QUID 2017, pp. 746-752, Special Issue N°1- ISSN: 1692-343X, Medellín-Colombia

THE INVESTIGATION OF RAW MATERIALS AND CERAMIC TILES, PRODUCED AT THE FACTORY "LASSELSBERGER" IN UFA

(Recibido el 23-05-2017. Aprobado el 30-08-2017)

Almir M. Salakhov
Kazan Federal University,
Institute of Physics,
salakhov8432@mail.ru

Vladimir P. Morozov
Kazan Federal University,
Institute of Geology and Petroleum Technologies

Alexey A. Eskin
Kazan Federal University,
Institute of Geology and Petroleum Technologies

Regina A. Ariskina
Kazan Federal University, *Institute of Engineering*

Kristina A. Ariskina
Kazan Federal University, *Institute of Chemistry*

Amir I. Gumarov
Kazan Federal University, *Institute of Physics*

Michael V. Pasynkov
Kazan Federal University, *Institute of Physics*

Abstract. The paper presents the results of investigations of the elemental-phase composition and the structure of furnace charge for production of floor and facing tiles at the “Lasselsberger” factory (Ufa). Thermal, electron-microscopical and X-ray investigation of raw materials for the production of ceramic tiles have been performed: clay of the Nizhneuvelsk deposit, kaolin of the Kiembaevsk deposit, kaolin-sand mixture, quartz-feldspar raw material of the Malyshevsk deposit and dolomite of the Balakovo deposit. The processes, occurring in the furnace charge of the facing and floor tiles, with the rise of the burning point were established. On the basis of the obtained data, it was found, that in case of the accelerated factory burning, the same basic structure formation processes occur as in case of the slow burning on the Shimadzu diffractometer: the decomposition of clay minerals, the destruction of carbonates, the synthesis of calcium and mullite silicates, and the formation of glass phase. However, there are some differences in the phase composition and mass content of separate phases. The initial composition of the facing tiles, produced at the factory “Lasselsberger”, was corrected.

Keywords: ceramic tiles, X-ray diffraction analysis, tile relaxation process, destruction of clay minerals, correction of furnace charge.

Citar, estilo APA: Salakhov, A., Morozov, V., Eskin, A., Ariskina, R., Ariskina, K., Gumarov, A. & Pasynkov, M. (2017). The investigation of raw materials and ceramic tiles, produced at the factory "Lasselsberger" in UFA. *Revista QUID (Special Issue)*, 746-752.

1. INTRODUCTION

According to the statistics, given over the last 5 years, the world production of ceramic tiles has significantly increased (AMICO Consulting Company, 2017, Company "Express-Obzor", 2017). One of the world's leading manufacturers of ceramic tiles and a relatively young representative of this industry in the Russian market is the Austrian company "Lasselsberger" (the Republic of Bashkortostan, Ufa). Their total production of floor and facing tiles is 6.5 million square meters. The technology of production and equipment of the factory provide for the use of exclusively local raw materials. In the process of tiles burning high-speed roller furnaces are used, while the procedure itself takes no more than 60 minutes. The facing tiles are burned at a maximum temperature of 1135°C during 7-8 minutes. The burning temperature of the floor tiles is 1200°C, the time of burning is 7-8 minutes. Then there is the phase of rapid tiles cooling, in the temperature range 1200-750°C, which lasts no more than 3 minutes. From the research point of view, both the characteristics of the raw materials, used in the production of ceramic tiles, and the production technology are of great interest (Pietro Mazzacani, Giovanni Biffi, 1997; Augustinik A.I. 1975; Zhukov A.D. et al., 2013; Gorbunov G.I., Zvezdin D.F., 2003; Zakharov A.I. et al., 2013; Bender, 2004; Giovanni Biffi, 2003).

One of the production problems at the factory of the company "Lasselsberger" (the Republic of Bashkortostan, Ufa) is the strong relaxation of the facing tiles after burning. Thermal coefficient of linear expansion (TCLE) of the ceramic glaze is always smaller than the crock TCLE, so the tile in the cooling zone, after the glaze hardens, takes a convex form. However, after the setting, it becomes less convex, up to the point, that the center retains a convex deformation, and the edges become concave. In this case, the process of relaxation has unpredictable duration.

Thus, the aim of this work is to investigate the elemental-phase composition and the structure of furnace charge, used for production of floor and facing tiles at the "Lasselsberger" factory, to identify their characteristics as a result of high-temperature burning, and also to solve the problem of long relaxation of the facing tiles after burning.

2. MATERIALS AND METHODS

The clays of the Novoorsk and Nizhneuvelsk deposits, kaolin of the Kiembaevsk deposit, as well as the quartz-feldspar raw materials of the Malyshevsk deposit (47%) and dolomite of the Balakovo deposit (2.5%) are used in the composition of furnace charge for the production of floor tiles. Liquid glass is used as fluxing agent. For the production of facing tiles, the abovementioned clays are used with the addition of kaolin-sand mixture, while feldspars are excluded, and the proportion of dolomite is increased to 12.5%.

Thermal investigations were performed using the "STA 443 F3 Jupiter" synchronous gravimetric analysis device (Netzsch, Germany) with the Netzsch Proteus Thermal Analysis software for reading the thermogravimetry (TG) curves and differential scanning calorimetry (DSC) curves, in the temperature range 50-1200°C.

Changes in the phase composition of the charge, depending on the temperature, were investigated by the method of high-temperature X-ray diffraction analysis (HT-XRDA), using "Shimadzu XRD-7000S" diffractometer, in the range of 50-1200°C. The process of heating the samples was carried stepwise, at a rate of 100 degrees per hour. At a predetermined temperature point, the sample was kept for 30 minutes, then the diffraction pattern was recorded for 50 minutes. The processing of the obtained data of HT-XRDA was carried out using the software DIFFRAC-plus Evaluation Package with standards file cabinet PDF-2 ICDD. To carry out a comparative analysis of the qualitative and quantitative phase composition of the burned furnace charges and the corresponding floor and facing tiles, X-ray investigation were carried out on the "D2 PHASER BRUKER" analyzer.

Surface morphology and elemental analysis of the floor and facing tiles samples were investigated by the methods of scanning electron microscopy (SEM) with "Carl Zeiss microscope", equipped with spectrometer "Energy 350 Oxford INCA". Elemental analysis was carried out in a low-vacuum mode with a probe-electron energy of 20 keV. For a given electron energy, the depth of sounding of the tiles was 1 μm.

3. RESULTS AND DISCUSSION

Table 1 presents the results of studies of the mineral composition of the investigated raw materials, by the XRF method. In the work (Petelin A.D., 2015) the presence of montmorillonite was not found in the clay of the Nizhneuvelsk deposit. Our investigations showed, that in this clay a significant proportion of montmorillonite, kaolinite and mixed-

layer clay minerals were found. There was no montmorillonite in the raw kaolin of the Kiembaevsk deposit and in the kaolin-sand mixture (Table 1).

Table. 1: Quantitative mineral composition of raw material samples

Material short text	Mineral composition, %									
	Quartz	Microcline	Albite	Montmorillonite	Mixed-layer clay minerals	Muscovite	Chlorite	Kaolinite	Calcite	Dolomite
Clay of the Nizhneuvelsk deposit	37,43			13,12		8,90	0,44	40,12		
Kaolin of the Kiembaevsk deposit	47,36		4,18			9,25		39,21		
Kaolin-sand mixture	64,59					3,84		31,57		
Quartz-feldspar raw material	46,52	9,03	34,41			10,04				
Dolomite	2,11		0,04						7,14	90,71

According to the material composition, the clay of the Novoorsk deposit is kaolinite with the admixture of hydromica. The aleuritic and psammitic fractions, whose content in clays is up to 6-8%, are represented mainly by quartz (N.F. Solodkiy et al. “Mineral and raw materials base of Ural for ceramic, refractory and glass industries”).

According to the thermal analysis of the charge, the destruction of clay minerals is accompanied by an endothermic effect at 187°C in a charge for the production of facing tiles, and at 182°C in a charge for the production of floor tiles (Figures 1-2, Table 2).

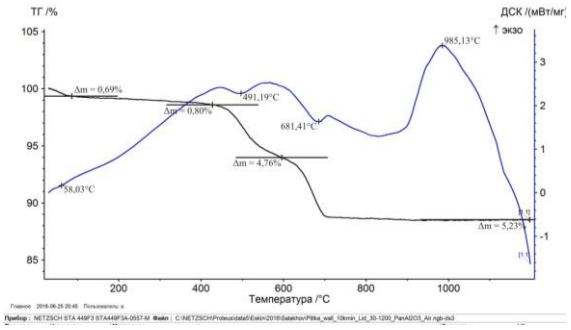

Figure 1. Differential scanning calorimetry (blue) and thermogravimetry (black) curves of charges for the production of facing tiles.

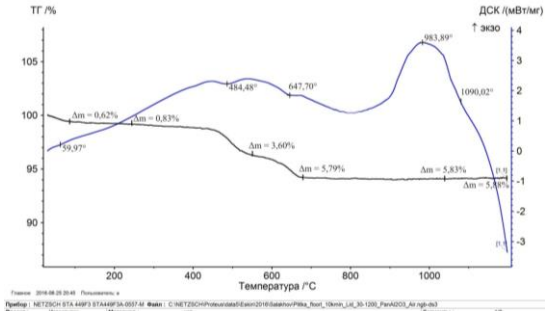

Figure 2. Differential scanning calorimetry (blue) and thermogravimetry (black) curves of charges for the production of floor tiles.

Table 2: Thermal effects and weight losses of charges for the production of tiles.

Item №	Thermal effect	T_{max}, °C	Weight loss of the sample, %	Interpretation
1	endo	58,03 / 59,97	0,76 / 0,62	Removal of adsorbed water.
2	endo	187,01 / 182,02	1,11 / 0,83	Removal of interlayer water from montmorillonite.
3	endo	491,19 / 484,48	5,74 / 3,60	Removal of OH groups from kaolinite.
4	endo	681,41 / 647,70	11,25 / 5,79	Removal of CO_2. Thermal destruction of dolomite.
5	exo	985,13 / 983,89	-	The ordering of the amorphous phase and the formation of new crystalline phases.
6	endo	- / 1090,02	11,48 / 5,88	Dehydration of mica, melting of quartz and feldspars.

Note. The values in the table are for facing / floor tiles.

The significant exothermic effect, determined by us, (Table 2) with a maximum in the temperature range 980-1050°C, indicates significant processes of structure formation. It can be assumed, that the exo-effect is connected with the partial crystallization of the liquid glass.

The data, obtained during the charge thermal study of tiles, produced by the “Lasselsberger” factory, complete the results of the X-ray diffraction analysis.

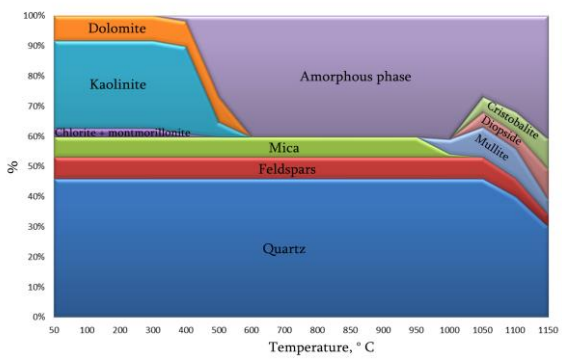

Figure 3. The diagram of change in the phase composition of charge for the production of facing tiles, obtained by the method of high-temperature X-ray diffraction analysis.

So, according to the data of HT-XRDA of charge for the production of facing tiles (Figure 3) with the increase in temperature the following reactions are taken place.

At temperatures above 300-400°C chlorite and montmorillonite disappear, and the products of their thermal destruction in the form of crystalline phases are not detected, which indicates their X-ray amorphous structure.

At temperatures above 500°C, kaolinite and dolomite disappear, and the products of their thermal decomposition are also not detected. Only at temperatures above 1000°C mullite and cristobalite (products of synthesis from decomposed kaolinite components) appear, and the expected products of dolomite decomposition - periclase MgO, calcite and CaO lime, are not detected at all. In our opinion, they "bind" with the products of chlorite and montmorillonite decomposition, forming an amorphous phase.

At temperatures above 950°C, there is the thermal destruction of mica; and then (> 1050°C), CaMg (Si_2O_6) diopside and Ca_2Mg (Si_2O_7) akermanite crystallize. Quite possibly, that their appearance is due to the presence of potassium oxide in the medium, as a result of mica decomposition, which "stimulates" their formation. At the same temperatures above 1050°C, partial melting of quartz and feldspar begins.

It is important to consider the behavior of the amorphous phase, which begins to appear with the disappearance of chlorite and montmorillonite. Two temperature maxima of its development are observed. At temperatures of 600-1000°C, the increased content of the amorphous phase is a result of the clay minerals decomposition and the impossibility of new formations development of crystalline phases. The appearance of the latter - mullite, cristobalite, akermanite and diopside - at temperatures of 1050-1100°C prevents the development of an amorphous phase (glass phase), that explains the porous structure of the facing tile. However, at a temperature of 1100°C, the content of the amorphous phase increases again, which is due to the beginning of feldspars and quartz melting.

It should be noted, that cristobalite was found in the process of high-temperature X-ray diffraction analysis of facing tiles charge. Its presence can be considered as undesirable, because it is known, that at 160°C the beta-alpha transition leads to a significant change in the specific volume of the order of 4% (Krasnikov G. Y. et al. “The system “silicon - silicon dioxide” of submicron VLSI”). In the crock of the facing tiles, cristobalite is not found.

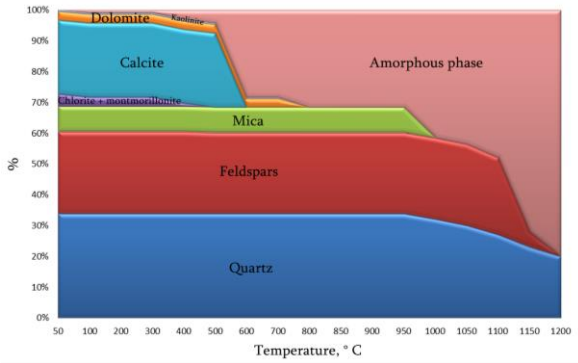

Figure 4. The diagram of change in the phase composition of charge for the production of floor tiles, obtained by the method of high-temperature X-ray diffraction analysis.

According to the data of HT-XRDA of charge for the production of floor tiles (Figure 4) with the increase in temperature the following reactions are taken place.

As in the previous experiment, chlorite and montmorillonite disappear at temperatures above 300-400°C, and the products of their thermal destruction are not detected in the form of crystalline phases, that indicates their X-ray amorphous structure.

At temperatures above 500°C, kaolinite disappears, the products of its thermal destruction - mullite and cristobalite - are not detected. Carbonates - dolomite and calcite - decompose at temperatures above 700°C and there are also no products of their thermal decomposition (MgO periclase, calcite and CaO lime). Therefore, we must admit, that the products of thermal destruction of kaolinite and carbonates form a single X-ray amorphous phase.

There is the thermal destruction of mica at temperatures above 950°C. At temperatures above 1050°C, there is the melting of quartz, and to 1200°C - almost complete melting of feldspars. No new crystalline phases were detected. The products of thermal decomposition of the named minerals, form a stable X-ray amorphous phase - the glass phase, the content of which in the object of investigation increases with increasing temperature.

The differences in the thermal behavior of the press powders of the facing tiles and the floor tiles, in our opinion, are explained by the differences in their mineral and chemical composition. The increased content of the amorphous phase in the floor tile, and the absence of crystalline neoplasms, can be explained by the higher content of alkaline elements in its composition. On the contrary, their lower content in the tile facing press powder determines a smaller content of amorphous phase (glass phase) in its crock, and a higher content of alkaline earth elements leads to the formation of Ca-Mg pyroxenes and amphiboles.

It should be noted, that the phase composition of tile samples, obtained as a result of investigation on the diffractometer “Shimadzu” (Figures 3-4), differs from the phase composition of products from the same charge, obtained as a result of rapid burning at the factory “Lasselsberger” (Table 3). First of all, this content of the amorphous phase in the ceramic sample (in the process of burning on diffractometer “Shimadzu”, liquid-phase sintering is more intensive). The phase composition is distinguished by the presence of some crystalline new formations.

Table. 3: Phase analytical quantification data for facing and floor tiles, produced by the factory “Lasselsberger”.

Tile sample	Mineral composition (only crystalline phase), %			
	Quartz	Albite	Gehlenite	Mullite
Facing tiles	63,5	22,0	5,0	9,5
Floor tiles	63,2	26,7	-	10,1

Note. The content of the amorphous phase in the sample of the facing tile is 24%, in the sample of the floor tile - 61%.

Electron microscopic photograph of the fragment surface of floor tile is presented in Figure 5.

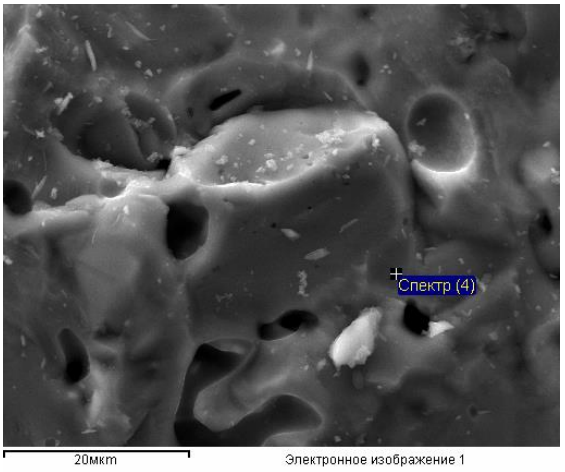

Figure 5. The image of the floor tile fragment, obtained from the scanning electron microscopy. Elemental composition of the X-ray spectrum of section, designated as "Spectrum (4)": O – 57,06, Na – 1,77, Mg – 0,47, Al – 10,56, Si – 27,06, K – 1,59, Ca – 0,70, Ti – 0,32, Fe - 0,48 %.

In the sample of floor tiles, the grains are densely bonded together by an amorphous phase; a monolithic structure is observed. On the contrary, a non-conformal and unequigranular structure was revealed for the sample of the facing tile (Figure 6).

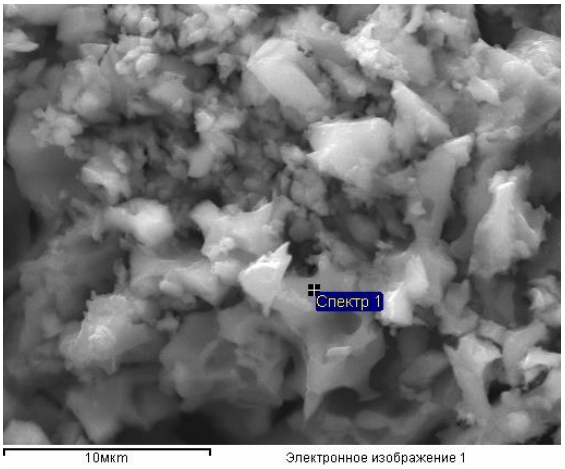

Figure 6. The image of the facing tile fragment, obtained from the scanning electron microscopy. Elemental composition of the X-ray spectrum of section, designated as "Spectrum 1": O – 71,61, Na – 0,32, Mg – 0,43, Al – 4,53, Si – 21,91, K – 0,15, Ca – 0,86, Ti – 0,07, Fe - 0,10, Mo – 0,04 %.

This structure of the facing tile sample indicates the high porosity of the object and, as a result, the low mechanical strength. The nature of such porosity is residual or relict, formed due to the porosity of the press powder and the coming out from the minerals of the gas phase. It was not possible to detect the glass phase, both in the sample of the floor tile and in the sample of the facing tile.

4. DEDUCTIONS

In order to solve the problem of long relaxation of the facing tiles after burning, the authors proposed to correct the composition of the charge, by reducing the content of kaolinite, because thermal coefficient of linear expansion of mullite is substantially smaller than that of quartz. Such a correction of charge corresponds to the trends in modern tile production. Thus, according to Italian researchers (Giovanni Biffi, 2003), in recent years, there has been a significant adjustment of the raw material composition for the production of tiles, in the direction of reducing the share of plastic clays and increasing the share of feldspars, and other non-plastic materials. This resulted in a significant reduction in the drying and burning time, and a decrease in the density of the burned material. At the same time, this caused a decrease in the strength of raw materials and an increase in costs for the dispersion of raw materials, but these factors were recognized by Italian experts as less significant.

5. CONCLUSIONS

1. Facing tiles are characterized by high porosity and a lower content of amorphous phase, compared to the floor tile. That is the result of the different chemical composition of the initial charges. In the composition of the floor tiles, it was revealed more high content of alkaline elements, which contribute to the formation of low-melting eutectics, than in the facing tiles, where higher content of alkaline earth elements leads to the formation of Ca-Mg pyroxenes and amphiboles.

2. Cumulative analysis of the obtained data has shown, that in the process of accelerated burning of charge at the factory, there are the same basic processes of structure formation, as in the process of slow (standard) burning. However, in case of standard burning, the process of amorphous phase formation is more intensive (HT-XRDA on the diffractometer “Shimadzu”).

3. The reduction of kaolinite in the factory charge for the production of facing tiles can eliminate the formation of unwanted phases (cristobalite), and unpredictable process of tiles relaxation.

ACKNOWLEDGEMENTS

The work is performed according to the Russian Government Program of Competitive Growth of Kazan Federal University.

REFERENCES

AMICO Consulting Company. (2017). *Marketing research "Russian market of ceramic tiles in 2010-2015. And the forecast for 2016-2020*. Moscow. p. 141

Augustinik, A. I. & Ceramics, L. (1975). Stroyizdat (Leningrad Branch). p. 592.

Bender, W. (2004). Vom Ziegelgott zum Industrieelektroniker. Bundesverb and der Deutschen Ziegelindustrie e.V. Bonn. 2004. 436 p.

Biffi, G. (2003) *Book for the production of ceramic tiles.* Faenza Editoriale. 2003. 376 p.

Express-Obzor (2017). *The overview of ceramic tiles market in Russia: operational data 2010-2016 and forecast for 2019*. Moscow. p. 100.

Gorbunov, G. I. & Zvezdin, D. F. (2003). Ceramic tiles. Technology of production and new proposals. *Russian Chemical Journal*. 47(4). p. 55-60.

Krasnikov, G. Y. & Zaitsev N. A. (2003). *The system "silicon - silicon dioxide" of submicron* VLSI. Moscow: Tekhnosfera, p. 384.

Mazzacani, P. & Biffi, G. (1997). Handbook for the technician of ceramics production. p.191.

Petelin, A. D., Saprykin, V.I., Klevakin, V.A. & Klevakina, E. V. (2015). The peculiarities of application of the Nizhneuvelsk deposit clays in the production of ceramic bricks. Construction materials, 4, p. 28-30.

Solodkiy, N. F., Shamrikov, A. S. & Pogrebenkov, V. M. (2009). *Mineral and raw materials base of Ural for ceramic, refractory and glass industry. Reference manual. Edited by prof. G.N. Maslennikova*. Tomsk: Publishing house of Tomsk Polytechnic University. p. 332.

Zakharov, A. I., Guseva T.V., Vartanyan M.A., Molchanova Y. P., Averochkin E. M. & Kastritskaya S. V. (2013). Improvement of energy efficiency of ceramic tiles production: comparative analysis of domestic and foreign experience. Construction Materials, 8, p. 41-43.

Zhukov, A. D., Gorbunov, G. I. & Belash, N. A. (2003). Energy-saving technology of ceramic tiles. Bulletin of Moscow State University of Civil Engineering, 10, p. 122-130.