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Properties of porous glass ceramics based on siliceous rocks

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Abstract. Porous glass ceramic materials are widely used in the construction industry. Foam glass ceramics are obtained from industrial wastes, rocks of various chemical and mineralogical composition and other raw materials. Samples of foam glass ceramic materials obtained by burning the mechanically activated charge were studied. Siliceous rocks from six deposits were ground together with thermonatrite ($Na_2CO_3 \cdot H_2O$). The resulting charge was burned at a temperature of 850 °C. The following properties were determined experimentally: bulk density, compressive strength, water absorption, sorption humidity, thermal conductivity, application limit temperature, thermal and chemical stability of samples. In order to obtain glass ceramic materials with a uniform porous structure, the total amount of cristobalite and the amorphous phase in the composition of siliceous rock has to be more than 44.5 %. The amount of quartz, calcite and muscovite in the rock should not exceed 12 %. The bulk density of the samples decreases with an increase of heilandite share in the charge composition. The maximum compressive strength of the developed materials is 6 MPa with a bulk density of samples equal to 290 kg/m^3. The water absorption of samples decreases to 2.5 % (by volume) with an increase of diatomite share in the charge composition for more than 39.5 %. The minimum thermal conductivity of glass ceramics (0.0583 W/m °C) was revealed at a sample density of 180 kg/m^3. Insufficiently high values of thermal stability index (167–183 °C) are associated with the presence of both amorphous phase and crystalline minerals in the material, which have different thermal expansion coefficients. The application limit temperature of the material reaches 850 °C. The developed materials demonstrated high chemical stability after boiling in water, an aqueous HCl solution, as well as in an alkaline solution. Regarding a number of indicators, porous glass ceramic materials based on siliceous rocks are superior to foam glass and can be used as thermal insulation of pipelines, industrial plants (melting furnaces, boiler equipment), etc.

1. Introduction

Porous glass ceramic materials are widely used in the construction industry. Glass ceramic materials have high strength, low heat conductivity, high stability to harsh chemical environments, a wide range of operating temperatures, etc. They are used as insulators in the construction of industrial and civil facilities, nuclear power plants, gas and oil industry enterprises [1–3].

In industrial and civil engineering, foam glass ceramic materials from glass waste are widely used [4–6]. Glass ceramics based on industrial wastes, such as slag from metallurgical production [7–9], lead-zinc mine tailings [10], red mud [11], etc., possess decent physical, mechanical, thermal and physical properties. A large number of researches are devoted to developing the compositions and studying the properties of porous glass ceramic materials from siliceous rocks (diatomite, tripoli, opoka) [12–19]. Technologies for the production of porous glass ceramics are also diverse. Materials are obtained by the method of co-melting the components [20], by method of mixing the components in the molten state [21], by foaming a colloidal suspension [22], etc. Porous glass ceramic from siliceous rock is obtained mainly in the form of bulk materials [13–19]. Diatomite, opoka, zeolite-containing rocks are activated with aqueous solutions of alkalis, then they are granulated and burned after that. The equipment deteriorates rapidly with this production technology, as a result of exposure to alkalis. Burning the charge is accompanied with the release of harmful substances (NaOH) into the atmosphere [23]. This issue is resolved by replacing the alkaline solution with an alkaline component (for example, $Na_2CO_3 \cdot H_2O$) in dry form. The components have to be mixed using joint grinding method (mechanochemical activation). Structural defects accumulate in the particles of a solid body during

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intense grinding, phase transformations occur, as well as amorphization of minerals in the crystal structure [24, 25]. The practice of obtaining block porous glass ceramic materials by burning joint ground siliceous rock (tripoli) and an alkaline component (Na_2CO_3) is described in the research [26].

Siliceous rocks from various deposits have significant differences regarding chemical and mineralogical composition. The impact of chemical composition of raw materials on the physical, mechanical, thermal, physical and other properties of glass ceramic materials is described in detail in scientific literature. It was determined that the strength characteristics of glass ceramics increase with increasing the amount of Al_2O_3 in the mixture up to 18 % [27]. According to the studies [28, 29], the increase in the alumina amount in the mixture to a certain extent reduces the thermal conductivity and thermal expansion coefficient of porous glass ceramic samples. The impact of CaO content in the material composition on various properties of glass ceramic samples from glass wastes and fly ash was described in detail in article [30]. Their obtained results indicate a density increase and a simultaneous decrease in compressive strength of samples. The calcium oxide content in the material composition increases and is more than 4.25 %. An increase in the density of glass ceramic materials, which are based on slag from copper production, with an increase of calcium oxide in the composition was also noted in the study [31]. The positive effect of Fe_2O_3 in the material composition on increase in the strength characteristics of glass ceramics was determined [32]. Almost all of the above mentioned results were obtained while studying glass ceramic samples based on artificially created glasses or industrial wastes. There are only few studies describing the impact of chemical and mineralogical composition of siliceous rocks on the properties of porous glass ceramic materials obtained by burning a mechanochemically activated charge (siliceous rock + fluxing agent).

The research goal is to determine the impact of chemical and mineralogical composition of siliceous rocks on the physical, mechanical, hydrophysical and thermophysical properties. The chemical stability of the foamed glass ceramic samples obtained by burning a mechanochemically activated charge needs to be determined as well.

Objectives:

- to determine the impact of chemical and mineralogical composition of siliceous rocks on the bulk density, compressive strength, as well as on water absorption and sorption humidity of foam glass ceramic samples;
- to determine the thermal conductivity, thermal stability and application limit temperature of the production samples of foam glass ceramic materials;
- to determine the stability of developed material samples in water or aqueous solutions of acids and alkalis.

2. Methods

2.1. Materials

In order to obtain foamed glass ceramic samples, siliceous rocks from six deposits were used, five species of tripoli and one diatomite (humidity ≤ 1 %). The chemical and mineralogical composition of the rocks is given in Table 1 and 2, respectively.

Table 1. The chemical composition of the rocks.

Comp. number	Chemical composition, % mass									
	SiO_2	CaO	Al_2O_3	Fe_2O_3	K_2O	MgO	TiO_2	Na_2O	SO_3	Other
R1	69.6	6.9	7.1	2.0	1.5	1.0	0.3	0.0	0.1	11.5
R2	68.5	6.8	6.8	1.8	1.5	1.0	0.3	0.2	0.1	13.0
R3	67.9	7.7	7.6	2.0	1.6	1.1	0.3	0.2	0.1	11.5
R4	56.4	12.5	8.7	2.7	2.0	1.2	0.4	0.2	0.1	15.8
R5	62.3	11.3	6.7	2.0	1.4	0.9	0.3	0.1	0.0	15.0
R6	81.5	1.5	5.3	2.1	1.0	0.9	0.2	0.2	1.8	5.5

Table 2. The mineralogical composition of the rocks.

Comp. number	Mineralogical composition, %						
	Quartz	Calcite	Heulandite	Muscovite	Cristobalite	Tridymite	Amorphous phase
R1	11.6	12.3	16.8	12.6	24.7	2.0	20.0
R2	11.4	12.1	19.0	10.8	24.6	2.1	20.0
R3	10.8	12.8	19.2	14.4	21.1	1.7	20.0
R4	11.1	22.4	19.8	14.3	11.4	1.0	20.0
R5	8.5	21.3	19.6	9.9	19.2	1.5	20.0
R6	14.3	0.0	0.0	10.7	0.0	0.0	75.0

Thermonatrite with a main substance mass fraction of at least 99 % was used as fluxing agent. The chemical formula is $Na_2CO_3 \cdot H_2O$.

2.2. Compositions and manufacturing technology of samples

Samples of foamed glass materials were produced according to the technology described below. First, the siliceous rock was ground together with fluxing agent ($Na_2CO_3 \cdot H_2O$). The grinding was carried out in a Retsch PM 400 planetary ball mill for 90 minutes (the rotation speed of the grinding jars was 250 rpm). Then, the resulting charge was poured into metal molds and burned in a muffle furnace (the molds were pre-treated with kaolin paste). The charge burning program is as follows: heating to a temperature of 600 °C at a rate of 4.5 °C/min, holding at 600 °C for 1 hour, heating to 850 °C at a speed of 4.5 °C/min, holding at 850 °C for 30 minutes. Holding at a temperature of 600 °C is necessary in order to remove excess gases formed due to the decomposition of individual minerals from the charge's composition (calcite, muscovite, etc.). After cooling the mold with the obtained material together with the furnace to 40 °C, the mold was disassembled, and the samples were removed for further testing.

The studied charge compositions are presented in Table 3. The compositions are selected based on previously conducted experimental studies of obtaining glass ceramic materials with an optimal porous structure (pore diameter not more than 2 mm). The results are partially described in the study [26].

Table 3. Compositions studied in the research.

Composition number	Charge composition, %						
	Siliceous rock (chemical composition see Table 1)						Thermonatrite
	R1	R2	R3	R4	R5	R6	
C1	79	–	–	–	–	–	21.00
C2	75.05	–	–	–	–	3.95	
C3	71.10	–	–	–	–	7.90	
C4	67.15	–	–	–	–	11.85	
C5	–	79.00	–	–	–	–	
C6	–	75.05	–	–	–	3.95	
C7	–	71.10	–	–	–	7.90	
C8	–	67.15	–	–	–	11.85	
C9	–	–	79.00	–	–	–	
C10	–	–	75.05	–	–	3.95	
C11	–	–	71.10	–	–	7.90	
C12	–	–	67.15	–	–	11.85	
C13	–	–	–	39.50	–	39.50	
C14	–	–	–	34.00	–	45.00	
C15	–	–	–	–	44.40	34.60	
C16	–	–	–	–	42.00	37.00	
C17	–	–	–	–	39.50	39.50	

2.3. Analytical techniques

2.3.1. Physical and mechanical properties

The density and compressive strength of foamed glass ceramic materials were determined using dry cubic samples with a face size of 90±5 mm. The maximum destructive force when determining the compressive strength was adopted as the value, at which the sample collapsed with cracking or crumpled in the surface layers by 10 % of the initial height value. The final result was the average value of the test results of five samples for each composition.

2.3.2. Hydrophysical properties

Water absorption (W_V) of foamed glass ceramic materials by volume was determined by measuring the water mass adsorbed by a dry sample when completely immersed in water for 24 hours. The tests were carried out on cubic samples with a face size of 50±5 mm. Before testing, the samples were dried to constant weight at a temperature of 105±5 °C. The formula for determining water absorption (W_V, %) is as follows:

$$W_V = \frac{m_1 - m}{V \cdot \rho_W} \cdot 100, \tag{1}$$

where m is mass of the sample, previously dried to constant weight, g;

m_1 is mass of the sample saturated with water, g;

V is volume of the sample, cm^3;

ρ_W is the density of water, g/cm^3.

The sorption humidity (W_S) of foamed glass ceramic materials was determined for samples with the mass of 5±0.5 g. The samples were placed in glass beaker and dried to constant weight. Then the glasses with samples were placed in artificially created steam-air medium (relative air humidity: 40 %, 80 %, 97 %, temperature is 20±2 °C). Every 5 days within 1 month, the moisture content of the samples was determined by weighing. The temperature of the room, in which the samples were weighed, was 20±2 °C; the relative air humidity was 60±10 %. The formula for determining the sorption humidity (W_S, %) of the samples is as follows:

$$W_S = \frac{m_1 - m}{m - m_2} \cdot 100, \tag{2}$$

where m is mass of the dried sample in a glass beaker, g;

m_1 is the mass of the sample in a glass beaker after the end of the sorption process, g;

m_2 is mass of dry glass beaker, g.

When determining the hydrophysical properties, the average value of the test results for three samples of each composition was taken as the final result.

2.3.3. Thermophysical properties

The thermal conductivity (λ) of samples was determined by the probe method using the MIT–1 device (probe diameter 6 mm). The studies were carried out on dry cubic samples with a face of 90±5 mm at a temperature of 25±2 °C. In the center of cube face a hole was drilled with a diameter of 6 mm and a depth from 50 to 60 mm, into which the probe was immersed.

The application limit temperature of foamed glass ceramic materials was determined by the residual change in sample size (90×40×40 mm) after aging at a given temperature. Dry samples were placed in a muffle furnace in one row in height. The temperature in the furnace was increased at a rate of 10 °C/min to a temperature, which is 50 °C less than maximum. Then it was increased at a rate of 2 °C/min for the last 50 °C before holding. The samples were kept at the testing temperature for 2 hours. The samples were cooled together with the furnace down to room temperature. Linear temperature shrinkage ($-\Delta l$) or growth thermal expansion ($+\Delta l$) during sample heating was calculated in percent by the following formula:

$$\Delta l = \frac{l - l_1}{l} \cdot 100, \tag{3}$$

where l is the sample height before heating, cm;

l_1 is the sample height after heating, cm.

The thermal stability (ΔT) of the samples was determined according to the temperature difference of the alternately heated and cooled samples, at which cracks occurred. Dry cubic samples (face length equals 50±5 mm) were kept for 30 minutes in a thermostat at a temperature of 110 °C. Then, the samples were removed from the thermostat after no more than 10 seconds and immersed in a water tank (water temperature is 20±2 °C). The immerse duration of samples in water is 65±5 seconds. The experiment was repeated with an increase in the thermostat temperature by 10 °C until cracks appeared on all samples. The thermal stability (ΔT, °C) of each sample was calculated by the following formula:

$$\Delta T = T_T - T_W - T_t, \tag{4}$$

where T_T is thermostat temperature, at which a crack on the sample appeared, °C;

T_W is temperature of the coolant in the tank, °C;

T_t is thermostat temperature difference between the subsequent and previous tests, 10 °C.

The average value of test results for three samples of each composition was taken as the final result, when determining the thermophysical properties.

2.3.4. Chemical stability

The chemical stability (X) of foamed glass ceramic materials was determined using powder samples (fraction 0.315–0.630 mm). The weight loss of the samples was determined after boiling for 3 hours in distilled water, in aqueous solution of 6N HCl, and in a mixture of equal volumes of 1N solutions of Na_2CO_3 and NaOH. 5±0.0005 g of the prepared sample were placed in a flask and filled with 100 cm^3 of reagent. The flask was connected to a reflux condenser. After boiling the contents of the flask for 3 hours, an aggressive liquid was drained from it, and the sample was washed with distilled water. The washed sample was poured onto a funnel with an ashless paper filter, together with distilled water. The funnel with the filter and the test sample was calcined in an oven at a temperature of 800±25 °C, cooled in a desiccator above $CaCl_2$ and weighed.

The formula for determining chemical stability (X , %) is as follows:

$$X = \frac{m - m_1}{m} \cdot 100, \tag{5}$$

where m is the sample mass before the test, g;

m_1 is the sample mass after testing, g.

The final result was adopted as the average value of the test results for three samples of each composition.

3. Results and Discussion

3.1. Physical and mechanical properties

The results of studying the impact of chemical and mineralogical composition (siliceous rock + thermonatrite) of the charge on the bulk density and compressive strength of porous glass-ceramic samples are presented in Fig. 1. During the experiment, 17 compositions of five samples each were tested.

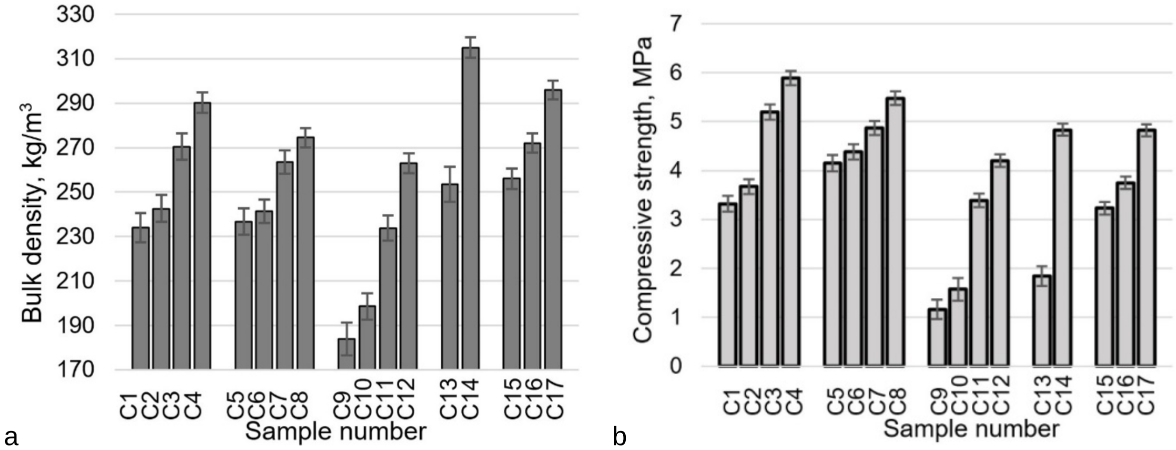

Figure 1. Bulk density (a) and compressive strength (b) of samples.

According to the obtained data (Fig. 1, *a*), an increase in the diatomite amount (rock R6) in the charge composition causes the bulk density of porous glass ceramic samples to increase linearly. For example, the density of samples increases by almost 25 % when 15 % of tripoli (rock R1) is replaced with diatomite (compositions C1 and C4, respectively) in the charge composition. This is probably due to the fact that the decrease in the bulk sample density (when replacing part of tripoli with diatomite) is a consequence of a heulandite (a mineral from the zeolite group) content decrease in the charge composition. As per researches [15, 26], the zeolite group minerals are ones of main sources for pore formation in the production of glass ceramic materials based on siliceous rocks (for one charge heating). According to studies carried out, samples C1, C5 and C11 have the lowest bulk density (≈ 230 kg/m^3). The heulandite content in the rock, from which the samples are made, is 17–19 %. The results obtained when testing samples of compositions C9 and C10 were not taken into account, since they had an uneven porous structure. The samples of C14 composition have the highest density (≈ 315 kg/m^3). In this case, the heulandite amount in the rock is the smallest (8.5 %).

Despite the deterioration of some indicators, such as density increase, the introduction of diatomite into the charge is necessary in some cases. For example, tripoli R4 and R5 contain a large amount of calcite (>

20 %). Without adding diatomite to the charge, it was not possible to obtain foamed glass ceramic materials based on these rocks. Samples based on tripoli R5 (21.5 % $CaCO_3$) have a uniform porous structure when at least 45 % of tripoli is replaced by diatomite in the charge. Based on the composition with tripoli R4 (22.4 % $CaCO_3$), it was possible to obtain porous glass ceramic materials with not less than 50 % of diatomite content from the total mass of siliceous rocks in the charge. According to the data in Table 2, the diatomite used in the study consists of an amorphous phase for 75 %, which is characterized by high reactivity. When diatomite is introduced into the charge, the fluxing agent amount increases at a lower temperature, the material has a uniform structure [14, 18]. In addition, the amount of calcite decreases with replacing the part of tripoli by diatomite in the charge composition. As is known [33], calcite contributes to the production of melt in the charge at high temperatures.

The pore structure of glass ceramic materials based on tripoli R3 becomes uniform, when at least 10 % of tripoli is replaced by diatomite in the charge. The main difference between the mineralogical composition of tripoli R3 from R1 is an increased muscovite content (by 1.8 %), as well as a lower amount of cristobalite (by 3.6 %). However, foam glass ceramic samples based on tripoli R1 have uniform porosity even without the diatomite inclusion. Therefore, in order to obtain a uniform porous structure of glass ceramic materials based on the presented siliceous rocks, the total amount of cristobalite and the amorphous phase has to be more than 44.5 %. The amount of quartz, calcite and muscovite should not exceed 12 %.

According to the studies (Fig. 1, b), it was found that the compressive strength of porous glass ceramic samples (C1–C12) is linearly dependent on their bulk density. These samples were obtained using tripoli R1–R3, which differ slightly in chemical and mineralogical composition. The samples of C4 composition have the highest compressive strength (≈ 6 MPa) for. The bulk density of the samples is 290 kg/m^3. The compressive strength of the developed porous glass ceramic materials with an equal bulk density is greater than that of foam glass from glass waste and coal fly ash (fly ash) [1, 4, 5, 10, 30].

Samples of foamed glass ceramic materials based on tripoli R4 and R5 have lower compressive strength compared to samples based on rocks R1–R3 (with equal bulk density). For example, at almost the same density (≈ 290 kg/m^3), the compressive strength of C17 samples is almost 20 % lower than the strength of C4 samples. According to the data in Table 1, this is most likely due to a decrease in Al_2O_3 amount in the material composition. A decrease in the strength characteristics of glass ceramic materials due to a decrease of aluminum oxide in their composition was represented in various researches [27–29].

3.2. Hydrophysical properties

The results of studying the water absorption for foamed glass ceramic samples based on siliceous rocks are presented in Fig. 2.

According to the scientific literature [16, 17], it is known that the water absorption of porous glass ceramic materials depends on the source of pore formation, the rate of temperature rise and burning, etc. Analyzing the data obtained (Fig. 2) showed that the water absorption of samples of the developed materials depends primarily on their bulk density. Samples of C9 composition have the greatest water absorption by volume (≈ 32 %). The bulk density of the samples is 180 kg/m^3. And the least water absorption (≈ 2.5 % by volume) is in samples of compositions C14 and C17. The density of these samples is 315 kg/m^3 and 295 kg/m^3, respectively.

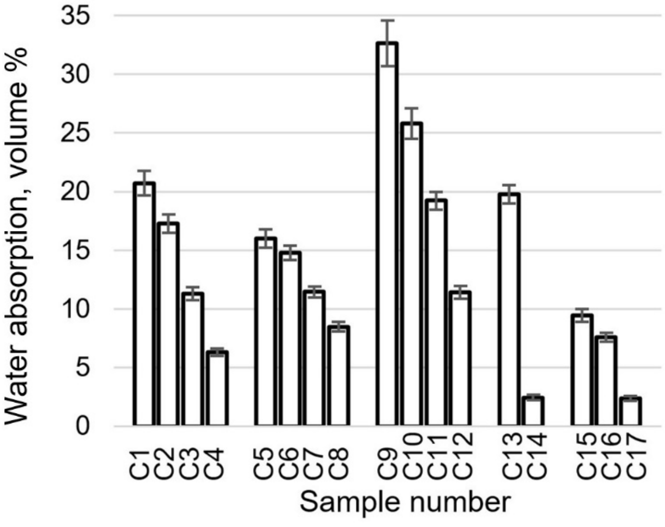

Figure 2. Water absorption of samples.

It should be noted that the amount of water adsorbed by the samples decreases with an increase of diatomite content in the initial charge composition. For example, the water absorption of C3 composition samples (7.9 % of diatomite) is almost 50 % higher than the composition of C16 (37 % of diatomite) at an almost equal value of the bulk density (≈ 270 kg/m^3). As noted earlier, this is due to the prevalence of closed pores in the material structure due to an increase in the amount of fluxing agent at a lower temperature.

According to the results of experimental studies regarding determining the sorption humidity of samples of developed foam glass ceramic materials, the following was determined. After 30 days of holding the samples at a temperature of 20±2 °C and a relative humidity of 40, 80 and 97 %, the sorption humidity of the material does not exceed 0.07, 0.10, 0.14 %, respectively. The mass of samples continues to increase. The impact of chemical and mineralogical composition of siliceous rocks (used for the research) on the equilibrium moisture content of samples from developed materials is not exposed at this stage. According to researches [16, 17], the sorption humidity index for samples of foam glass and foamed glass ceramic is stabilized for some compositions only after 1 year of testing. Our results after 30 days of testing correlate with data obtained by other authors [16, 17].

3.3. Thermophysical properties

The results of the thermal conductivity test for porous glass ceramic samples, which are based on siliceous rocks with various bulk densities, are presented in Fig. 3. During the experiment, three samples for each of 17 compositions were tested.

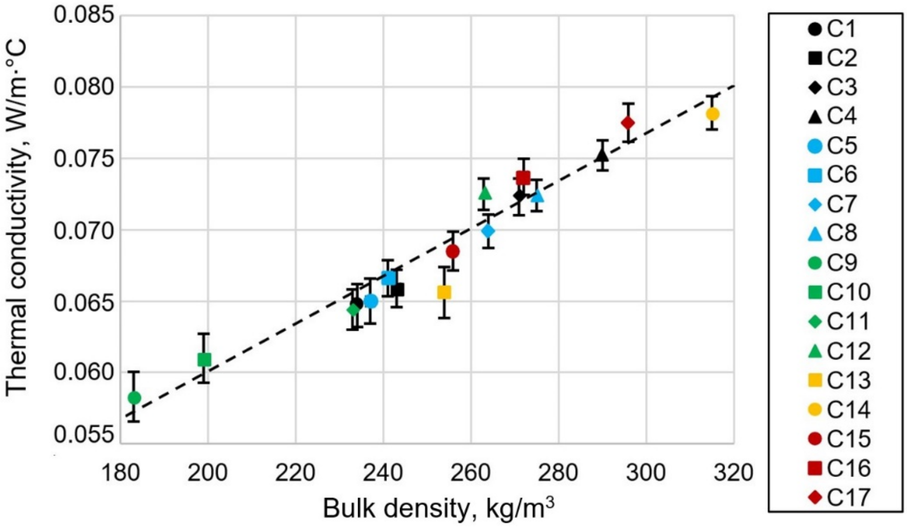

Figure 3. Thermal conductivity of samples.

According to the data presented in Fig. 3, the thermal conductivity of dry samples increases linearly from 0.0583 to 0.0782 W/m·°C with an increase in the material density from 180 to 320 kg/m^3. The dependence of thermal conductivity (λ, W/m·°C) on the density of studied materials is represented by the following formula:

$$\lambda = \frac{0.02\rho + 3.2}{120}, \tag{6}$$

where ρ is the bulk density of the material in the dry state, kg/m^3.

The approximation certainty factor is R^2 = 0.9405.

As a result of conducted research, it was found that the density of dry porous glass ceramic materials from siliceous rocks with a thermal conductivity of not higher than 0.060 W/m·°C should be less than 200 kg/m^3. For thermal conductivity of not more than 0.070 W/m·°C the density has to be less than 260 kg/m^3. No significant impact of the chemical and mineralogical composition of siliceous rocks (used in the study) on the thermal conductivity of developed material samples was detected. The results obtained correlate with the data of many researchers [11, 14, 20, 28].

According to various studies [1, 27, 28], the building materials used for the thermal insulation of industrial equipment must have high thermal stability (not to collapse under abrupt temperature changes). The results of testing the thermal stability of porous glass ceramic samples from siliceous rocks are represented in Fig. 4.

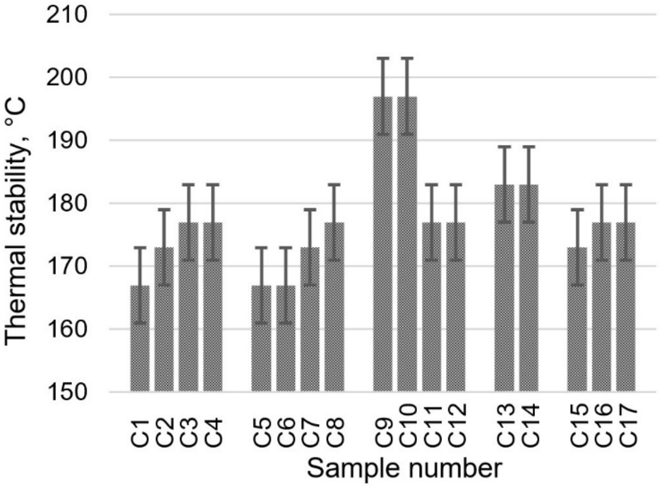

Figure 4. Thermal stability of samples.

Analyzing the data presented in Fig. 4, it can be concluded that the thermal stability of developed material samples is within the 167–183 °C range. Insufficiently values of the indicator are apparently associated with the presence of both amorphous phase and crystalline minerals in the material. They have different thermal expansion coefficients. As a result, with an abrupt temperature drop of more specific intervals, the material is destroyed by internal stresses. As was determined earlier [26], the ratio of crystalline to amorphous phase is approximately 40:60 for the foamed glass ceramic materials based on siliceous rocks. Samples of compositions C9 and C10 withstood temperature gradient of almost 200 °C. Such effect is likely associated with the open porosity of the material, as evidenced by the high rate of water absorption of the samples (Fig. 2). According to the test method, heated samples were immersed in water. Penetrating into the material, it contributed to a more uniform cooling. Consequently, the thermal stability of the samples increased.

It should be noted that the thermal stability of foamed glass ceramic samples increases with an increase in the diatomite content in charge composition. Disregarding the test results of C9 and C10 composition samples, the compositions with a diatomite content in the charge of more than 39.5 % (C13 and C14) have highest thermal stability (183 °C). The lowest value of the indicator is for samples (compositions C1, C5, C6), for which the diatomite content in the charge does not exceed 3.95 %.

In terms of thermal stability, porous glass ceramic materials from siliceous rocks are comparable to foamed glass ceramic from industrial wastes, but slightly inferior to foamed glass [27, 28].

The results of studies on determining the application limit temperature of the developed materials (residual changes in the size of the samples after holding for 2 hours at a given temperature) are presented in Table 4.

Table 4. Residual changes in the size of samples after holding for 2 hours at a given temperature.

Comp. number	Residual changes in the size of samples after holding for 2 hours at a given temperature, %*		
	750 °C	800 °C	850 °C
C1	0.00	–0.10	–0.21
C2	0.00	–0.10	–0.29
C3	0.00	–0.12	–0.49
C4	–0.12	–0.43	–1.17
C5	0.00	–0.13	–0.39
C6	0.00	–0.29	–0.75
C7	0.00	–0.31	–0.97
C8	–0.17	–0.34	–2.32
C9	0.00	0.00	–0.15
C10	0.00	–0.11	–0.27
C11	0.00	–0.18	–0.43
C12	0.00	–0.30	–0.88
C13	–0.06	–0.18	–1.04
C14	–0.76	–0.82	–3.04
C15	–0.11	–0.68	–5.36
C16	–0.13	–0.76	–4.71
C17	–0.22	–0.78	–5.48

* − The standard deviation (σ) of the results does not exceed 0.02 % (from 0 to – 1 % for the results).

Analyzing the data in Table 4 shows that individual compositions of the developed materials (C1–C3, C5–C7, C9–C12) can be operated at a temperature of ≤ 850 °C. After holding for 2 hours at a temperature of 870 °C, the sizes of samples of all compositions decreased by more than 1 %. With an increase of the charge diatomite content to more than 11.85 % in the composition, the application limit temperature of the samples decreases to 800 °C. After holding the samples for 2 hours at a temperature of 850 °C, their sizes decreased by only 0.15 % (C9 composition), and decreased by more than 5 % for C17 composition. According to the data in Tables 1 and 3, a C9 composition sample was obtained from siliceous rock (R3) with an Al_2O_3 content of ≈ 7.6 % (the amount of diatomite is 0). The total amount of aluminum oxide in the C17 charge does not exceed 6 %. According to the researches [27–29, 32], the stability of ceramic materials to prolonged exposure to high temperatures increases with an increase in the amount of Al_2O_3 and decreases with an increase in Fe_2O_3. It is likely that the increased content of Fe_2O_3 (2.7 %) in the composition of siliceous rock (R4) contributed to a decrease in the application limit temperature of samples based on it (C13, C14) up to 800 °C. It is important to note that the amount of alumina in the charge, from which samples C13 and C14 are made, is approximately 7 %.

Regarding the application limit temperature, the developed materials are comparable to foamed glass ceramic from industrial waste, and significantly exceled foamed glass [28]. The application limit temperature of the latter rarely exceeds 600 °C [1]. Porous glass ceramic materials based on siliceous rocks (presented in the research) can be used as thermal insulation of industrial equipment, such as melting furnaces, boiler equipment, etc.

3.4. Chemical stability

Table 5 presents data on the weight loss of foamed glass ceramic samples (crushed to a fraction of 0.315–0.630 mm) after 3 hours of boiling in various chemical media.

According to the experimental data, with an increase in the diatomite content in the charge composition, the dissolution of powdery glass ceramic samples decreases upon boiling for 3 hours in water, an aqueous HCl solution, and also in alkaline solution. The pattern is typical for samples obtained from a charge based on siliceous rocks R1–R3 (compositions C1–C12). Thus, the mass of developed material samples based on R1 composition tripoli (sample C1) decreased on average by 0.9 % after 3 hours of boiling in water. In an alkaline solution it decreased by 7.51 %, and by 3.62 % in an acid solution. When replacing 15 % of tripoli with diatomite, the weight loss of samples (C4) after 3 hours of boiling in water is on average 0.36 %. For an alkaline solution this value is 7.16 %, and for acid solution – 1.78 %.

Table 5. The change in mass of samples after boiling in various chemical media for 3 hours.

Comp. number	The change in mass of samples after boiling in various chemical media for 3 hours, %					
	Average value			Standard deviation (σ)		
	H_2O	6N HCl solution	1N Na_2CO_3 solution + 1N NaOH solution (1:1)	H_2O	6N HCl solution	1N Na_2CO_3 solution + 1N NaOH solution (1:1)
C1	0.90	7.51	3.62	0.08	0.45	0.25
C2	0.75	7.44	2.37	0.06	0.52	0.17
C3	0.57	7.33	1.94	0.05	0.44	0.10
C4	0.36	7.16	1.78	0.03	0.36	0.11
C5	0.74	7.43	3.6	0.05	0.45	0.22
C6	0.58	7.38	2.48	0.05	0.44	0.12
C7	0.49	7.24	2.03	0.04	0.51	0.14
C8	0.42	7.13	1.94	0.03	0.50	0.12
C9	0.61	6.99	3.41	0.05	0.35	0.24
C10	0.54	6.71	2.97	0.04	0.40	0.15
C11	0.48	6.35	2.74	0.04	0.44	0.14
C12	0.32	6.13	2.51	0.03	0.31	0.18
C13	0.86	6.45	2.08	0.06	0.38	0.17
C14	0.99	6.38	1.91	0.09	0.43	0.10
C15	0.08	6.51	1.97	0.01	0.46	0.12
C16	0.33	6.43	1.89	0.02	0.32	0.13
C17	0.89	6.42	1.87	0.08	0.39	0.13

The dissolution of samples from a charge based on siliceous rocks R4 and R5 (compositions C13–C17) is greater with an increase of diatomite content in the mixture. After 3 hours of boiling in water, samples of composition C15 lost only 0.08 % by weight. At the same time, samples of composition C17 lost 0.89 %. Both variants of samples were obtained on the basis of tripoli with the R5 composition. There is by 4.9 % more diatomite in the C17 charge composition than in C15. The chemical stability of these samples in HCl and alkaline solutions varies slightly. Samples lost on average 1.91 % after 3 hours of boiling in a HCl solution, and 6.46 % after boiling in an alkaline solution.

According to the researches [34, 35], the chemical stability of glass-ceramic materials depends on many factors. The main influence is provided by their chemical and mineralogical composition. Pisciella P. in the study [31] came to the conclusion that the chemical stability of glass ceramics primarily depends on the material's structure formation. As mentioned above, the amount of fluxing agent increases at a lower temperature with the introduction of diatomite in the charge composition. This possibly contributes to the material's structure formation, characterized by greater chemical stability. It was determined that the chemical stability of glass ceramic materials is directly affected by the content of CaO in the composition [32]. The chemical stability increases with a decrease in calcium oxide in the material composition. According to the data in Table 1, the CaO content in the diatomite used (R6) is several times lower compared to tripoli (R1–R5). When replacing part of tripoli in the mixture with diatomite, the amount of calcium oxide in the calcined material decreases. Apparently, this also contributes to an increase in the chemical stability of the samples.

The experimental tests of foamed glass materials showed their high chemical stability in water, in an aqueous HCl solution, as well as in an alkaline solution. Regarding this indicator, the developed materials excelled foamed glass [11, 34, 35]. The above mentioned allows recommending porous glass ceramic materials to be used as insulation of pipelines, industrial plants, etc.

4. Conclusions

The impact of chemical and mineralogical composition of siliceous rocks on the properties of porous glass ceramic samples is studied. The samples were obtained by burning a mechanochemically activated charge. Siliceous rocks from six deposits were ground together with thermonatrite ($Na_2CO_3 \cdot H_2O$). The resulting mixture was burned at a temperature of 850 °C. The following properties were experimentally determined: bulk density, compressive strength, water absorption, sorption humidity, thermal conductivity, application limit temperature, thermal and chemical stability of samples. The major findings of the research are as follows:

1. The bulk density of the samples depends more on the mineralogical composition of the siliceous rocks, from which they were made. In order to obtain glass ceramic materials with a uniform porous structure, the total amount of cristobalite and the amorphous phase in the rock composition has to be more than 44.5 %. The amount of quartz, calcite and muscovite in the charge composition should be less than 12 %. The bulk density of the samples decreases with an increase in the heulandite content in the charge composition.

2. The compressive strength of the developed materials is linearly dependent on their bulk density. Moreover, this indicator decreases with a decrease in the amount of Al_2O_3 in the charge composition. The greatest compressive strength (≈ 6 MPa) was found in samples with a bulk density of 290 kg/m^3. The compressive strength of the developed porous glass ceramic materials with an equal bulk density is several times higher than that of foamed glass from waste glass and coal fly ash.

3. Water absorption of samples of developed materials decreases with a diatomite content increase in the charge composition. The greatest water absorption by volume (≈ 32 %) is in samples based on a charge without diatomite. The least absorption (≈ 2.5 %) is in samples obtained from a charge with a diatomite content of at least 39.5 %. The decrease in water absorption as a result of replacing part of tripoli with diatomite is apparently due to the prevalence of closed pores in the material structure. This is due to an increase in the amount of fluxing agent at a lower temperature.

4. The thermal conductivity of dry foamed glass ceramic samples from siliceous rocks increases almost linearly from 0.0583 to 0.0782 W/m·°C with an increase in the material density from 180 to 320 kg/m^3. No significant effect of the chemical and mineralogical composition of siliceous rocks (used in the study) on the thermal conductivity of the samples was revealed.

5. The thermal stability of the foam glass ceramic samples increases from 167 to 183 °C with diatomite content increase in the charge composition from 0 to 39.5 %. Insufficiently values of the indicator are apparently associated with the presence of both amorphous phase and crystalline minerals in the material. They have different thermal expansion coefficients.

6. The application limit temperature of porous glass ceramic materials reaches 850 °C. This indicator for samples decreases to 800 °C with an increase of diatomite in the charge composition of more than 11.85 %. It was determined that the application limit temperature decreases with a decrease in the amount of Al_2O_3 in the charge composition, as well as with an increase in Fe_2O_3.

7. The developed materials showed high chemical stability after boiling in water, in an aqueous HCl solution and in alkaline solution. It was determined that the dissolution of powdery glass ceramic samples

upon boiling for 3 hours in chemical media decreases with diatomite content increase in the charge composition.

8. Considering the number of indicators, porous glass ceramic materials based on siliceous rocks excel foamed glass and can be used as insulation for pipelines, industrial plants (melting furnaces, boiler equipment), etc.

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