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A STUDY OF MECHANISM OF GLAZE FORMATION IN THE PROCESS OF BURNING GLAZED BRICK ON THE BASIS OF BEIDELLITE CLAY AND MINERAL COTTON WASTE PRODUCTS

Problem statement. It is essential to establish the values of temperature coefficient of linear expansion of glaze and ceramic material containing beidellite clay and waste products of mineral cotton, and to examine the mechanism of glaze formation in the course of burning by means of infrared spectroscopy and electronic microscopy.
Results. The formation of glaze of type ЩЛСО involves glass phase separation which precedes crystallization process.
Conclusions. The study of thermoprocessed monoliths shows that liquation structure considerably decreases at temperatures of 700 °C and 950 °C. Temperature interval of liquation is a function of glaze thermal treatment conditions. It is shown that crazing resistance of glazed products is determined by correlation of average temperature coefficients of linear expansion of mass and glaze, therefore, to obtain heat-resistant glazed ceramic brick with temperature coefficient of linear expansion $6.53 \cdot 10^{-4}$ °C, it is necessary to use glaze of type ЩЛСО with temperature coefficient of linear expansion $6.45 \cdot 10^{-4}$ °C.

Keywords: glazed brick, beidellite clay, heat resistance, wettability, crock, kaolin, glaze frit, IR spectrum, liquation.

Introduction

Application of ceramic glazed brick for facing of facades gives a building a more aesthetic look, extends its durability and makes it possible to cut down its operating costs. Given constant repairs involved, the cost of a surface with a ceramic facing is 2—3 times as small as compared with other types of building facings [4].

The authors of [1—3] had studied a principal chance of using beidellite clay and wastes of mineral cotton production in the manufacture of ceramic brick. Although there appears to have been no study made of the production of glazed brick based on the above components.

Thermal resistance of glazed ceramic materials is largely dependent on a right choice of ceramic shards and glazing. In actual practice, a glazing content is fitted to one of ceramic materials, not the reverse, i. e. changes have to be made to a glazing content if they do not fit [5, 6]. The same glazing cannot be used in all types of ceramic materials. While making a decision as to whether glazing for composite ceramic materials is good enough or not, it is necessary to consider their firing temperature, the color of plates following the firing and agreement between the coefficients of thermal expansion of ceramics and glazing. If a coefficient of thermal expansion of glazing is smaller than one of a ceramic material, glazing comes off [5—7]. If a coefficient of thermal expansion of glaze is higher, it cracks (glaze crazing), for which reason choosing the right glazing content is crucially important.

The thermal coefficient of linear expansion is of considerable importance in the selection of glazing, even though some researchers believe that this coefficient plays a mere orientational role, while glazing elasticity is paramount [5, 6]. It is proven by researchers [5, 6] that elasticity of glazing does not result in crazing even at considerable differences of thermal coefficients of linear expansion of ceramic material and glazing.

Many components of low-melting glazings used mainly in facing tile are soluble in water, hence the mixture of these materials is first alloyed (fritted) and the melt is poured into water afterwards and is then ground adding a clay material and water.

1. Theoretical idea of the interaction between shards and glazing

One of the main problems of chemistry and ceramic material technology is a question about the interaction and bonding strength between shards and glazing. Adhesion of phases in heterogeneous systems is estimated by the ratio of their surface energy, surface tension between the adhesion phases [5]. Adhesion is attained both by the Van der Waals forces between the phases and by emerging intermediate junctions. Damping between the components is routinely used in the evaluation of a possible interaction between the phases. Some authors believe that there is invariably some chemical interaction in a fine surface layer in the interface of the phases if a ceramic shard is properly wetted with glazing mass [5]. There is also an assumption that poor wetting with glazing mass is accounted for by a negative electric charge on the surface of ceramics.

According to [9], the thermal coefficient of linear expansion is of great importance when choosing glazing, whereas according to [5], it has a merely orientational value, with elasticity of glazing playing a much greater role. The aim of the present article is using a dilatometer, to estimate thermal coefficient of linear expansion for ceramic materials and glazing and by means of infrared spectroscopy and electron microscopy to study the mechanism of glazing formation in the burning process. This technique helps to find out the areas of glazing elimination and therefore to minimize it.

Some scientists assume that similarity of structures and types of intracrystalline bonds of both phases is an aid to a better wetting, which is why those components that are used in ceramic shards are added to glazing to achieve it.

It is known that kaolin (Table) is added to almost all light glazing, thus it is necessary that kaolin is added into brick for a better adhesion between brick and glazing and a better wetting as well.

Table

Contents of frits and their thermal coefficient of linear expansion

Component	Content of glazing, mass %			
	ЛГ-77	24/75	ЩЛСО	Н-23
Silica sand	23.3	13	47.4	48.4
Kaolin	4.5	13	8.7	5.3
Boric acid	30.8	39	16.7	23.5
Sodium carbonate	6.7	2.5	5.8	6.3
Zinc oxide	1.4	-	2.7	-
Zircon	11.2	12	8.2	5.0
Calcium borate	16.2	-	-	-
Cryolite	2.6	5	-	-

End of Table

Component	Content of glazing, mass %			
	ЛГ-77	24/75	ЩЛСО	Н-23
Carbonic barium	3.3	-	3.8	-
Cobalt sulphate (over 100 %)	0.03	0.02	-	-
Chalk	-	9.5	6.1	1.1
Strontium carbonate	-	6	-	-
Carbonic magnesia	-	-	1.1	2.9
Fluorosilicate natrium	-	-	-	2.9
Potassium nitrate	-	-	-	1.8
Thermal coefficient of linear expansion, 10^{-4} °C	6.37	6.4	6.45	6.28

2. Production of glazed brick

Two contents have been examined to produce glazed ceramic brick, mass %:

1) beidellite clay— 57, Chapaev kaolin — 8 (approximate average of kaolin content in glazings), “regulus” — 35;
2) beidellite clay — 57, Chapaev kaolin — 8, product of purification of cupola waste smoke gases from cupola when obtaining a melt in the production of mineral cotton (VPR of mineral cotton) — 35.

Chapaev kaolin was quite sufficiently studied in [4]. Averaged chemical content of Chapaev kaolin is made up of the following oxides, mass %:

– SiO_2 — 69.8;
– Al_2O_3 — 16.38;
– Fe_2O_3 — 3.10;
– CaO — 3.02;
– MgO — 1.42;
– R_2O — 0.20;
– losses in the course of ignition — 5.08.

According to the overall content of $Al_2O_3 + TiO_2$, it belongs to semiacid clays with a high content of coloring (Fe_2O_3 of over 3 %). According to the content of particles of below $1 \cdot 10^{-3}$ m in size (30…35 %), the material under examination is defined to be coarsely dispersed, moderately plastic according to its plasticity (plasticity number — 10…15), low sensitive according to its sensitivity to drying, high-melting according to its refractoriness (refractoriness — 1520…1550 ^oC), moderately caking with the caking interval of 100…120 ^oC.

The mineral content of Chapaev kaolit is represented by the following minerals, mass. %:

- kaolin — 45…50,
- felspar — 20…30,
- quartz — 10…20,
- calcite — 2…4,
- ferric oxide — 1…3,
- organic impurities (humic substances) — 1.8…2.

3. Estimating the thermal coefficient of linear expansion of ceramic brick and glazing

The thermal coefficient of linear expansion of ceramic brick and glazing was evaluated using the dilatometer method. The research was carried out on fillets sized 5×5×50 mm cut out from ceramics and glazing by recording made during the heating of the samples with the temperature range of 200…700 ^oC using the dilatometer ДКВ-5А fitted with a recorder. The heating rate was 3 ^oC/min. The thermal coefficient of linear expansion was evaluated based on the data of the dilatometer research.

The samples used in the dilatometer research were prepared by the fusion of glazing in porcelain "boats". In this case, the mode of burning of the samples is to fit the mode of burning of the items. It is of particular importance to sustain the same rate of cooling. This requirement is obligatory and only provided it is met, can one be sure that the structure of a synthesized sample (fillet) turns out to be identical or sufficiently close to the structure that the cooled down glazing on the surface has. In case the temperature drops sharply, there is a chance of hardening that heavily impacts the dilatometric curve of the glazing. It lies above the curve of the slowly cooled down sample and has a typical area before the point of glass-transition temperature [8].

4. Studying the microstructure of ceramic materials

The microstructure of ceramic materials was studied with an electronic microscope РЭМ-200 and Japanese electronic microscope JEM-7A. Their resolution is $2 \cdot 10^{-8}$ m in the continuous zoom range from 18000 to 40000 and from 1000 to 25000 times, accelerating voltage is 30 and

80 kWatt respectively. The evaporation of silver with purity of 99.9 % on the surface of the samples of about $1 \cdot 10^{-8}$ m thick was performed in VUP-4 (vacuum universal post) to obtain a conductive layer that is crucial to the operation of РЭМ. The conditions for evaporation on the surface of the sample for the operation of JEM-7A are a carbon film and palladinized grid.

The infrared absorption spectrums of the samples were examined with a spectrophotometer *Specord*-75IR. The samples were prepared in the form of a powder slurry with petrolatum oil. The decoding of the obtained infrared spectrums is carried out by comparing them with those of the known substances according to typical absorption bands whose frequency of maximums in three-dimensional (laminated, circular) and one-dimensional chain-like groups is 1000…1100 cm^{-1} and 900…1000 cm^{-1} in isolated groups $[SiO_4]^{4-}$ [7].

A number of lines or bands in a spectrum, their frequency and intensity give information about the presence or these or those symmetry elements in a substance being examined. Hence the frequency of absorption maximum is 1010…1260 cm^{-1} for cristobalite, 980…1200 cm^{-1} for quartz and 1027…1195 cm^{-1} for quartz glass [7]. The bond ≡Si−O−Si≡ (at different angles) is typical of these grids. The major clay mineral in Chapaev kaolin is kaolin, while product of purification of waste smoke gases of mineral cotton ВПР showed to have an elevated content of calcium oxide of 31.2 and 23.6 % in content respectively [1—3] that is a major oxide of chalk. The content of kaolin and chalk in 24/75 glazings and ЩЛСО is 13 and 9.5 %; 8.7 and 6.1 % respectively (see Table).

Individual cases of low thermal resistance [5] with similar values of thermal coefficient of linear expansion may be caused by a number of reasons. For instance, glazing “did not ripen”, i. e. it still contains some non-dissolved quartz. Crazing resistance of glazed items is mostly determined by the ratio of average thermal coefficient of linear expansion of the mass and glaze at the temperature ranging from the room one resulting in softening of the glaze, i. e. till there are no stresses in it. Depending on this ratio, residual stretching and compression stresses may occur in the glaze. Since the ultimate strength during the compression of glazes (glasses) is way higher than during stretching, it is necessary to use the masses with a higher thermal coefficient of linear expansion than that one of a coating glaze [5, 6].

The research showed that in order to obtain a thermal resistant glazed ceramic brick of Content 1 with thermal coefficient of linear expansion $6.53 \cdot 10^{-4}$ °C, the glaze of the ЩЛСО brand with the thermal coefficient of linear expansion $6.45 \cdot 10^{-4}$ °C should be used (see Table). The thermal resistance of glazed ceramic brick coated with the ЩЛСО glaze was 155 °C, 110, 130 and 100 ° C respectively for one coated with the ЛГ-77, 24/75 and Н-23 glazes.

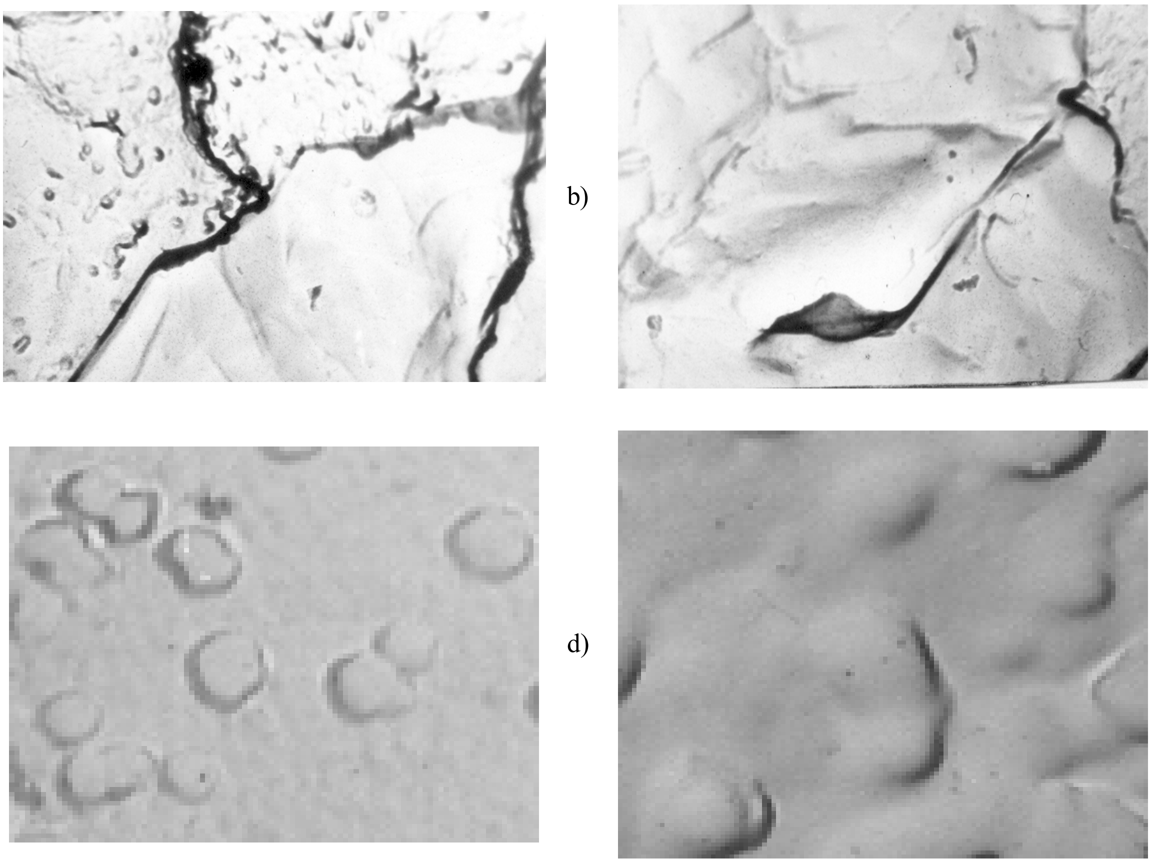
For ceramic brick of Content 2 with the thermal coefficient of linear expansion $6.41 \cdot 10^{-4}$ °C, it is essential to use the 24/75 glaze with the thermal coefficient of linear expansion $6.4 \cdot 10^{-4}$ °C and a higher chalk content (see Table). The thermal resistance of glazed ceramic brick coated with the glaze 24/75 was 140 °C, 90, 120 and 100 °C for one coated with the ЛГ-77, ЩЛСО and Н-23 glazes respectively. Therefore, in order to obtain a thermal resistant ceramic glazed brick (with the thermal resistance of 150 °C), it is necessary to use Content 1 and the ЩЛСО glaze.

The mechanism of glaze formation is seen as a sequence of processes resulting in crystal and other formations that are responsible for light scattering power of a material. The research of glaze ЩЛСО monoliths was carried out by the infrared spectroscopy and electronic and microscopic methods.

In order to obtain the monoliths, the ЩЛСО fritt was fused in crucibles at 1250 °C and afterwards swiftly poured onto a metal plate. Only such monoliths that exhibited no signs of opalescence were made use of and heat treated at a temperature range of 400…950 °C for 15 h.

The electronic and microscopic research showed that a sample of Content 1 fused at 400 °C did not noticeably split into to drops and matrix (Fig. 1a), at 600 °C it is observed to split into a drop phase and matrix (Fig. 1b). The research showed that the glass stays transparent as a result of the monoliths being heat treated at 600 °C and then get a milky white color, whilst staying X-ray amorphous.

The electronic and microscopic research of the glaze coatings presents problems related to obtaining sample replics fused at the area of the elimination temperature while the glaze is still poorly melted and has a lot of incompletely dissolved clay particles (kaolin) introduced during the milling. The electronic and microscopic research of such milky white samples using the replic method with a preliminary pickling of the surface of a fresh cleavage with 3 % HF showed that the glaze glass had undergone some changes. The drops are complex and mostly round shaped and to 3 mkm in size from the fractions that are largely dependent on the heat treatment temperature.



a) b) c) d)

Fig. 1. Microstructure of the ЩЛСО glaze, burning temperature, °C:
a) 400, magnification ×5000; b) 600, magnification ×4000;
c) 700, magnification ×5500; d) 950, magnification ×6000

Many scientists (see, e. g. [5—9]) believe that it is very rarely the case in glaze coatings that the drops have a ball shape and are significantly away from one another (Fig. 1b). It is more often that the electronic and microscopic research of glazes of wide content 'ranges' indicated an elimination structure with fairly small-sized drops (0.03…0.05 mkm) and their close location as in the 24/75 glaze at the burning temperature of 600 °C (Fig. 2a).

The electronic and microscopic research of glaze coatings (ЩЛСО glaze, Fig. 1c) showed that an increase in burning temperature up to, as in the 24/75 glaze at 600 °C (Fig. 2a), is accompanied by spreading, i. e. a decrease in the drop concentration and by a loss of their clear contours at 950 °C (Fig. 1d and 2b). Such an elimination structure typical of a number of industrial glazes can be arbitrarily called a residual one [9].

Fig. 3 presents the spectrums of the ЩЛСО glaze at its initial state and after it was heat treated at 400, 500, 600, 700 and 950 °C.

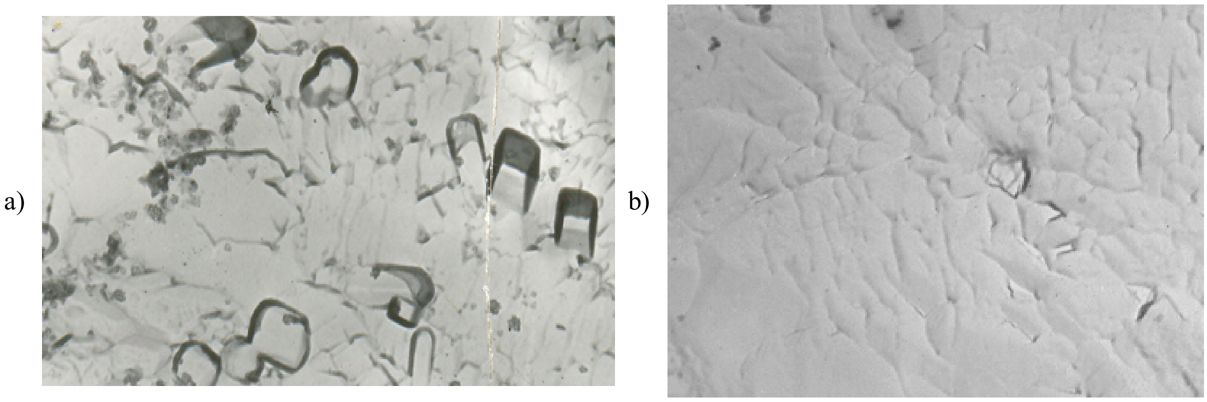


Fig. 2. Microstructure of the 24/75 glaze, burning temperature, °C:
a) 600, magnification ×50000;
b) 950, magnification ×60000

The glaze spectrum before the heat treatment, as noted in [9] as well, has four intensive absorption bands with the following maximums: 470, 710, 1030 and 1370 cm^{-1}. The bands of 1370 and 710 cm^{-1} are typical of combinations involving a three-dimensional boron presented by isolated groupings $[BO_3]^{3-}$ [9].

As Fig. 3 suggests, the glaze under investigation showed no noticeable changes at 400 °C. The spectrums of the glaze that was heat treated at 500 and 600 °C are similar and differ from the initial one due to a cleavage step marked 1250 $см^{-1}$, 1370 cm^{-1} at the right shoulder of the band and a weak maximum peak at 525 cm^{-1}. The above changes culminate at 700 °C when apart from a stronger intensity of the peak of 525 cm^{-1}, a cleavage step also appears at the left shoulder of the band of 1370 cm^{-1}. A split of the band into three components (with peaks of 1250, 1370, 1440 cm^{-1}) is caused by the polymerization of the triangles $[BO_3]^{3-}$ [9], this being the case, only one of the elimination phases can be enriched in boron.

Elimination starts at the edges of the fritt grains before they even start melting and then goes deep down affecting grains entirely or partially depending on their size, content and burning conditions. It is followed by the process of crystal formation after the glaze is almost completely melted (lgη = 3-3.5 pas·sec).

According to the authors of [9], depending on to what extent each of the two above processes is completed in glazing, areas of the following four types: 1 — propagation of crystals (Fig. 1a); 2 — simultaneous presence of crystals and residual elimination drops (Fig. 1b); 3 — homogeneous elimination structure (Fig. 1c); 4 — unchanged glass (Fig. 1d).

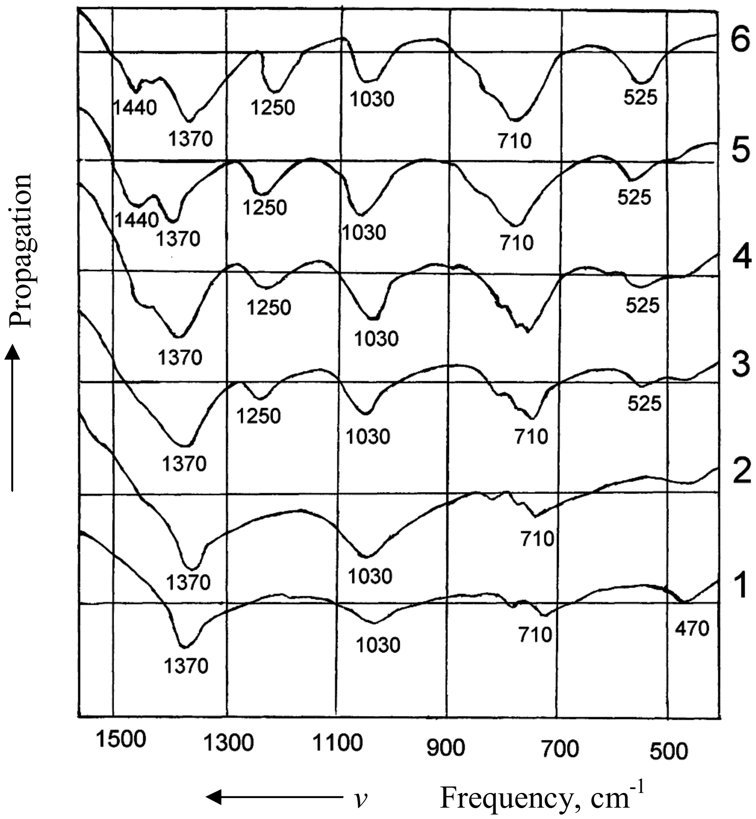


Fig. 3. Infrared spectrums of initial and burnt ЩЛСО glaze:
1 — initial glaze; 2 — glaze burnt at 400 °C;
3 — the same at 500 °C; 4 — the same at 600 °C;
5 — the same at 700 °C; 6 — the same at 950 °C

Conclusions

It has been found that the process of the ЩЛСО glaze formation is accompanied by a phase separation in glass (elimination) that is followed by crystallization.

The research of heat-treated monoliths showed that elimination structure drops sharply at the temperature range of 700 to 950 °C. The temperature interval of elimination is a function of conditions of glaze heat treatment.

The research showed that in order to obtain thermal resistant glazed ceramic brick of Content 1 with the thermal coefficient of linear expansion $6.53 \cdot 10^{-4}$ °C, the ЩЛСО glaze with the thermal coefficient of linear expansion $6.45 \cdot 10^{-4}$ °C should be used.

The thermal resistance of glazed ceramic brick coated with the ЩЛСО glaze was 155 °C and 110, 130 и 100 °C respectively for one coated with the ЛГ-77, 24/75 and Н-23 glazes.

For ceramic brick of Content 2 with the thermal coefficient of linear expansion $6.41 \cdot 10^{-4}$ °C, it is necessary to use the 24/75 glaze with the thermal coefficient of linear expansion $6.4 \cdot 10^{-4}$ °C and a higher chalk content.

Thermal resistance of glazed ceramic brick coated with the 24/75 glaze was 140 °C, 90, 120 and 100 °C respectively for the one coated with the ЛГ-77, ЩЛСО and H-23 glazes.

Hence, in order to obtain thermal resistant ceramic glazed brick (with thermal resistance over 150 °C), Content 1 and the ЩЛСО glaze should be used.

References

1. Ye. V. Vdovina, Ye. S. Abdrakhimova, V. Z. Abdrakhimov, “A Study of Structural Transformations of *Fe* at Various Temperatures of Burning of Beidellite Clay Brick and Combustion Products of Basalt Charge by the Method of Nuclear Gamma Resonance Spectroscopy”, Bashkirskiy Khimicheskiy Zhurnal, vol. 14, N 2 (2007), 96—99.
2. Ye. V. Vdovina, Ye. S. Abdrakhimova, V. Z. Abdrakhimov, “Determination of Blackheart at Beidellite Clay Brick Burning and Combustion Product of Basalt Charge”, Bashkirskiy Khimicheskiy Zhurnal, vol. 14, N 2 (2007), 102—104.
3. Ye. V. Vdovina, Ye. S. Abdrakhimova, “A Study of Heat-Mass-Exchange Processes at Ceramic Materials Burning”, Bashkirskiy Khimicheskiy Zhurnal, vol. 14, N 5 (2007), 110—112.
4. V. Z. Abdrakhimov, Ye. S. Abdrakhimova, *Chemical Technology of Ceramic Brick with the Use of Anthropogenic Raw Material* (Samara, 2007) [in Russian].
5. P. P. Budnikov, et al., *Chemical Technology of Ceramics and Refractories* (Moscow, 1972) [in Russian].
6. A. I. Avgustinik, *Ceramics* (Lenizdat, 1975) [in Russian].
7. G. V. Kukolev, *Chemistry of Silicium and Physical Chemistry of Silicates* (Moscow, 1965) [in Russian].
8. V. F. Pavlov, *Physical Chemical Basis of Building Ceramics Burning Products* (Moscow, 1977) [in Russian].
9. O. S. Grum-Grzhimailo, K. K. Kvyatovskaya, “Mechanism of Baffle Formation in Boric- Zirconium Glazes”, in *Coll. paper of NIIStroikeramiki* (Moscow, 1979), vol. 54, pp. 127—145.