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Frost Resistant Porous Ceramics

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Extremely actual problem of these days is the production of ceramics which is resistant to frost under exploitation and jointly effective (porous), because these ceramic wall articles will be particularly suitable for building the facades which are being exploited under aggressive conditions (e.g. a seaside zone). Such a brick building will have a low coefficient of thermal conductivity and will be resistant to frost (the surface of the bricks will not decay). The porous and at the same time frost resistant (under exploitative conditions) ceramic material was obtained, when composition of formation mix was as follows: (59.2 – 72.8) % of clay, (7.2 – 10.8) % of sand, (3.2 – 4.8) % of crushed bricks, (10.4 – 15.6) % of sawdust and (6.4 – 9.6) % of milled glass. When ceramic samples were formed and burned under regime (maximum burning temperature is to 1100 °C), ceramics which exploitation frost resistance is more than 300 cycles, total open porosity is 40 %, and the predicted coefficient of thermal conductivity is (0.37 – 0.42) W/mK.

Keywords: ceramics, exploitation frost resistance, physical-mechanical and structural parameters.

INTRODUCTION

Currently produced ceramic articles are either frost resistant (designed for facade masonry) or effectively porous having low coefficient of thermal conductivity. Due to the good sound isolation properties of effectively porous products, they are suitable for building partitions. They may be also applied for low-rise buildings because of their low degree of strength [1]. The value of thermal conductivity coefficient of blocks produced in Lithuanian Rokai and Palemonas factories (with the typical composition of clay, sand, crushed bricks, sawdust, peat and coal) is The blocks with the composition often of clay, sand, chip (the chip of baked ceramics), sawdust, peat and coal is 0.19 W/mK, and frost resistance hardly reaches 25 cycles, compressive strength is 7.5 MPa – 10.0 MPa.

The standard solid bricks for building facades have the coefficient of thermal conductivity of 0.81 W/mK, and frost resistance, which is determined using volumetric method, is also quite low of 75 – 100 cycles [2 – 3], therefore, under the atmospheric action the decomposition of ceramic masonry facades or surfaces of blocks starts already in few years after construction. It includes flaking, cracking and crumbling.

Therefore, the very topical object of investigation worldwide is the research on composition and manufacturing technology of ceramic formation mix, having low coefficient of thermal conductivity and being frost resistant under exploitation. Recovering of waste is very important too.

Ways of obtaining resistant to frost ceramics are presented in patents [4 – 7]. The properties of ceramics which is obtained are as follows: compressive strength is from 20 MPa to 35 MPa, frost resistance, which is determined using volumetric freezing method, is from 75 to 150 cycles, and water absorption is to 5 %.

There are described methods of how to obtain ceramics with higher frost resistance in the works enumerated, however such articles are of quite low porosity (their water absorption is lower than 5 %). Moreover, frost resistance was determined using volumetric freezing method, which most often does not disclose real long-lasting effect of ceramic articles.

Thus, the ceramic articles are mostly resistant to frost under exploitation (baked ceramics which water absorption is not higher than 5 %), or porous (effective ceramics which water absorption is more than 5 %), and having lower coefficient of thermal conductivity, however they are resistant to frost to a low degree under exploitation [8].

The authors [9 – 12] determined, that using zirconium oxide it is possible to obtain ceramics with porosity from 40 % to 75 %. The size of the granules of ceramics obtained is lower than 70 nm. The scientists [12] determined how the porosity of ceramics changes while burning at different temperatures. Burning ceramic samples at 750 °C – 1100 °C temperature, the porosity of material obtained varies from 45 % to 75 %, and the coefficient of thermal conductivity is reduced to 0.1 W/mK.

The ceramic articles described in the patents [13 – 16] have the properties as follows: the coefficient of thermal conductivity is (0.15 – 0.42) W/mK, density is (379 – 1800) kg/m^3, porosity is (20 – 50) %. However, ceramics with bigger porosity presented in these works is not frost resistant.

We failed to find in literature any description of ceramics which would be frost resistant and at the same time effective under exploitation. Ceramics with similar properties was only presented in patents [17 – 18]. Ceramics with composition of clay (70 – 80) % and anthracite (20 – 30) %. The properties of this ceramic are as follows: density is (1100 – 1200) kg/m^3, compressive strength is (8.8 – 14.6) MPa, frost resistance is 75 cycles, water absorption is (19.5 – 26.9) %. However, 75 cycles are not sufficient for frost resistance in order to use articles under harsh conditions; moreover, this indicator was also determined using volumetric freezing method, which is not used for the examination of the impact on exploitation factors.

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The composition of ceramics presented in patent [18] is: (78 – 85) % clay, (14.5 – 15) % sand, (1 – 2) % anthracite, small dispersal magnesia or dolomite, or (4.5 – 6) % calcite. The ceramics produced has (16.72 – 20.57) % water absorption while vacuuming, (21.4 – 34.03) % reserve of porous volume, and its frost resistance is up to 1000 cycles. Frost resistance of ceramics with such a composition would be sufficient. Moreover, it is determined by method according to p. 5 GOST 7025-78: 1978 [19]. There is also presented the main indicator – reserve of porous space which influences exploitation frost resistance in this patent. However, more expensive additions were used during the experiments of the research described.

The aim of our research was to obtain resistant to frost under exploitation and at the same time porous ceramics, made of local raw materials and waste, suitable for constructing seaside facades [1].

RAW MATERIALS AND INVESTIGATION METHODOLOGY

The semi manufactures were shaped into dimensions of (70×70×70) mm, later they were dried and burned under the best time and temperature regime. The composition of formation mix was selected as follows: (59.2 – 72.8) % of clay sieved through sieve with 0.63 mm holes (its chemical composition is presented in Table 1), (7.2 – 10.8) % of sand sieved through sieve with 0.63 mm, (3.2 – 4.8) % of crushed bricks sieved through sieve with 1.25 mm holes, (10.4 – 15.6) % of sawdust sieved through sieve with 1.25 mm holes and (6.4 – 9.6) % milled glass sieved through sieve with 0.63 mm holes. The microstructure of main raw materials is presented in Fig. 1. The microstructure was tested with a scanning electron microscope Zeis Evo LS 25. According to microstructure of raw materials we saw, that the least particle size is in the main raw material – clay. When particle size is less, than burning processes of ceramics are accelerated. Particles of all raw materials have irregular form, however they lock very well.

Using synchronization method during investigations, it was determined that maximum burning temperature is 1100 °C, as afterwards samples lose their shapes or it is obtained a ceramic sliver with many defects.

The ceramic samples burned and cooled were used for setting physical-mechanical and structural parameters. The density and water absorption of the samples were being set using standard methods [20]. The density was assessed

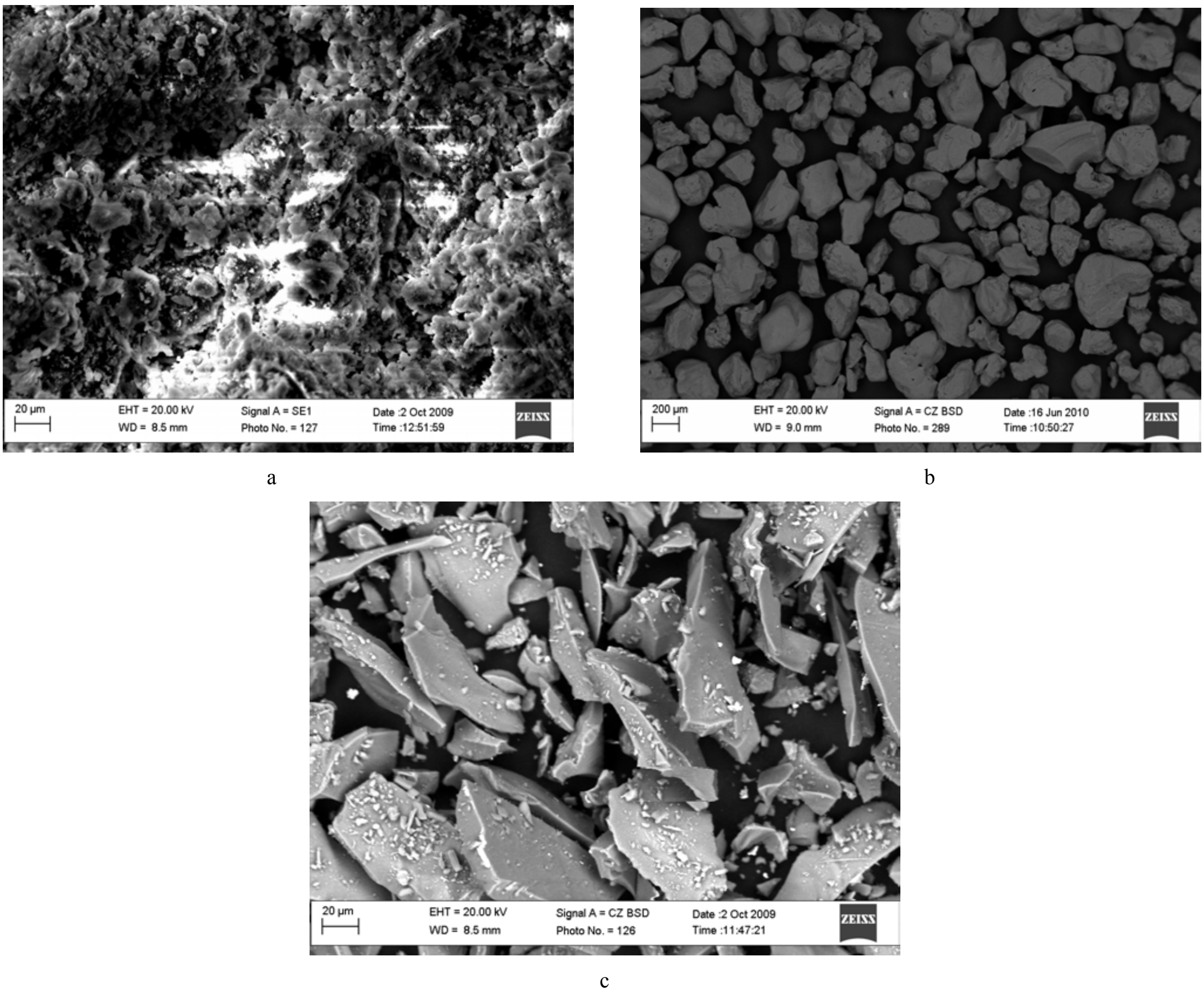

Fig. 1. Microstructure of raw materials: a – clay; b – sand; c – milled glass

Table 1. The average chemical composition of the main raw material (clay)

Chemical composition, %							
SiO_2	Al_2O_3+TiO_2	Fe_2O_3	CaO	MgO	K_2O	Na_2O	L.O.I.
48.31	18.94	6.28	7.19	3.26	1.42	0.19	11.7

as proportion of the mass and the volume of dry product. During our research water absorption was tested at atmospheric pressure in the water of (20 ±5) °C for 72 h. Compressive strength was being set according to LST EN 772-1:2003 [21]. The coefficient of thermal conductivity was calculated according LST EN 1745:2002 [22]. Frost resistance (by *F*, cycles) was determined according to LST 1985:2006 [23] using one-side cooling method. The exploitation frost resistance forecasted according to the methodology of parameters of structure [24 – 25] calibrated according to LST 1413.12:1998 [26]. Exploitation frost resistance as physical parameter of facade ceramics can be characterized as being able to prevent defects from being filled with water because of the migration processes [24].

Further, the formulas for forecasting exploitation frost resistance are presented, as the effective porosity of the samples is lower than 26 % [24 – 25].

$$F_{RE1} = 0.231\frac{R^{1.068}D^{1.345}G_1^{0.275}G_2^{0.663}}{N^{0.285}g_1^{0.833}}, \quad (1)$$

$$F_{RE2} = 0.223\frac{R^{1.465}D^{0.759}G_1^{0.383}G_2^{0.852}}{N^{0.168}g_1^{1.034}}, \quad (2)$$

where: F_{RE1} is the beginning of the decomposition of the samples in cycles; F_{RE2} is the end of the decomposition of the samples, in cycles; *R* is the reserve of porous volume, %; *D* is the qualified thickness of the wall of capillaries, %; G_1 is the capillary rate of mass flow in a vacuum in a direction of freezing, g/cm^2; G_2 is the capillary rate of mass flow in a vacuum in a perpendicular direction of freezing, g/cm^2; *N* is degree of structural inhomogeneity, units; g_1 is the capillary rate of mass flow, set under normal conditions, g/cm^2.

Further, according the formulas [25] for calculations of structural parameters used for forecasting exploitation frost resistance was determined.

The phase analysis of the powder of burned samples was performed by X-ray diffraction. The used main instrument was difractometer DRON-7, used a cobalt anode, the wavelength λ = 0.1792 nm. The X-ray diffraction were decoded according to the standard tables where the values of the interplanar distances *d* and relative intensity *I* are presented [27 – 28]. The data of difractometer analysis was analyzed using computer program “Origin 5.0”.

RESULTS AND ANALYSIS

The average values of physical-mechanical and structural parameters of ceramic samples determined and counted are presented in Table 2 and Table 3 respectively.

As it is seen from the data presented in Table 3, the porous ceramics was obtained (water absorption is much bigger than 5 %). Its compressive strength is higher than 15 MPa, and therefore such ceramics is suitable for building low-rise buildings. The exploitation frost resistance determined according to [23] is higher than 300 cycles. According to the authors of the standard [23], while maintaining 100 freezing-thawing cycles, ceramic articles without any sign of decomposition can be used under extremely harsh atmosphere conditions, where strong winds, wet weather, cold, or sun and heat in summer are predominant The value of the coefficient of thermal conductivity is quite low, and it would become much lower while producing bricks or blocks from such ceramic chip with various empty areas.

Table 2. The average values of physical-mechanical parameters

ρ, kg/m^3	S_b, %	f_c, MPa	W_{72h}, %	λ, W/mK	*F*, cycles
1556	12.44	15.32	12.98	0.38	> 300

Note: ρ – density, S_b – general contraction, f_c – compressive strength, W_{72h} – the water absorption determined under normal conditions after 72 hours, λ – the coefficient of thermal conductivity, *F* – the exploitation frost resistance determined according to the [23].

Table 3. The average values of structural parameters

R, %	W_e, %	W_p, %	*D*, %	*N*, units	G_1, g/cm^2	G_2, g/cm^2	g_1, g/cm^2
47.5	20.2	38.5	1.9	0.03	1.4	1.4	1.2

Note: *R* – the reserve of porous volume, %; *D* – the qualified thickness of the wall of capillaries, %; G_1 – the capillary rate of mass flow in a vacuum in a direction of freezing, g/cm^2; G_2 – the capillary rate of mass flow in a vacuum in a perpendicular direction of freezing, g/cm^2; *N* – degree of structural inhomogeneity, units; g_1 – the capillary rate of mass flow, set under normal conditions, g/cm^2.

Placing the obtained values of structural parameters into the (1) and (2) formula, the forecasted exploitation frost resistance was calculated. Ordinary samples begin to decompose as their effective porosity is lower than 26 %, (there were 108 cycles obtained), and the end of the decomposition is 234 cycles. According to the requirements of the standard LST 1413.12:1998 [26], such ceramic production can be also used under extremely harsh weather conditions.

It was determined in the work [29] that one-side regime of freezing-thawing according to LST EN 1985: 2006 is less aggressive than one-side regime of freezing-thawing according to LST 1272-92:1993 [30] and LST 1413.12:1998 [26] methodologies. The reason was based on methodology used during cyclic thaw for extremely short period of watering. Because of that the influence of water migration processes, which lead to the decomposition of ceramic samples, decreases greatly. Therefore, it was suggested that in order to produce articles suitable for their usage under extremely harsh weather conditions such articles must go through 300 cycles according to new LST EN 1985: 2006 [23] standard, and this would match 75 – 100 cycles of invalid LST 1272-92:1993 [30] standard which were determined using one-side freezing-thawing method. Consequently, the ceramic body we obtained meets the requirements for exploitation frost resistance according to methodologies presented in above mentioned standards.

The main additions of the formation mass which enable to obtain desired effect (exploiting ceramics which is resistant to frost and jointly porous) are sawdust and milled glass. Adding more than 16 % of sawdust to the formation mix the number of defects increases and frost resistance starts to decrease. While adding less than 10 % sawdust the product of desired porosity is not obtained. When the amount of milled glass in the formation mass is reduced to 6 % and less percents, it is impossible to obtain resistant to frost ceramics, and when increasing the amount of milled glass to 10 % and more percents, it is impossible to obtain porous ceramic body. Moreover, when our limits on the amount of glass in the formation mix are exceeded, glass mass starts to diffuse into surface, the strength of the product decreases.

In addition, it is determined that maximum burning temperature and duration, which were selected, made very significant impact on the properties of ceramics.

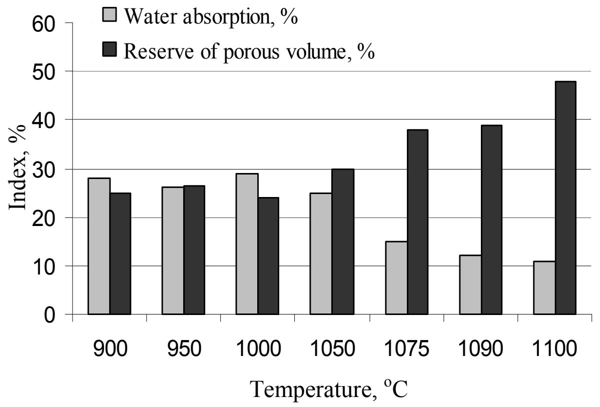

Fig. 2. The influence of burning temperature on water absorption and reserve of porous volume

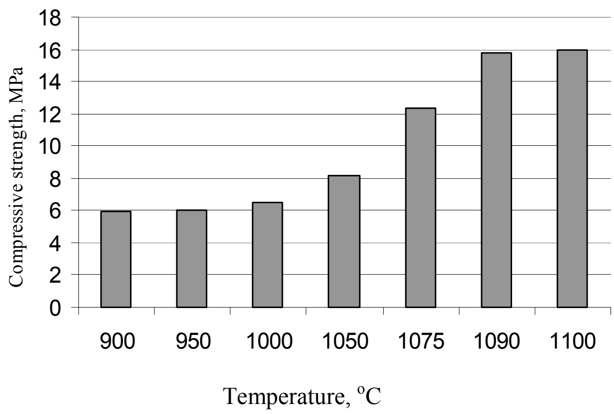

Fig. 3. The influence of burning temperature on compressive strength

Figures 2 and 3 show how water absorption, reserve of porous volume and compressive strength change as maximum burning temperature is increased from 900 °C to 1100 °C.

It is obvious from Figures 2 and 3 that physical, mechanical and structural parameters which change slightly while increasing burning temperature from 900 °C to 1050 °C, therefore ceramic samples were being burned at higher temperature. While increasing maximum temperature of ceramic samples from 1050 °C to 1100 °C, it was noticed the increase in reserve of porous volume (approximately from 29 % to 48 %) and compressive strength (approximately from 8 MPa to 16 MPa), where water absorption decreased (approximately from 26 % to 12 %).

According to the results of the research it was determined that optimal burning temperature while producing exploitation frost resistant and at the same time porous ceramics is 1100 °C.

According to frost resistant porous ceramics micro-structure (Fig. 4) we could say, that in the samples composed closed pores and they are very small (< 5 µm).

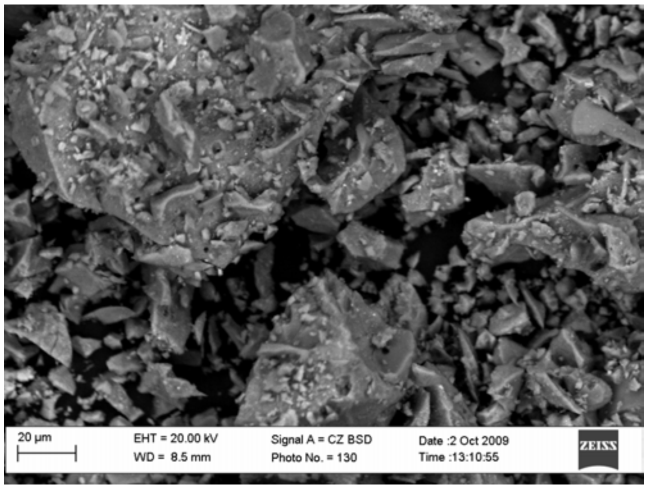

Fig. 4. Microstructure of milled frost resistant porous ceramics samples

When X-rays diffraction analysis of burned samples under different regimes was performed, it is determined such their composition in phases.

These minerals are determined in all the batches: quartz *Q* (SiO_2), which intensive peaks are 0.154, 0.167, 0.182, 0.198, 0.213, 0.229, 0.246, 0.335, 0.424 nm, hematite *F* (Fe_2O_3), which intensive peaks are 0.170, 0.184, 0.220, 0.251, 0.270 nm, anortite *A* ($CaO[Al_2Si_2O_8]$ or $CaOAl_2O_32SiO_2$), which intensive peaks are 0.213, 0.251, 0.321, 0.324, 0.370, 0.376, 0.406, 0.643 nm, and diopside *D* ($CaOMgO2SiO_2$), which intensive peaks are 0.175, 0.184, 0.203, 0.213, 0.220, 0.251, 0.256, 0.295, 0.300 nm (Fig. 5). Part of the quantity of grounded glass in formation mix in respond with other components of formation mix crystallized and formed such new minerals as anortite, diopside, and part of the glass remained of amorphous structure. The researchers [31] demonstrated too, that burned at higher than 1000 °C temperature ceramic samples, which consist from main raw material

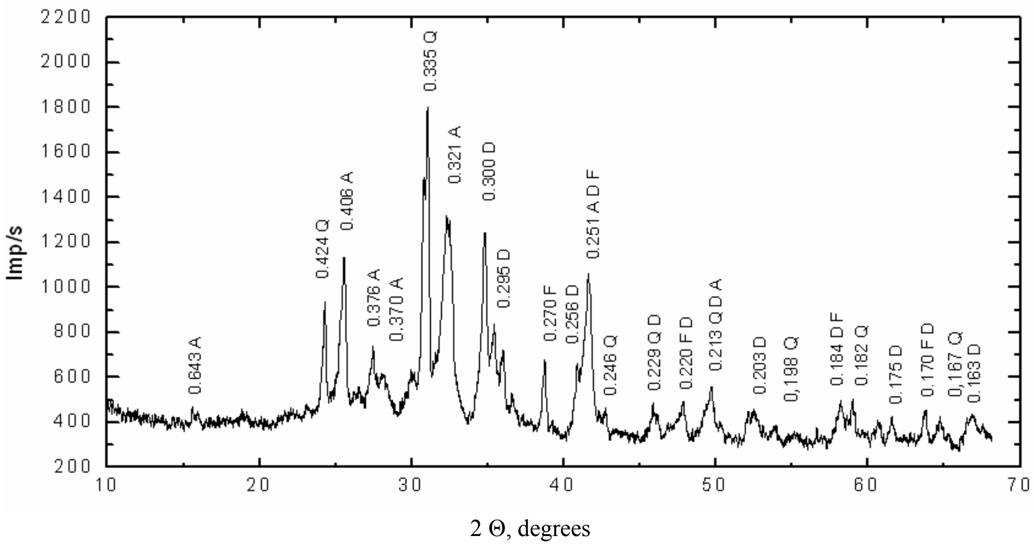

Fig. 5. X-ray diffraction pattern of the sample (as burning temperature is 1100 °C)

illite clay compose from such minerals as diopside, quartz, anortite and hematite.

Ceramics from thermodynamically stable crystals is resistant to frost under exploitation.

CONCLUSIONS

1. The porous and at the same time frost resistant (under exploitative conditions) ceramic material was obtained, when composition of formation mix was as follows: (59.2 – 72.8) % of clay, (7.2 – 10.8) % of sand, (3.2 – 4.8) % of crushed bricks, (10.4 – 15.6) % of sawdust and (6.4 – 9.6) % of milled glass. Such ceramics exploitation frost resistance determined according to LST EN 1985:2006 is more than 300 cycles; the forecasted frost resistance, which methodology is developed according to LST 1413.12:1998, is 108 cycles for the beginning, and 234 cycles for the end of sample decomposition. The total open porosity is about 40 % and the coefficient of thermal conductivity is 0.38 W/mK. Such ceramics can be used for the production of wall articles for facades, especially for the facades which are being exploited under harsh conditions (e. g., seaside zone).
2. Part of small dispersal glass in respond with other components of formation mix crystallizes and forms such new minerals as anortite and diopside, and part of glass remains of amorphous structure. Ceramics from thermodynamically stable crystals is resistant to frost while it is being exploited. Thermodynamically stable crystals enable to obtain ceramic articles with better mechanical properties.

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