of various additives to the composition of the ceramic mass was not considered.

In [6], the change in critical humidity, equilibrium humidity, degree of dryness, etc. during drying of clay under the condition of changing technological parameters to improve the energy and economic stability of refractories production was investigated. The parameters of the dryer were adjusted: the temperature was from 40 to 60 \(^\circ\text{C}\), the humidity was increased in the range of 30–70 \%; at an air flow speed of 1.3 m/s. According to the correlation analysis between the working parameters and the drying performance, the mathematical optimization of the drying mode was carried out. According to the assessment of the influence of the drying mode on the quality of the dried refractory samples, the optimal result of two types of clay was obtained: temperature 50 \(^\circ\text{C}\), humidity 40 \%. The study did not pay attention to the composition of raw materials and additives that ensure fire resistance and optimal drying of products.

According to the results of research [7], the values of sensitivity to drying of clay mixtures, obtained by determining the index of sensitivity to drying – Bigot (DSI-B) and the index of sensitivity to drying – Ratzenberger (DSI-R), decreased with an increase in the amount of sand, grog and pottery additives stone. The correlation of the results of the measurement of the sensitivity index of both methods was confirmed, which allows to safely use these methods in further research. An improvement in the drying properties of the clay body was observed due to the addition of non-plastic additives, but without reference to the drying temperature and time.

In a study [8], during the evaporation drying step, \(TiO_2\) ceramic layers with a graded porous structure had a strong tendency to warp and crack due to the resulting difference in capillary pressure in the upper and lower side pores. When tested with four drying methods, the most successful method is a combination of microwave drying and subsequent critical point drying. At the same time, there is a reduction or elimination of capillary forces and for the production of flat dried samples without cracks. Although no drying mode was selected for building ceramics, this study can be used as an example of manipulations made to select the optimal drying mode.

The addition of zeolite rock \((10–30 \text{ wt. } \% )\) to brick clay acts as a moisture absorbent and non-plastic additive, reducing the drying sensitivity index by 3–4 times, without impairing the cohesiveness of the materials at work [9]. The effectiveness of zeolite additives depends on their dispersion, content and temperature regime.

The addition of zeolites has a beneficial effect on the resistance to cracking of raw products during drying and ensures automatic loading of dry products into the oven without defects. Improvement of the drying properties of clay raw materials is achieved by transferring part of the free water introduced from the hydrated clay into a bound state by introducing it into the channel-framework space of zeolite minerals. The work does not indicate the effect of the introduction of the additive on the drying process.

In work [10], sawdust was added as a partial replacement of the zeolite-poor rock in the samples. The percentage of replacement was 0 \%, 2 \%, 4 \%, 6 \%, 8 \% and 10 \% by weight of the zeolite-poor rock. The results confirmed that the addition of sawdust to the low-zeolite rock minimized the bulk density of the samples to 1.45 from 1.6 g/cm\(^3\). Sawdust can be effectively used as a pore former in stone bricks with poor zeolite content, because the porosity has increased to 37.37 from 31 \%, improving its thermal insulation characteristics. This can lead to the production of lightweight bricks due to the increased number of pores formed by the combustion of sawdust organic content, as shown in TG-DTA analysis. The heat released during sawdust combustion can contribute to the heat requirements of the manufacturing process. Instead, their compressive strength decreased from 14.5 to 6.7 MPa, and water absorption increased. However, their strength was greater than desired by the standards. The thermal conductivity of the samples containing 8 \% sawdust decreased from 0.37 to 0.14 W/mK, corresponding to a 37 \% decrease compared to the blank sample. The mechanical and physical characteristics of bricks were also affected by the temperature of sintering and drying, but the dependence of their flow was not indicated.

Based on the study [11], it is possible to draw a conclusion about the drying characteristics of construction ceramics made with the use of lubricant-cooling waste. Due to the physical and chemical processes in the clay-water-surfactant system, the duration of drying is reduced,
thermal energy is saved, and the amount of waste is reduced. This is a very promising study for the introduction of secondary waste processing, but there is no compliance of the obtained samples with existing regulatory documents to confirm the possibility of such use in practice.

The composition of mineral binding components (clay and zeolite rock) with ash-containing solid fuel combustion waste (ash microspheres) on the physical and mechanical properties of highly porous heat-insulating ceramic materials is considered in [12]. The pore-forming effect of ash microspheres together with low-melting clay is due to the porous macrostructure of the ash component (the presence of hollow spherical particles) and the nature of the physicochemical processes in the «clay – ash microspheres» and the «zeolite – ash microspheres» system (synthesis of anorthite and mullite, which increases molar volume). Also, pore formation is due to structural (channel) porosity of zeolite minerals.

The use of zeolite rock as a binder in a mixture with ash microspheres with a content of up to 60–95 wt. %, modified with zeolite-lignosulfonate slip, makes it possible to obtain highly effective construction and heat-insulating ceramic bricks with a compressive strength of 18–30 MPa, a bulk weight of 930–1100 kg/m³ and a thermal conductivity of 0.22–0.31 W/m·K at a firing temperature of 950–1000 °C. The work takes into account the main technological parameters, in addition to the drying mode of the manufactured shard.

Therefore, based on the analysis of literature data, it can be concluded that in order to choose the optimal technological regime for the production of construction ceramics, it is necessary to investigate the effect of zeolite additive on the physical and mechanical properties of ceramic products based on local low-melting raw materials at optimal drying and firing temperatures.

Thus, the aim of research is to obtain a ceramic material based on local low-melting clay with the use of zeolite as a non-deficient natural additive, which will contribute to the reduction of air shrinkage and sensitivity to drying of the ceramic mass.

To achieve the aim, the following objectives must be completed:
1. To study the chemical and mineralogical composition of the studied local low-melting clay and zeolite rock.
2. To investigate the drying properties of products based on local low-melting clay with the addition of zeolite-containing rock.
3. To work out the technological modes of drying ceramic masses.

2. Materials and Methods

The object of research is the physical and chemical processes of forming the structure and properties of ceramic masses, based on local low-melting clay raw materials of the Kyiv region and zeolite-containing rock, which occur during their drying and firing.

The subject of research is a comprehensive study of low-melting clay of the Kyiv region, the disadvantage of which is high sensitivity to drying. The addition of zeolite-containing rock to the ceramic mass based on low-melting clay will optimize its drying properties, contributing to the formation of a structure with improved operational properties of building ceramics.

Modern physico-chemical methods were used to solve the tasks – X-ray phase, thermal (TG, DTG, DTA) methods of analysis, chemical methods of research of raw materials and masses based on them, which made it possible to evaluate the peculiarities of the structure formation of ceramic materials. To determine the suitability of local low-melting clay for the manufacture of ceramic products, systematic studies were conducted on the development of mass compositions, as well as the main characteristics of the manufactured products.

In the work, a plastic method of preparing the raw material mixture and forming the samples was used. When developing ceramic masses for the production of building ceramics, it is necessary to take into account their sensitivity to drying, the change in the linear dimensions of the samples during drying and firing, the limit of compressive strength and water absorption.

In order to study the influence of the addition of zeolite on the technological properties of ceramic masses based on low-melting raw materials, the following charges for the production of construction ceramics were studied, which are listed in the Table 1.

<table>
<thead>
<tr>
<th>Components</th>
<th>Content of components in batches, wt. %</th>
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<tbody>
<tr>
<td>Clay</td>
<td>100  90  85  80</td>
</tr>
<tr>
<td>Zeolite</td>
<td>–   10  15  20</td>
</tr>
</tbody>
</table>

To determine the phase composition of materials, a modernized X-ray diffractometer DRON-3M (Joint Stock Company «Bourevestnik»), equipped with a computer system for automatic recording of diffraction data, was used. Filtered CuKα radiation, Ni filter was used. The analysis of the obtained data was carried out using the «Match» program. Phase identification is performed according to the international database of standard X-ray diffraction data (PDF-2 database of ICDD). Adjustment of the background level and approximation of the peaks was carried out using the «Fityk» program [13].

Ceramic samples for research were fabricated by the molding technique, using a technological mode as close as possible to the process of manufacturing ceramic products for construction purposes. For this, the clay was first crushed, and then ground in fine grinding rollers and runners. The zeolite-containing mineral rock was first dried at a temperature of 200–250 °C, and then crushed to a size of less than 1 mm. Grinding of zeolite was carried out in ball mills, and then added to the original clay in amounts of 10, 15 and 20 %. The prepared components were sifted through a sieve, mixed and closed with water to normal forming humidity. After laying for a day, samples with a size of 50×50×50 mm and beams with a size of 60×15×10 mm were formed by the method of plastic pressing at a humidity of 18–22 %. Mass leaching must be carried out to ensure the flow of mass exchange processes between clay and zeolite in full. Molded samples were dried to a moisture content of 3–6 %. Drying was carried out in an oven at 100 °C to a constant mass. Firing was carried out in an electric furnace at 950 °C.
3. Results and Discussion

To regulate the drying properties of low-melting clay, a zeolite-containing rock was used as a mineral admixture. The chemical analysis of low-melting clay of the Kyiv region is given in [14]. According to the results of chemical analysis, zeolite rock contains: SiO₂ – 65.45; Al₂O₃ – 12.75; Fe₂O₃ – 1.37; TiO₂ – 0.18; CaO – 2.21; Na₂O – 3.17; MgO – 0.52; l.d.r. (losses during roasting) – 14.33.

The peculiarity of the structure of the mineral-forming component of zeolite-containing rocks determined their choice for regulating the drying properties of low-melting clays. Zeolites are hydrous aluminosilicates of light gray or green alkaline and alkaline earth metals and have a porous structure. They have an internal system of channels, thanks to which they are able to absorb molecules of various substances. In general, the volume of pores and channels can reach 50 %.

The diffractogram of zeolite rock (Fig. 1) has significant differences compared to clay. The amorphous halo is much more intense and this indicates the relative majority of amorphized dispersed matter. SiO₂ exists in three forms: (I) – +* – SiO₂ (PDF file 0086-2237) – quartz; (II) – +% – SiO₂ (PDF file 0082-1235) – cristobalite; and (III) – + previously mentioned phases, there are peaks +* – Al₂O₃ (PDF file 0075-1864) and +% – Na₂O (PDF file 0089-39).

As a result of the conducted research, it was established (Table 2) that the addition of zeolite in the amount of 10–20 % to low-melting clay contributed to increasing its sensitivity to drying.

For low-melting clay, it is 54 s, and when zeolite is added, it increases to 58 s (sample 90:10), 61 s (sample 85:15), and 65 s (sample 80:20).

Also, the mechanical compressive strength in the dry state, which is an important physical and mechanical indicator for the further process of production of building ceramics, increased.

The conducted studies showed that with an increase in the amount of zeolite additive from 5 to 15 % by weight to low-melting clay contributed to the strengthening of the semi-finished product in the dry state to 8.9 MPa. The addition of zeolite practically did not affect the forming humidity and plasticity.

One of the important indicators of the drying properties of clay raw materials is air shrinkage, which indicates a decrease in the size of the products during their drying. The addition of zeolite admixture contributed to the reduction of air shrinkage, which has a positive effect on the stability of the external dimensions of the products. For ceramic clay mass, it was 8.1 %, and for masses with a sample ratio of 90:10, it was 7.4 %; for sample 85:15 – 7.1 % and for sample 80:20 – 6.9 %.

Among the strengths of this study, it should be determined that due to the limitation of high-quality clay raw materials in many regions, the possibility of using low-melting clays for the production of building ceramics is shown. The composition of low-melting clays requires

Table 2

<table>
<thead>
<tr>
<th>Technological indicators</th>
<th>Fusible clay</th>
<th>Zeolite impurity content, %</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>10</td>
<td>15</td>
</tr>
<tr>
<td>Molding humidity, %</td>
<td>24.5</td>
<td>21.4</td>
</tr>
<tr>
<td>Plasticity number</td>
<td>13.5</td>
<td>13.1</td>
</tr>
<tr>
<td>Air shrinkage, %</td>
<td>8.1</td>
<td>7.4</td>
</tr>
<tr>
<td>Sensitivity to drying, s</td>
<td>54</td>
<td>68</td>
</tr>
<tr>
<td>Dry compressive strength, MPa</td>
<td>8.0</td>
<td>8.4</td>
</tr>
</tbody>
</table>

Fig. 1. Diffractogram of a zeolite sample with designation of the main phases

Fig. 2. Thermal curve of zeolite rock

The results of the differential thermal analysis showed that the zeolite-containing rock is characterized by slow, continuous dehydration. The main part of zeolite water, about 70 % of the total mass loss, is removed already at 300 °C. Complete dehydration occurred already at 900 °C (Fig. 2).

In order to completely remove the adsorbed water, the zeolite was first dried at a temperature of 200–250 °C, and then crushed to a size of less than 1 mm. Thanks to this, a homogeneous fine-grained mass was formed, from which up to 70 % of the total zeolite water was removed for better opening of the pore space. Table 2 presents the technological properties of the ceramic mass with the addition of zeolite in amounts of 10, 15, and 20 %.
the use of additives that will improve the technological properties of ceramic masses based on them. One of these can be zeolite-containing mineral rocks. The use of these materials as a raw material admixture will contribute to the expansion of the use of local raw materials in the production and will have a positive effect on the technical and economic performance of the enterprise for the production of construction ceramics.

The use of zeolite-containing mineral rock will contribute to the formation of a strong structure and improvement of the physical and chemical properties of the products after drying. This additive increases the sensitivity of the ceramic mass to drying and reduces air shrinkage. It is very important that the mechanical compressive strength of the dried samples increases.

The weaknesses of this study are related to the fact that the developments are based on the need to first dry the zeolite-containing mineral rock at a temperature of 200–250 °C. And this will contribute to a slight increase in energy consumption.

In the future, it is very important to consider the optimal methods of preparing zeolite-containing mineral rock as an additive (purification, enrichment, etc.), which can significantly affect the quality of products and a higher price and greater demand.

It is also necessary to research and select production parameters and the composition of raw materials in order to reduce energy costs and use them rationally and energy-efficiently. This will reduce the cost and increase the environmental friendliness of production.

It is important to investigate the effect of components that will lower the firing temperature without impairing the strength of the material. Creation and selection of the optimal improved formulation is always a promising direction of research in production, which will reduce energy costs, the amount of defects and increase quality.

This work may be interesting for foreign manufacturers due to the low cost of low-melting clays in the Kyiv region and in Ukraine as a whole.

A threat to this study is the presence of an analogue additive that will provide better physicochemical properties of the samples and will not lose to the zeolite-containing mineral rock in terms of cost. In the world, the use of expanded clay, galvanic sludge, glass production waste, ash and sawdust as part of the ceramic mass is also being considered. Each of these additives can be promising when considered in the technology of ceramic production, but there is still no clear dominant competitor in terms of properties.

4. Conclusions

1. When evaluating the suitability of zeolite-containing rock as an admixture to low-melting clay for the production of building materials, its chemical and mineralogical composition was studied. Its composition includes clinoptilolite, heylandite and mordenite, and as impurities there are quartz, iron oxides, titanium and a small amount of clay minerals.

2. The conducted studies showed that it is possible to use the zeolite-containing rock additive for the production of building ceramics (bricks). A slight decrease in moldng humidity and plasticity did not affect the molding properties of the ceramic mass.

3. Introduction of zeolite-containing rock up to 20 wt. % as an admixture to low-melting clay contributed to an increase in its sensitivity to drying by 1.5 times without deterioration of cohesion, due to which the crack resistance of the ceramic mass increased.

4. It was established that when the zeolite-containing rock was added, an increase in the compressive strength of the samples after drying to 8.9 MPa was also observed. This ensures the possibility of defect-free automatic landing and transportation of the dried semi-finished product.

5. Improvement of the drying properties of low-melting local raw materials is achieved by transferring part of the free water of the clay into a bound state by transferring it into the pore space of the zeolite-containing rock.

Conflict of interest

The authors declare that they have no conflict of interest in relation to this research, whether financial, personal, authorship or otherwise, that could affect the research and its results presented in this article.

Financing

The research was conducted without financial support.

Data availability

The manuscript has no associated data.

References

APPLICATION OF PROCESSES STIMULATED BY NONEQUILIBRIUM PLASMA FOR LARGE-TONNAGE DECONTAMINATION OF SOILS

The object of research is a new, potentially effective and practical process for the decontamination of radioactive soil, based on combination of plasma hydroseparation and plasma activation. The cleaning effect is ensured by the destruction of the bonds of radionuclides with soil particles due to a series of electrophysical discharges at which active particles and shock waves appear. In a designed setup, the process of plasma-chemical treatment is implemented in a plasma cell with a self-sustaining pulsating mode of burning an electric discharge, which occurs in an aqueous solution. The setup realizes a resonant increase in the intensity of shock waves, turbulence and multiple expansion of the core, such that the expansion of the plasma-liquid interface becomes a real basis for scaling up the setup. Regardless of the material of the electrodes and in a wide range of electrical conductivity (measured from 100 to 5,000 μS/cm), the restructuring of the combustion regime is accompanied by an increase in the size and stabilization of the luminous zone, fragmentation of bubbles, and an increase in the rate of their evacuation from the discharge zone. The main factors of such a restructuring are the channel dimensions and temperature of the solution. Various materials of the walls of plasma-chemical reactor have been tested: plexiglass, ceramics and stainless steel with the thickness of 2 mm. The maximum increase in the amplitude of resonance oscillations depends on the cell radius. A dynamic pressure, which in an individual discharge is about 5–15 mm of the water column at the mouth of the discharge, increases to 150–200 mm of the water column at the bottom of the plasma cell at resonance. An increase in efficiency is achieved by an optimal choice of the duration of the current phase and the distance between the electrodes, which is 15–30 mm. The voltage drop is 70–80 % across the spark discharge, the rest falls across the solution. The transition of the discharge to a periodic pulsating current mode with an increase in the temperature of the solution has been found. Tests on a mobile plasma-chemical facility for the process of plasma co-precipitation of radionuclides $^{137}$Cs, $^{134}$Cs and $^{90}$Sr with ferrocyanide sorbents under real conditions of hydroseparation of contaminated soil from fields around the Fukushima Daiichi have shown a decrease in organic substances in water by 40 times, and of radioactivity by 75 times.

Keywords: electric discharge, water solution, electrohydraulic resonance soil decontamination, radionuclides, plasma cell, active particles.

1. Introduction

The problem of radioactive waste (RW) is an extremely complex issue of nuclear activity in general and nuclear energy in particular [1]. The experience of eliminating the consequences of accidents at the Chornobyl and Fukushima nuclear power plants [2–7] indicates that the existing system of radioactive waste management in real