

This paper reports research into the development of compositions of engobe coatings for ceramic bricks and investigating the influence of technological production factors on their physical and mechanical properties. The results of this work make it possible to solve the task of expanding the range and improving the operational properties of building ceramics.

The data obtained have made it possible to establish physicochemical processes occurring during the formation of the phase composition and structure of engobe coatings. This has revealed the possibilities for designing engobe for various types of ceramic bricks, which differ in technological parameters of production and operational properties.

The charge compositions were designed in a three-component system "refractory clay – quartz sand – cullet", taking into account the possibility of their practical implementation in large-tonnage production. It has been established that the most important condition for obtaining high-quality products is the correlation of shrinkage and temperature coefficients of linear expansion of the ceramic shard and engobe coating. To prevent various defects, these indicators should vary by no more than 10 %.

The crystal-phase composition of engobe is represented by β -quartz and a small amount of devitrite, which are evenly distributed in a vitreous dense layer of coating on the surface of the ceramic shard.

Distinctive features of the results relate to the fact that a solution to the problem of designing engobe coatings for ceramic bricks has been proposed and the physicochemical bases of production have been highlighted. This paper also suggests ways to achieve coordination of finely dispersed coatings with coarse-grained ceramic masses by shrinkage and thermal processes.

The results reported here could be applied in typical production of face, clinker, and in some cases – ordinary brick or ceramic stone with firing temperatures of 950–1150 °C

Keywords: engobe, rheological properties, ceramic brick, thermal expansion, crystal phase, shrinkage

DESIGNING ENGOBE COATINGS FOR CERAMIC BRICKS

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Received date 07.04.2023

Accepted date 17.06.2023

Published date 30.06.2023

How to Cite: Khomenko, O., Tsyhanenko, L., Tsyhanenko, H., Borodai, A., Borodai, D., Borodai, S. (2023). Designing engobe coatings for ceramic bricks. *Eastern-European Journal of Enterprise Technologies*, 3 (6 (123)), 77–87.

doi: <https://doi.org/10.15587/1729-4061.2023.279918>

1. Introduction

Construction ceramics is the most common and demanded material used for the erection and cladding of buildings [1]. The products have high physical and mechanical properties, provide an optimal indoor climate, and do not emit toxic substances [2].

However, the consumer seeks to surround himself with bright, aesthetically attractive and extraordinary things, and exclusive design solutions require the development of new finishing materials. In this sense, the natural coloring of ceramic bricks, which is formed as a result of heat treatment of low-melting clays, limits the possibility of their use in modern construction projects. Therefore, there is a need for new technological solutions that will expand the color gamut of ceramic bricks and the ability to create decorative effects with their help.

To this end, the application of engobe coatings on the front surface of the brick is the optimal solution, in contrast to the volumetric coloring of products [3]. This technique does not require the introduction of expensive coloring components into the charge in significant quantities, and at the same time makes it possible to obtain bright spectral colors and a homogeneous surface of ceramic material.

Engobe coatings qualitatively selected to the ceramic base, in addition to decorative, perform a protective function. It implies reducing the porosity of products by creating a dense outer layer [4], which slows down the destruction of their structure under the influence of environmental factors.

The limited production of engobe domestic products is associated with certain difficulties in production, as well as the lack of in-depth basic research. In particular, there is no universal approach to the development of charge compositions of coatings for bricks with different firing tem-

peratures. The basic properties of the cover layer and their dependence on technological factors are not sufficiently studied. The physicochemical processes of phase formation and formation of the structure of coatings are not covered, the issue of adhesion of engobe to the ceramic base and coordination of their shrinkage processes is not elucidated.

Therefore, designing and examining engobe coatings for building ceramics is an urgent task in terms of improving the basic properties of construction products and expanding their range.

2. Literature review and problem statement

Engobe coatings in ceramic technology differ significantly in composition, basic properties, and have a variety of purposes.

In ancient times, engobe was used to decorate household ceramics, in particular – red-figure painting [5]. Engobe based on red finely ground clay was applied to the surface of ceramic dishes, and then, after firing, painted scenes were created using black varnish.

The most studied and widely used engobe relates to the production of ceramic tiles and porcelain stoneware, as transition layer between ceramic base and glaze to balance the difference in their coefficients of thermal expansion.

In [6], the possibility of replacing expensive frit, which is specially made by cooking glass melt at temperatures of 1500 °C and above, by a secondary product. The composition of engobe is within the following limits, wt%: clay 1040, feldspar 040, cullet 1040, quartz 040, zircon 020. Coatings after firing have water absorption of 820 wt%, which is sufficient for the intermediate layer between the ceramic base and glaze but unacceptable for the outer layer of building ceramics.

The authors of [7] investigated the processes of degassing ceramic granite through a layer of engobe and glaze during firing at temperatures up to 1200 °C. The results showed that the tiles somewhat complicated the process of removing gases from the shard due to the presence of layers of engobe and glaze, which leads to the formation of additional pores in the shard of 0.83.0 microns in size. But the cited paper does not investigate the effect of changes in the compositions of engobe on these processes, and also does not consider the ratio of shrinkage of the ceramic base and coatings, which is often the cause of defects in the form of cracks [8].

In the manufacture of engobe for tiles, they suggest the use of secondary products, in particular ceramic sludge from a wastewater treatment plant [9]. Ceramic sludge together with cullet is fused at 1420 °C and frit is obtained, which is introduced into the composition of engobe together with clay, kaolin, feldspar, zirconium, talc, and bentonite. After firing tiles at 1150 °C, an engobe of high quality is obtained on their surface, with an indicator of thermal expansion close to a ceramic base. But the implementation of this technology in large-tonnage production will require high energy costs since it includes an additional operation of sludge fusion.

Engobe for ceramic tiles was investigated in [10], using frits based on diopside, zircon, and titanium. The introduction of these components helps increase the opacity of coatings and their permeability to form a high-quality intermediate layer between the ceramic base and glaze. But for ceramic bricks, such engobe is impractical to use since it

is necessary to obtain a strong densely baked engobe for the outer layer.

As part of engobe for porcelain stoneware, in [11] it is proposed to use pharmaceutical waste from glass, which is a mixture of used medical ampoules in order to reduce the negative impact of these wastes on the environment and preserve mineral raw materials. The designed engobe with a content of up to 30 wt% of glass waste is used as a transition layer between ceramic base and glaze in the production of porcelain stoneware with a firing temperature of 1185 °C.

In building brick technologies, firing temperatures are lower. Only in some clinker brick productions can firing occur at 1150 °C or more [12]. But more often in the manufacture of facial products, these temperatures are within 1050–1100 °C [13], and under conditions of energy shortage, studies are underway to further reduce them [14]. Thus, the difference in engobe for ceramic bricks is that their composition and technological parameters of production should contribute to the formation of a dense engobe layer with water absorption indicators of up to 1.0 % at temperatures 1000–1150 °C.

Engobe samples for Dan Kwian pottery were developed in [15]. It has been established that the best composition of engobe contains, wt%: kaolinite clay 10, zirconium silicate 10, sodium feldspar 40, and quartz 40. This composition of engobe is optimal for creating a beautiful appearance of the surface of ceramics with a firing temperature of up to 1200 °C. The color and surface of the engobe samples are opaque white and glossy, respectively. Obviously, this engobe does not sinter at low temperatures to a dense state since it contains up to 60 % by weight of refractory components. The only relatively low-melting component is feldspar but depending on the chemical composition, it only begins to melt at 1130 °C [16].

There are data on engobe for ceramic tiles, which reduce its light absorption ability [17]. To this end, it is proposed to include frit with a high diffuse reflection coefficient (0.95), which is able to increase the reflective properties of tiles from 0.69 to 0.75. However, it is also noted that the growth of this ratio is limited due to crystallization, which has not yet been fully controlled. In [18], the influence of coloring pigments on the properties of reflective engobe for roof tiles was investigated. It has been established that the presence of zirconium oxides and chromium oxides in the composition of engobe increases its diffuse reflection coefficient, while the presence of cobalt and iron oxides leads to its decrease.

The authors of [19] propose to use engobe coatings to improve the aesthetic performance of ceramic bricks. Coatings include clay, cullet, limestone, and a by-product of the steel industry. The resulting engobe have a light and dark brown color and make it possible to get ceramic bricks with an attractive appearance. But the cited work does not sufficiently disclose the dependence of the properties of engobe on the composition and temperature of firing products.

Engobe coatings can be relevant not only for expanding the color gamut of ceramic bricks [20] but also for creating self-cleaning facades of buildings [21].

However, the problem of developing engobe coatings for ceramic bricks is not sufficiently illuminated. The peculiarities of the development of engobe compositions for bricks burned at different temperatures, the possibilities of regulating the rheological properties of engobe slurries, even

insufficiently formulated requirements for engobe as the final product of firing have not been disclosed.

Therefore, it is necessary to devise a systematic approach to the selection of compositions of engobe coatings for ceramic bricks obtained with different technological parameters.

3. The aim and objectives of the study

The aim of this study is to establish the dependence of the basic properties of engobe coatings for ceramic bricks on the charge composition and technological factors of production. This will make it possible to devise a basic approach to the development of decorative and protective coatings for ceramic bricks and formulate requirements for their basic properties.

To accomplish the aim, the following tasks have been set:

- to justify the choice of raw materials for the design of engobe;
- to investigate the rheological properties of engobe slurries and establish their dependence on the composition and technological parameters of production;
- to investigate the basic properties of engobe samples and establish their dependence on the composition and technological parameters of production;
- to investigate the processes of formation of engobe coatings on the surface of ceramic bricks and determine the basic conditions for the coordination of engobe with the ceramic base;
- to investigate the peculiarities of the formation of the phase composition and structure of engobe, to establish the basic composition of the coating and to formulate the basic requirements for the properties.

4. The study materials and methods

The object of our study is the compositions of engobe coatings for ceramic bricks.

The main hypothesis of the development was to establish the possibility of influencing the physical and mechanical parameters of engobe coatings by changing the ratio of components in the charge composition of the engobe and the technological parameters of the process, which led to the formation of the required phase composition and coating structure. At the same time, special attention should be paid to the study of the processes of coordination of the parameters of ceramic products and engobe during drying and firing.

The study assumes that the most rational for the development of engobe compositions and the establishment of dependences of their indicators on technological factors and conditions for the formation of the phase composition of coatings is a three-component system “refractory clay – quartz sand – cullet”. This system contains common and non-scarce raw materials and is easily managed and predictable.

To determine the indicators of shrinkage, water absorption, and hardness of coatings, the engobe slurries of a given composition were used to make samples-tiles the size of 30×30×5 mm by casting into gypsum molds; they were dried and burned at appropriate temperatures. To determine the indicators of the temperature coefficient of linear expansion,

stick samples with a size of 5×5×50 mm were similarly prepared.

To determine the covering capacity and whiteness, engobe slurries were applied to ceramic brick samples 50×30×10 mm in size, which were made of ceramic charge of controlled composition.

Chemical analysis of raw materials was determined using the X-ray fluorescence spectrometer Zetium (PANalytical B. V., The Netherlands).

The rheological properties of slurries and the physico-mechanical parameters of the samples were evaluated using standard methods. The readiness of the slurry was determined by the indicator of the sieve residue No. 0063, which was not more than 0.5 %. The yield strength of the slurry, which is the time of outflow of 100 ml of suspension through a hole of 4 mm in size, was measured using a Ford bowl. Shrinkage indicators were determined by changing the size of semi-finished samples before and after drying and firing. The water absorption of the sintered materials was estimated by the amount of water absorbed in the open pores of the sample after saturation in vacuum.

The hardness of the coatings was assessed on the Mohs scale by scratching the surface of the samples with a steel knife with a hardness index of 7.

The whiteness was measured using a WM-106 whiteness meter (Walcom, China).

The temperature coefficient of linear expansion was measured using a dilatometer DIL 402 Expedit Classic by Netzsch (Germany).

X-ray phase analysis was performed using X-ray analyzer DRON-3 (“Burevestnik”).

To study the microstructure of burnt samples, the raster electron microscope “REM1061” (NPP “Akademprilad”) was used.

5. Results of investigating the dependence of the properties of engobe on the charge composition and technological factors of production

5.1. Justification of the choice of raw materials

Our review of the scientific and technical literature showed that the experimental compositions of engobe coatings are very diverse and the number of components in the batch varies widely. However, the components, depending on their role in the composition of the engobe, can be divided into clay (clay or kaolin), lean (quartz sand, chamotte, battle products), and flux (cullet, pegmatite, feldspar).

Clay materials provide engobe slurries with suspension ability, prevent the deposition of stone particles, and are also the basis for the formation of the body of sintered material [22]. The task of lean materials is to create a “frame” of the coating and regulate shrinkage processes during drying and firing [23]. Flux ones are introduced into ceramic masses to intensify liquid-phase sintering and obtain dense durable material [24].

Therefore, for the development of engobe, the system «refractory clay – quartz sand – container cullet» was chosen; the chemical composition of raw materials is given in Table 1.

In this system, the contents of the components were changed, according to Table 2. In this case, the oxide composition of engobe differed as follows (Fig. 1).

The chemical composition of raw materials, wt%

Name of raw materials	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	CaO	MgO	K ₂ O	Na ₂ O	Loss on ignition
Refractory clay DN-1	51.1	34.5	0.7	0.1	0.5	0.5	2.0	0.5	10.1
Quartz sand PK-150-3	97.4	2.1	0.1	0.2	0	0	0	0	0.2
Container cullet	73.1	3.5	0.6	0	2.9	3.7	0	16.0	0.2

Table 1

Engobe No. 10 has the lowest yield strength (9.8 s) and humidity (32.2 %), engobe No. 1 has the highest indicators (20 s and 46.3 %, respectively).

The ability of ceramic slurries to stratify due to proofing was also evaluated. This phenomenon is dangerous because it leads to deformation, uneven shrinkage, and the

Table 2

Experimental compositions of engobe coatings, wt%

Component name	Composition number										
	1	2	3	4	5	6	7	8	9	10	11
Refractory clay	80	50	50	65	65	50	60	35	35	20	40
Quartz sand	10	10	40	10	25	25	20	25	40	40	30
Container cullet	10	40	10	25	10	25	20	40	25	40	30

occurrence of additional internal stresses in the microstructure of the samples, which, in turn, leads to a decrease in performance properties [26].

For visual assessment of deposition ability, samples-tiles 5×5×1 cm in size were cast from engobe slurries into gypsum molds, which were dried and burned at a temperature of 1100 °C. Evaluation was carried out by the presence of deformation of the samples (Fig. 2). The results are given in Table 4.

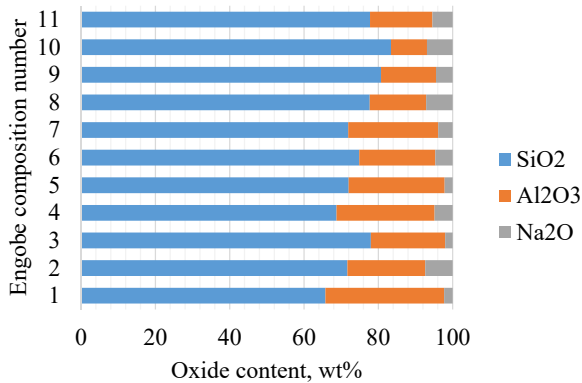


Fig. 1. The chemical composition of experimental engobe

Data in Fig. 1 demonstrate that the content of the basic oxides of the experimental system is within, wt%: 66–83 SiO₂, 10–32 Al₂O₃, 2–7 Na₂O. Such oxide composition limits allow covering a wide range of engobe compositions that can potentially be used in the brick industry.

5.2. Investigation of rheological and technological properties of engobe slurries

The rheological properties of engobe slurries determine their manufacturability (mobility, adhesion to the ceramic base, the quality of spreading on the surface of ceramics), as well as the physical and mechanical properties of baked coatings (porosity, strength, hardness). At minimum humidity, slurries should be easily transported by a slurry line, have sufficient filtration properties, and at the same time should not delaminate during long-term storage and during application to the surface of the ceramic product [25].

The rheological and technological characteristics of experimental engobe slurries are given in Table 3. As a diluent additive, the electrolyte reotane was added to all slurries in an amount of 0.2 mass parts.

Table 4

Visual assessment of the ability of engobe slurries to delaminate and deform specimens after firing

Composition number	1	2	3	4	5	6	7	8	9	10	11
Deformation	-	+	-	-	-	+	-	-	+	++	++
Stratification	-	++	-	-	-	+	-	+	++	+++	++

Note: “-” – no delamination/deformation, “+” there are signs of delamination/deformation, “++” – deformation/delamination is significant, “+++” deformation/delamination is strong

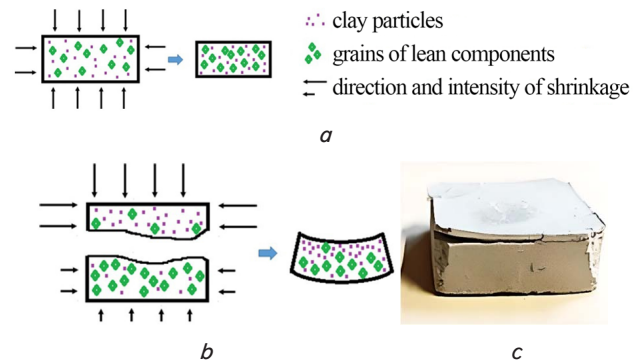


Fig. 2. Schematic representation of the distribution of shrinkage processes in the ceramic bulk: a – with high sedimentation resistance; b – with a tendency to stratification; c – illustration of engobe sample No. 10 with stratification

Data in Table 4 indicate that engobe slurries No. 2, 6, 9, 10, 11 have the ability to stratify and deposition.

5.3. Investigation of the basic properties of engobe samples during drying and firing

The physical and mechanical properties of engobe coatings play an important role in coordination with the ceramic base, as well as in assessing the properties of engobe ceramics. Fig. 3 shows the change in the indicators of air and fire shrinkage of engobe; Fig. 4 – water absorption at different firing temperatures.

Rheological and technological characteristics of experimental slurries

Table 3

Characteristic	Composition number										
	1	2	3	4	5	6	7	8	9	10	11
Viscosity (fluidity) 100 ml, s	20.0	14.2	14.4	17.0	14.1	14.7	15.7	15.1	11.5	9.8	13.3
Slurry moisture, %	46.3	43.0	43.2	43.3	45.2	41.2	43.0	36.7	39.3	32.2	37.7
Density (by pycnometer), g/cm ³	1.49	1.53	1.54	1.53	1.50	1.56	1.53	1.62	1.58	1.71	1.60

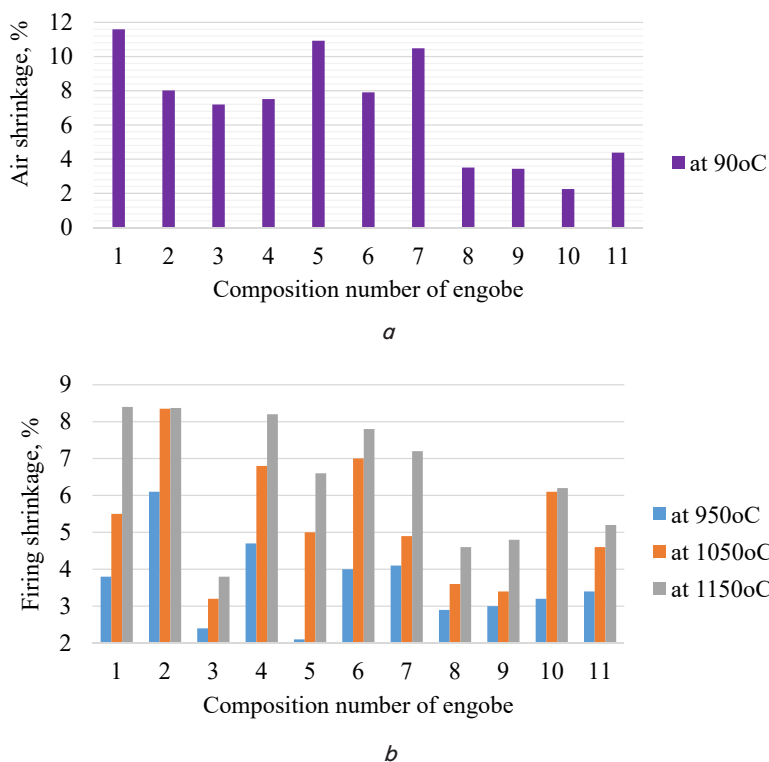


Fig. 3. Engobe shrinkage rates: a – air; b – firing

Data in Fig. 3 demonstrate that the minimum air shrinkage characterized for engobe No. 10, and the maximum – engobe No. 1. Fire shrinkage at all test firing temperatures is minimal for engobe No. 3.

In terms of water absorption, it can be noted that the most active sintering is observed for engobe No. 2 and 4, while samples No. 3 and 9 do not form a dense structure even at maximum firing temperature.

For ceramic materials on which glaze coatings are applied, in particular facing ceramic tiles, sanitary ceramics, electro porcelain, and others, one of the most important indicators is the temperature coefficient of linear expansion [27]. The discrepancy between the ceramic base and coating based on this indicator causes low adhesion strength and the presence of internal stresses in the contact zone, which can lead to chipping or cracking of the coating layer. Engobe contains less vitreous phase than glazes but water absorption indicators of the engobe layer are 10–12 times lower than that of the ceramic base due to the difference in structure and phase composition of these materials. Therefore, the danger of internal stresses is also high and, to minimize it, their thermal expansion indicators must be carefully monitored. Temperature coefficients of linear expansion of samples of experimental engobe after firing at 1100 °C are shown in Fig. 5.

The temperature coefficients of engobe coatings annealed at 1100 °C vary within $(51-89) \cdot 10^{-7} 1/°C$.

For experimental engobe samples, a qualitative assessment of hardness in the annealed state was carried out. To this end, a steel blade of a knife, whose hardness is 7 on the Mohs scale, scratched samples of engobe burned at different temperatures and we set the limit

at which the coatings were not damaged. The results are given in Table 5.

Table 5

Evaluation of the resistance of sintered engobe samples to scratching with a steel knife after firing at different temperatures

Composition number of engobe	Firing temperature, °C				
	950	1000	1050	1100	1150
1	++	+	-	-	-
2	+	-	-	-	-
3	+++	++	++	+	-
4	+	-	-	-	-
5	++	++	+	+	-
6	++	+	+/-	-	-
7	++	+	-	-	-
8	+	+	+/-	-	-
9	++	+	+/-	+/-	-
10	++	++	+/-	+/-	-
11	++	+	+/-	+/-	-

Note: “-” – no surface damage, “+” – minor trace, “++” – significant trace, “+++” – deep footprint, “+/-” – different on different surfaces of the same sample

From the above data it can be seen that engobe No. 2 and 4 form a dense surface with high hardness already at 1000 °C, unlike other samples, which acquire hardness at higher temperatures.

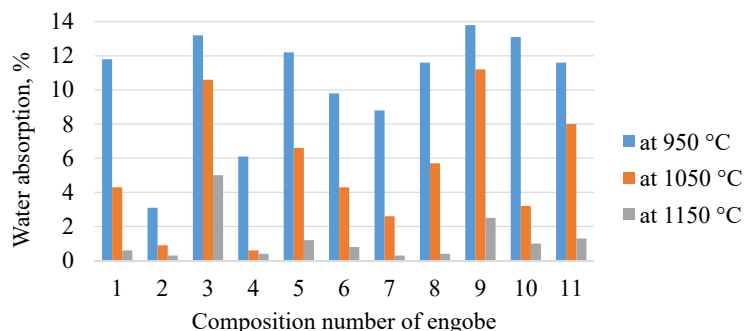


Fig. 4. Change in engobe water absorption indices

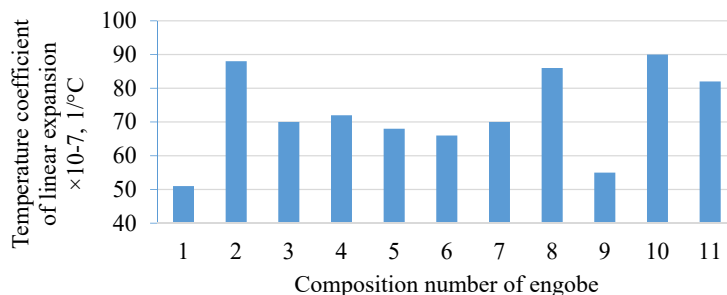


Fig. 5. Dependence of the temperature coefficient of linear expansion of experimental engobe after firing at a temperature of 1100 °C on its composition

5. 4. Investigating the processes of formation of engobe coatings on the surface of ceramic bricks

From the typical ceramic mass used in the production of building bricks, tile samples were prepared by plastic mold-

ing, on which experimental engobe coatings were applied by irrigation. Engobe slurries were applied to freshly formed tiles. This technique has advantages over the technique of coating dry samples since both the engobe and the ceramic base dry simultaneously and slowly, which reduces the risk of defects due to the difference in shrinkage (Fig. 6). If engobe is applied to dry samples, this risk increases significantly.

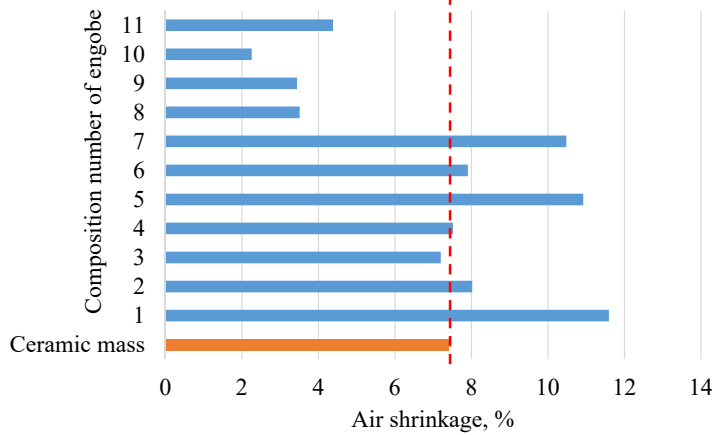


Fig. 6. Indicators of air shrinkage of engobe and experimental ceramic mass

The Fig. 6 shows that the most consistent in terms of shrinkage with ceramic mass are engobe No. 2–4, and 6.

Engobe samples were fired at a temperature of 1050 °C, which was determined as the most appropriate for sintering the base ceramic mass. The results of visual analysis of fired samples are given in Table 6.

Table 6

Visual analysis of engobe ceramics

Composition number	1	2	3	4	5	6	7	8	9	10	11
Whiteness, %	71	62	76	68	73	67	67	65	67	66	62
Cracks	-	-	-	-	-	-	-	-	-	-	-
Yellowness	-	++	-	-	-	++	-	+	-	-	++
Irregularity of pouring	-	++	-	-	+	-	+	+	-	-	-
Illumination of the shard	-	-	+	-	-	-	+	+	+	+	-
Visualization											

Note: 1. Studies are conducted at an engobe layer thickness of up to 100 microns.

2. The designations in the table correspond to: “-” – absence of defect, “+” – presence of defect, “++” – strong manifestation of the defect.

The table above shows that the most common defects of the samples are yellowness (No. 2, 6, 8, and 11), uneven pouring (No. 2, 5, 7, 8), and shard translucency (No. 3, 7–10). Engobe samples No. 1 and 4 have no defects.

5.5. Investigation of phase composition and microstructure of engobe coatings

The formation of the directed phase composition of ceramic materials and coatings makes it possible to control the properties of the finished product. For the analysis, an engobe of composition No. 4 was chosen, which turned out to be the

most rational according to the complex of properties obtained. Radiographs of samples of this engobe after firing at temperatures of 1000, 1100, and 1150 °C are shown in Fig. 7.

Fig. 8 shows radiographs of engobe No. 1 and No. 8.

The microstructure of engobe No. 4 and No. 3 on the surface of ceramic samples after firing at 1100 °C is shown in Fig. 9, 10, respectively.

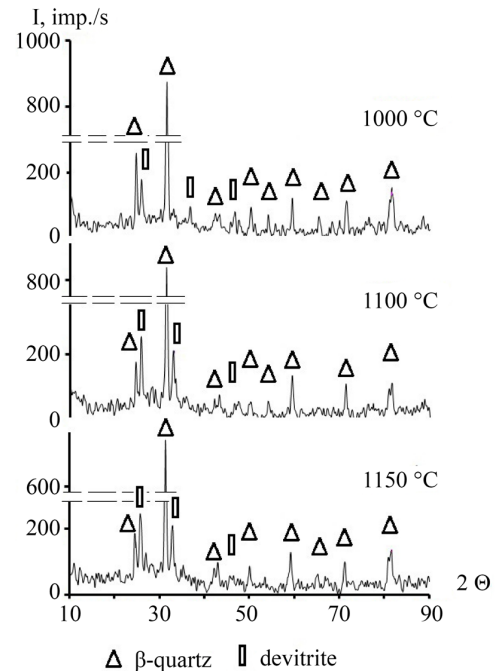


Fig. 7. Radiographs of engobe prototypes of composition No. 4

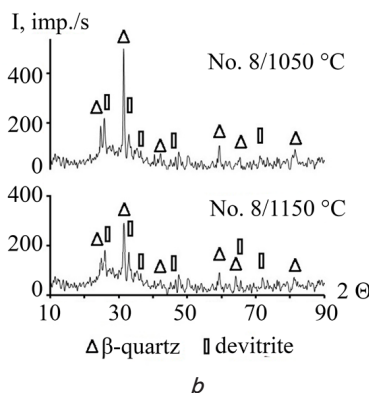
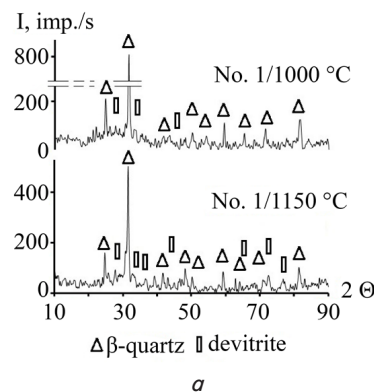


Fig. 8. Radiographs of experimental engobe: a – No. 1, b – No. 8

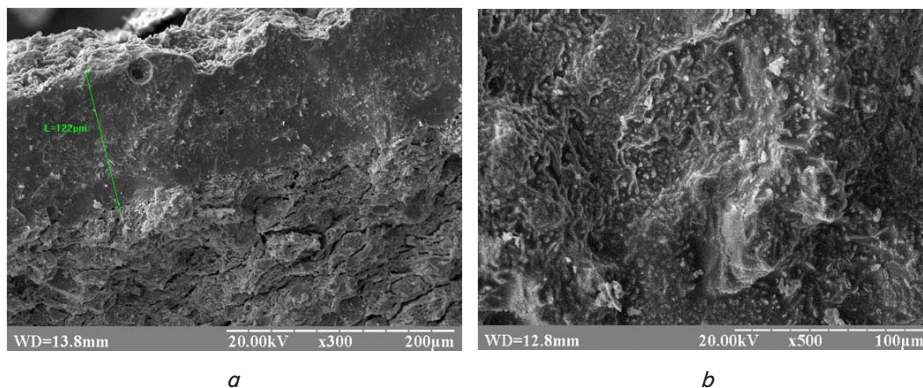


Fig. 9. The microstructure of engobe No. 4 on the surface of ceramic shard after firing at 1100 °C: *a* – cross-section; *b* – top view

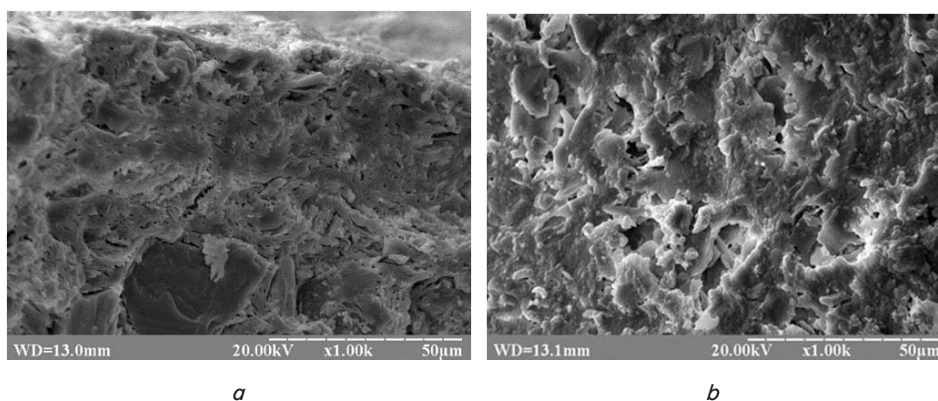


Fig. 10. The microstructure of engobe No. 3 on the surface of ceramic shard after firing at 1100 °C: *a* – cross-section; *b* – top view

Thus, as a result of our research, it was possible to obtain a complex of properties of experimental engobe and establish the physicochemical basis of its production. In almost all respects, engobe No. 4 has shown the most manageable and stable technological and operational properties, so it can be recommended for wider testing on various types of ceramic bricks.

6. Discussion of results of the development of universal coatings for ceramic bricks

The design of universal engobe coatings for various types of building ceramics (front, clinker) is a difficult task since these materials differ significantly in performance properties, the kinetics of shrinkage processes, and features of the formation of phase composition and structure [2, 12]. The system «refractory clay – quartz sand – cullet» in a significant approximation makes it possible to cover almost all possible combinations of known engobe in terms of filling with clay, lean, and glass-forming components. This makes it possible to investigate the physicochemical processes in the engobe material at each production stage and to establish the dependence of the basic properties of engobe on its composition and technological parameters of production.

Analysis of rheological and technological characteristics of engobe showed (Table 3) that with a decrease in the content of clay components in the composition of the slurry, the moisture required to achieve a fluid state decreases from

46.3 to 32.2 %. At the same time, the viscosity (fluidity) decreases from 20 to 9.8 s. The density of engobe slurries, on the contrary, increases since the content of lean components with a higher density increases, compared with clay minerals.

The engobe slurry of composition No. 1 with the highest clay content has a sufficiently high fluidity index (20 s) at maximum humidity (46.3 %), which indicates its increased viscosity. This makes it difficult to apply engobe to the surface of the ceramic product since the engobe spreads unevenly, which can lead to thickening of the layer in individual areas and the appearance of microcracks. The introduction of electrolytes can partially solve this problem but there are difficulties at a further stage – this engobe has the highest indicator of air and fire shrinkage, which complicates consistency with the ceramic base during drying and firing.

In terms of resistance to deposition, engobe No. 9–11 had problems. Their viscosity in comparison with engobe No. 1 is almost 1.82 times less (fluidity 9.8–11.5) and, due to

the low content of the clay component, these slurries are subject to strong delamination and deformation (Fig. 2). For the same reason, it is necessary to note the composition No. 2.

When applied to a ceramic sample of an engobe slurry capable of deposition, internal stresses in the structure may occur due to a violation of uniformity, which will contribute to the peeling of the coating even during the drying process.

Other types of engobe in terms of complex rheological properties turned out to be satisfactory while engobe No. 4 was noted as the most technologically advanced in terms of humidity (43.3 %), fluidity (17 s), suspension capacity, and homogeneity. The slurry spreads well over the surface of the brick, does not form gaps or craters, there is no cracking of the coating during drying of samples.

Analysis of the main indicators of properties, in particular the shrinkage of engobe during drying and firing, showed its significant difference depending on the content of lean components and the firing temperature. Shrinkage during drying varies from 11.6 to 1.6 %, and during firing from 8.5 % for engobe No. 1 at 1150 °C to 2.2 % for engobe No. 5 at 950 °C. Such a wide interval of change in coating shrinkage indicators opens up prospects for the possibility of selecting engobe for ceramic masses with almost any indicator of shrinkage. The intensity of shrinkage correlates well with the content of the clay component in the charge of engobe.

Fig. 3, *a* demonstrate that engobe masses containing 60–80 % clay have rather high air shrinkage rates: from 12.4 to 8.3 %. This may provoke the formation of internal stresses

during drying of the semi-finished product. With a decrease in the content of the clay component to 20 %, the air shrinkage of engobe decreases to 2.1 %.

From the given data in Fig. 6, it shows that water absorption of less than 1 % can be achieved at a temperature of 1050 °C for engobes No. 2, 4. When the temperature rises to 1150 °C, the number of engobe types that are sintered to almost zero water absorption expands to No. 1, 2, 4, 7, 8, 10. The density of coatings increases with increasing content – cullet from 10 to 40 wt%.

Engobe No. 4 is stable when sintered over a wide temperature range. After firing at 1050–1150 °C, the water absorption of samples is 0.50.6 % and remains virtually unchanged, so this engobe can potentially be used in the production of a wide range of ceramic bricks. For clinker bricks, the firing temperature of which approaches 1100 °C or more, engobe No. 6–8 can also be used.

However, it is necessary to pay attention to the indicators of the temperature coefficient of linear expansion of coatings (Fig. 5), which should be as close as possible to a similar indicator of the ceramic base [28]. In this sense, engobe No. 8 has a slightly overestimated coefficient compared to typical ceramic construction products, but No. 4, 6, and 7 remain satisfactory for this indicator in combination with the previously given properties.

Within the range of temperature coefficients of linear expansion of typical ceramic bricks $((50-70) \cdot 10^{-6} \text{ }^\circ\text{C}^{-1})$ or painted fine-stone masses [28], all engobe except No. 1, 2, 8, 10, 11 are found. Consequently, for most experimental compositions of engobe, it is possible to predict their maximum coordination in terms of expansion with the brick base on which the coatings will be applied.

Hardness determines the ability of ceramics to resist the indentation of other bodies, which is especially important, for example, during transportation and during bricklaying. The simplest and most affordable method for assessing the hardness of materials is the Mohs scale [29]. For ceramic bricks, this indicator is usually 56, for porcelain stoneware up to 8. For ceramic bricks, this indicator is not regulated by the requirements of the standard but quite fully makes it possible to characterize the degree of sintering and adhesion of the engobe to the ceramic base.

Data in Table 5 demonstrate that engobe hardness greater than 7 on the Mohs scale is acquired at different temperatures, starting from 1000 °C. After firing at 950 °C, none of the samples has such hardness, while engobe No. 9–11 reach more than 7 only at 1150 °C. There are also samples in which, due to delamination, surfaces with varying degrees of hardness were obtained, therefore, in Table 5 there are symbols «+–». Such engobe types are undesirable to use for bricks under these temperature conditions of firing.

Visual analysis of engobe ceramic samples showed (Table 6) that no sample had cracks on the surface, which probably turned out to be associated with a thin layer of the coating itself (up to 100 microns). But this thickness is not enough for high-quality coating of the ceramic shard – translucent areas appear, exposure of the smallest protrusions on the surface of the product is manifested, which reduces the visual perception of the engobe product as a whole. With an increase in the thickness of the engobe layer to 120–130 microns, most of these defects disappeared but cracks appeared on all engobe surfaces that differed from the ceramic mass in terms of shrinkage by more than 10 % (Fig. 6).

It is also necessary to note low whiteness – almost all engobe coatings are gray or beige and have a yellow tint, especially No. 2, 3, 6, and 11. This effect is exerted by an increased cullet content in the composition of engobe with a low content of quartz sand. An excess amount of the vitreous phase leads to the fact that even minimal impurities of iron oxides in raw materials cause undesirable coloring. For these compositions, «spots» in the form of vitrified areas are noticeable, which is caused by the ability of these slurries to precipitate. This is unacceptable for ceramic facing bricks.

The phase composition of engobe is represented by β -quartz SiO_2 with well-fixed diffraction maxima characteristic of quartz $d=4.25; 3.32; 2.45; 2.12; 1.98; 1.81; 1.66; 1.37 \text{ \AA}$, and devitrite $\text{Na}_2\text{Ca}_3\text{Si}_6\text{O}_{16}$ with diffraction maxima $d=5.23; 4.18; 3.79; 3.66; 3.45; 2.95; 2.11 \text{ \AA}$. At the same time, the phase composition practically does not change in the experimental temperature range – the intensity of the main diffraction maximum, characteristic of quartz ($d=3.32 \text{ \AA}$), only slightly decreases from 840 imp./s at 1000 °C to 660 imp./s at 1150 °C. This indicates a very slow dissolution of quartz in glass melt, the amount of which increases with increasing temperature.

The intensity of devitrite crystallization is very low – diffraction maxima practically do not exceed the intensity of 200 imp./s, which indicates its small content in experimental engobe.

If we compare radiographs of other engobe types (Fig. 8), we can find that they have similarities in qualitative phase composition – just as in engobe No. 4 the β -quartz and devitrite are identified, but the intensity of peaks is different. For example, almost only β -quartz is present in engobe No. 1, the devitrite phase is almost not formed due to the low amount of its source – cullet. The expected mullite crystalline phase, which is usually formed during the thermal transformation of kaolinite at 950–990 °C [30], is not registered since mullite in the temperature range of 1000–1200 °C recrystallizes and can be in its embryo state.

Engobe No. 8 contains a high amount of cullet, so the content of the crystalline phase in it is less and decreases with increasing temperature: the quartz crystalline phase dissolves in the glass melt, and the devitrite barely noticeably increases. This trend has a positive effect on the compaction of the engobe material, but reduces hardness, which is undesirable for decorative and protective coatings.

In Fig. 9, *a*, a dense, well-sintered layer of engobe No. 4, 122 μm thick, on the surface of a porous coarse-ceramic shard is clearly traced. The engobe layer is sufficiently vitrified, practically does not contain gas inclusions, which indicates intensive sintering of the coating during the period when the degassing of the shard has already been completed. The outlines of crystals with an average size of 515 microns in large quantities are recorded, which, according to the results of X-ray phase analysis, can be identified as β -quartz. Probably, the presence of a sufficiently high amount of quartz, firmly «cemented» by the vitreous phase, causes the high hardness of engobe No. 4 (after firing at 1000 °C, there is no trace of a steel knife when scratching the surface).

Fig. 10 shows for comparison the microstructure of engobe No. 3 on the surface of the ceramic shard after firing at 1100 °C. This engobe belongs to lean engobe, with a reduced content of cullet and clay, therefore, even at 1150 °C, it does not sinter to a dense state (Fig. 4).

Therefore, on the chip of the sample (Fig. 10, *a*), the boundary between the ceramic shard and the engobe coating

is practically not traced, and the engobe surface contains numerous micropores (water absorption of this engobe at 1100 °C is 7.5 %). On the one hand, such an engobe agrees well on shrinkage processes and thermal expansion with a ceramic base, which minimizes the likelihood of defects. And on the other hand, such a layer will not fully serve as a protective coating for the exterior cladding of the building, reducing the durability of products.

Thus, according to the complex of properties, engobe No. 4 turned out to be the most universal. It has the following rheological and technological indicators: fluidity, 17 s; humidity, 43 %; and density, 1.53 g/cm³. According to these parameters, the slurry spreads well over the surface of ceramic samples, does not crack during drying, and adheres well to the ceramic base. The thickness of the engobe coating layer should be 100–130 microns while the shard does not shine through, and small roughness is covered.

The engobe coating after firing in the range of 1050–1150 °C has water absorption of 0.6–0.5 %, temperature coefficient of linear expansion $66 \cdot 10^{-7} \text{ 1/}^\circ\text{C}$, Mohs hardness over 7, and can be used to decorate and protect the surface of a wide range of bricks. One of the main requirements when matching the engobe coating and ceramic base is the difference in shrinkage rates of both materials is not more than 10 %.

So, the advantage of the current study is that the physicochemical processes of engobe layer formation on the surface of the ceramic shard are comprehensively considered, the relationship between the composition of coatings, their structure, and operational properties is established. Unlike most works on engobe construction products [6–9, 11, 17, 18], where coatings for thin ceramics are developed, this paper reveals the algorithm for developing engobe coatings for building ceramics, which has a rough structure, which greatly complicates the coordination of coating and ceramics. In contrast to the few works on engobing bricks [19, 20], which offer engobe compositions with limited use, our paper formulates a systematic approach to the development of engobe. That has made it possible to establish the dependences «property – structure – composition», to reveal the possibilities of their regulation and adaptation of engobe coatings to brick production.

The solutions obtained in the process of research close the problematic part of the lack of a systematic approach to the development of engobe for ceramic bricks. The paper not only identifies the basic properties of the covering engobe layer, their dependence on the composition of the charge and technological factors, but also reveals the mechanisms of their regulation. The physicochemical processes of phase formation and formation of the structure of coatings are also illuminated, the issue of adhesion of engobe to the ceramic base and coordination of their shrinkage processes are disclosed.

When applying the above results in practice, as well as in further theoretical studies, it must be borne in mind that the only composition of engobe, which could be used for bricks of various types, is incredibly difficult to obtain. Even for one type of facing brick, ceramic masses with a wide range of shrinkage indicators, different features of sintering and structure formation are used in different industries. Therefore, the developed composition of engobe coating No. 4 with an acceptable set of properties may need to be modified in a particular production. But the highlighted physicochemical processes that occur in the experimental system can reduce the labor intensity of such research.

The limitations of the application of the developed composition of engobe No. 4 are the requirements for the ceramic mass – its air shrinkage should be $7.4 \pm 10 \%$, the sintering temperature should be 1050–1150 °C, and the thermal expansion index of the shard is $66 \cdot 10^{-7} \pm 10 \%$ 1/°C. Under other conditions, additional studies of the consistency of mass and coating are required.

The disadvantages of this work are that on the basis of this system it was not possible to obtain dense coatings on the surface of building bricks, which are burned at temperatures below 1000 °C due to insufficient sintering of any of the considered engobe. Probably, this requires more effective sintering components, or special mineralizing additives.

Further research may involve the adaptation of engobe to specific ceramic masses, the study of the possibility of replacing the components of the engobe in order to increase the whiteness of the surface, intensify sintering. The study of the role of coloring components in the formation of the engobe structure, including the use of production waste, is relevant. A possible area of research may also be the study of the effect of burning additives in the composition of ceramic masses on the formation of a solid engobe coating.

7. Conclusions

1. The choice of raw materials for the design of engobe has been substantiated. As basic, the system “refractory clay – quartz sand – cullet” was proposed, which includes raw materials available for the large-tonnage industry.

2. The rheological properties of engobe slurries were investigated and their dependence on the composition and technological parameters of production was established. The main requirements for engobe slurries established sufficient spreading over the surface of ceramic material and the absence of a tendency to deposition and deformation during subsequent drying and firing. Such requirements were satisfied by engobe with the following content of components, wt%: 50–65 refractory clay, 10–40 quartz sand, and 10–25 cullet. Indicators of the properties of these engobe are: fluidity, 15.117 s; humidity, 43–45 %; and density $1.52\text{--}1.54 \text{ g/cm}^3$. Engobe types with a higher content of clay components have difficulty with liquefaction and subsequently show increased shrinkage. If engobe types have a higher content of lean components, they are prone to delamination and deposition.

3. The basic properties of engobe samples were investigated and their dependence on the composition and technological parameters of production was established. Air shrinkage varies from 11.6 to 1.6 %, and fire shrinkage from 8.5 % to 2.2 %, depending on the content of the clay component in the coating and the firing temperature. Also, these parameters depend on the indicators of the temperature coefficient of linear expansion, which varied within $(51\text{--}89) \cdot 10^{-7} \text{ 1/}^\circ\text{C}$. Regarding the hardness index of coatings on the Mohs scale, values of more than 7 units were achieved at different firing temperatures also depending on the composition of the initial charge.

4. The processes of formation of engobe coatings on the surface of ceramic bricks have been investigated and the basic conditions for coordination of engobe with a ceramic base were determined. The main indicators by which the coordination of these two materials should be monitored are air and fire shrinkage and the temperature coefficient of linear expansion. The engobe coating should be applied to the ceramic base with a layer thickness of 100–130 microns,

but the indicators of shrinkage and thermal expansion of materials should not differ by more than 10 %. With a smaller thickness, the likelihood of defects such as peeling and cracking of coatings is reduced, but the decorative effect of the coating is reduced, as exposures and roughness of the surface appear.

5. The peculiarities of formation of phase composition and structure of engobe were investigated, the basic composition of the coating was established and the basic requirements to its properties were formulated. As an engobe, which provided samples with a complex of high physical and mechanical characteristics, composition No. 4 was chosen. The dense structure of the coating is formed at 1050 °C and lasts up to 1150 °C, which for the most part is a sufficient interval for firing front and clinker bricks. At the same time, water absorption of the layer is 0.50.6 %, temperature coefficient of linear expansion $66 \cdot 10^{-7} \text{ 1/}^\circ\text{C}$, hardness is more than 7 on the Mohs scale after firing at 1000 °C and above, whiteness is 68 %. The phase composition of engobe is represented mainly by β -quartz SiO_2

and a small amount of devitrite – the cullet crystallization product.

Conflicts of interest

The authors declare that they have no conflicts of interest in relation to the current study, including financial, personal, authorship, or any other, that could affect the study and the results reported in this paper.

Funding

The study was conducted without financial support.

Data availability

All data are available in the main text of the manuscript.

References

- Muneron, L.M., Hammad, A.W., Najjar, M.K. et. al. (2021) Comparison of the environmental performance of ceramic brick and concrete blocks in the vertical seals' subsystem in residential buildings using life cycle assessment. *Cleaner Engineering and Technology*, 5, 100243. doi: <https://doi.org/10.1016/j.clet.2021.100243>
- Khomenko, O.S., Datsenko, B.M., Fomenko, G.V. (2022) Determination of approaches to the development of ceramic compositions for the manufacture of facial bricks. *Voprosy khimii i khimicheskoi tekhnologii*, 6, 98-107. doi: <http://dx.doi.org/10.32434/0321-4095-2022-145-6-98-107>
- Pavlova, I. Sapozhnikova, M., Farafontova, E. (2020) The effect of manganese-containing pigment on the strength of ceramic bricks. *Materials Science Forum*, 989 MSF, 329 – 334 doi: <http://dx.doi.org/10.4028/www.scientific.net/MSF.989.329>
- Khomenko, O., Datsenko, B., Sribniak, N. et. al. (2019) Development of engobe coatings based on alkaline kaolins. *Eastern-European Journal of Enterprise Technologies. Technology organic and inorganic substances*, 6, 6 (102), 49-56. doi: <https://doi.org/10.15587/1729-4061.2019.188126>
- Mangone, A., Caggiani, M. C., Giannossa, L. C. et. al. (2013) Diversified production of red figured pottery in Apulia (Southern Italy) in the late period. *Journal of Cultural Heritage*, 14, 1, 82-88. doi: <https://doi.org/10.1016/j.culher.2012.03.011>
- Dal Bó, M., Bernardin, A. M., Hotza, D. (2014) Formulation of ceramic engobes with recycled glass using mixture design. *Journal of Cleaner Production*, 69, 243-249. doi: <https://doi.org/10.1016/j.jclepro.2014.01.088>
- Nieves, L.J. J., Natri, S., Lot, A.V. et. al. (2022) Influence of engobe and glaze layers on the evolution of porosity and permeability of single-fired porcelain tiles. *Applied Clay Science*, 228, 106635. doi: <https://doi.org/10.1016/j.clay.2022.106635>
- Kavanova, M. (2017) Characterization of the interaction between glazes and ceramic bodies. *Ceramics Silikaty*, 61(3), 1-10. doi: <https://doi.org/10.13168/cs.2017.0025>
- Nandi, V.S., Raupp-Pereira, F., Montedo, O.R.K., Oliveira, A.P.N. (2015) The use of ceramic sludge and recycled glass to obtain engobes for manufacturing ceramic tiles. *Journal of Cleaner Production*, 86, 461-470 doi: <https://doi.org/10.1016/j.jclepro.2014.08.091>
- Muge, T., Baran, T. (2020) Development of waterproof engobe layer for ceramic wall tiles. *Journal of Thermal Analysis and Calorimetry*, 140, 2, 555 – 565. doi: <https://doi.org/10.1007/s10973-019-08893-3>
- Samoilenko, N., Shchukina, L. (2019) Development of engobe composition with the use of pharmaceutical glass waste for glazed ceramic granite. *Eastern-European Journal of Enterprise Technologies*, 4, 10 (100). 6-12. doi: <https://doi.org/10.15587/1729-4061.2019.175922>
- Koleda, V.V., Mikhailyuta, E.S., Alekseev, E.V., Tsybul'ko, É.S. (2009) Technological particularities of clinker brick production. *Glass and Ceramics*, 66 (3–4), 132–135. doi: <https://doi.org/10.1007/s10717-009-9129-3>
- Subashi De Silva, G.H.M.J., Hansamali, E. (2019) Eco-friendly fired clay bricks incorporated with porcelain ceramic sludge. *Construction and Building Materials*, 228, 116754. doi: <https://doi.org/10.1016/j.conbuildmat.2019.116754>
- Benahsina, A., Haloui, Y. E., Taha, Y. et. al. (2022) Substitution of natural clay by Moroccan solid mining wastes to manufacture fired bricks. *Materials Today: Proceedings*, 58, 4, 1324-1330. doi: <https://doi.org/10.1016/j.matpr.2022.02.211>
- Luangnaem, C., Sathonsaowaphak, A., Kamon-In, O., Pimraksa, K. (2014) Development of engobe samples for Dan Kwian ceramic body. *Key Engineering Materials*, 608, 325 – 330. doi: <https://doi.org/10.4028/www.scientific.net/KEM.608.325>
- Johnson, L. A., McCauley, R. A. (2005) The thermal behavior of albite as observed by DTA. *Thermochimica Acta*. 437, 1–2, 134-139. doi: <https://doi.org/10.1016/j.tca.2005.06.039>

17. Governatori, M., Cedillo-González, E.I., Manfredini T., Siligardi, C. (2022) Solar reflective properties of porcelain tiles for UHI mitigation: effect of highly reflective frits in the engobe's formulation. *Materials Today Sustainability*, 20, 100255. doi: <https://doi.org/10.1016/j.mtsust.2022.100255>
18. Ferrari, C., Muscio, A., Siligardi, C. (2016) Development of a Solar-reflective Ceramic Tile Ready for Industrialization. *Procedia Engineering*, 169, 400-407. doi: <https://doi.org/10.1016/j.proeng.2016.10.049>
19. Zorigt, S., Jadamba, Ts., Tsevel, S. (2012) Synthesis and structural studies of face engobe layer's mass. *Proceedings 7th International Forum on Strategic Technology, IFOST*, 6357603. doi: <https://doi.org/10.1109/IFOST.2012.6357603>
20. Yatsenko, N. D., Rat'kova, É. O. (2009) Engobes for ceramic brick. *Glass Ceram.* 66, 93–94. doi: <https://doi.org/10.1007/s10717-009-9144-4>
21. Janus, M., Zając, K. (2019) Self-cleaning efficiency of nanoparticles applied on facade bricks *Nanotechnology in Eco-efficient Construction (Second Edition)*. *Materials, Processes and Applications Woodhead Publishing Series in Civil and Structural Engineering*, 591-618. doi: <https://doi.org/10.1016/B978-0-08-102641-0.00024-4>
22. Becker, E., Jiusti, J., Minatto, F. D. et. al. (2017) Use of mechanically-activated kaolin to replace ball clay in engobe for a ceramic tile. *Cerâmica*, 63 (367). doi: <https://doi.org/10.1590/0366-69132017633672077>
23. Bernasconi, A., Diella, V., Pagani, A. et. al. (2011) The role of firing temperature, firing time and quartz grain size on phase-formation, thermal dilatation and water absorption in sanitary-ware vitreous bodies. *Journal of the European Ceramic Society*, 31, 1353–1360. doi: <https://doi.org/10.1016/j.jeurceramsoc.2011.02.006>
24. Gültekin, E. E., Topateş, G., Kurama, S. (2017) The effects of sintering temperature on phase and pore evolution in porcelain tiles. *Ceramics International*, 43, 14, 11511-11515. doi: <https://doi.org/10.1016/j.ceramint.2017.06.024>
25. Shaikh, S.M.R., Nasser, M. S., Hussein I. et. al. (2017) Influence of polyelectrolytes and other polymer complexes on the flocculation and rheological behaviors of clay minerals: A comprehensive review. *Separation and Purification Technology*, 187, 137-161 doi: <https://doi.org/10.1016/j.seppur.2017.06.050>
26. Khomenko, O.S. (2018) Choice of ceramic masses for the manufacture of electrical ceramics. *Voprosy Khimii i Khimicheskoi Tekhnologii*, 1, 92-95.
27. Kavanová, M., Kloužková, A., Kloužek, J. (2017) Characterization of the interaction between glazes and ceramic bodies. *Ceramics-Silikáty*, 1 (3), 267-275. doi: <https://doi.org/10.13168/cs.2017.0025>
28. Venturelli, C., Paganelli, M. (2006) Thermo-mechanical behaviour of technical ceramic bricks, felt boards and fibres. *CFI Ceramic Forum International*, 83, 4, E18-E22.
29. Goncalves, R. A., Dal-Pont, G., Werneke, A. S. W. et. al. (2000) Determination of mohs hardness of glazed tiles by scratching tests. *Ceramic Technology Center*, 67-71.
30. Li, J., Lin, H., Li, J., Wu, J. (2009) Effects of different potassium salts on the formation of mullite as the only crystal phase in kaolinite. *Journal of the European Ceramic Society*, 29, 14, 2929-2936. doi: <https://doi.org/10.1016/j.jeurceramsoc.2009.04.032>
31. Kazmina, O., Tokareva, A.Y., Vereshchagin, V.I. (2016) Using quartzofeldspathic waste to obtain foamed glass material. *Resource-Efficient Technologies*, 2(1), 23-29. doi: <https://doi.org/10.1016/j.refffit.2016.05.001>