Low-Temperature Sintering of High-Siliceous Clay under
Conditions of Oxygen Deficiency

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Abstract:

In the work, the processes of phase reconstruction and properties of ceramics obtained from high-siliceous clay–sand, clay–cullet, and clay–sand–cullet mixtures are considered. It is possible to perform plastic molding of blanks from the given mixtures due to the presence of montmorillonite in clay and sand and sintering at 800 °C for 8 h under conditions of oxygen deficiency. Depending on the composition of the initial mixtures, specimens ranging in color from gray to black can be obtained. It has been established by the XRD, IR spectroscopy, and electron microscopy methods that the synthesized material is glass ceramics consisting of quartz, feldspars, and a glass phase. Depending on the content of the initial components in the mixtures, it is possible to obtain glass ceramics with high strength properties or coarse-pored glass ceramics whose properties are similar to those of foamed ceramics.

Keywords: High-siliceous clay; Sand; Low-melting glass; Sintering; Properties of ceramics.

1. Introduction

In [1], a technology that makes it possible to realize the low-temperature synthesis of bricks from high-siliceous clays by the method of plastic molding of blanks was presented, though it is known that ceramics of this type is usually obtained from clays by dry or semidry pressing of blanks with subsequent high-temperature sintering [1-6]. It was established that for the initiation of the plastic properties of the material, it is necessary to introduce a small amount of montmorillonite/bentonite and water into high-siliceous clay. In [1], as a...
plasticizing additive, sand containing a small amount of montmorillonite (Table I) was used. Moreover, to perform low-temperature sintering, a low-melting component should be added to high-siliceous clay. As such, a component, low-melting glass, namely, bottle cullet with a melting point of ~ (750-800) °C, playing the role of flux, was chosen. It turned out that the ceramics obtained from binary and ternary mixtures containing high-siliceous clay, sand, and cullet and sintered at 800 °C for 8 h had high strength properties.

| Type of material | Phase composition | Content, wt% |
|------------------|-------------------|--------------|
| Clay yellow      | plagioclases:     |              |
|                  | from NaAlSi$_3$O$_8$ to CaAl$_2$Si$_2$O$_8$ | 22           |
|                  | quartz (SiO$_2$)  | 45           |
|                  | phyllosilicates:  |              |
|                  | mica (d =10Å)     | 14           |
|                  | kaolinite (d = 7Å)| 11           |
|                  | montmorillonite (d = 14Å) | 8 |
| Sand black       | plagioclases:     |              |
|                  | from NaAlSi$_3$O$_8$ to CaAl$_2$Si$_2$O$_8$ | 38           |
|                  | quartz (SiO$_2$)  | 35           |
|                  | phyllosilicates:  |              |
|                  | mica (d =10Å)     | 8            |
|                  | kaolinite (d = 7Å)| 5            |
|                  | montmorillonite (d = 14Å) | 10         |
|                  | hematite (Fe$_2$O$_3$) | 2 |
| Glass            | amorphous material|              |

In view of the similarity of the mineralogical composition of the so-called “clay” and “sand” and the dominant content of quartz and plagioclases in them, it is more reasonable to assign these components to quartz–feldspar sands with a somewhat different composition [7-8]. It is known that, on the basis of high-siliceous sand, refractory ceramics is obtained at high firing temperatures [2, 3, 9-11]. For quartz–feldspar sand, precisely the presence of feldspar containing orthoclase, albite, and anorthite provides the flux-forming effect and sintering at 1050 °C [12-15]. To decrease further the sintering temperature and obtain high-strength ceramics, different additives, e.g., bone ash, cullet, etc. are introduced into the initial composition or compositions [16-26]. As a rule, ceramics sintered in air is reddish brown.

Since in modern civil engineering, bricks of different color are extensively used, the objective of the present work is three-fold: (1) to develop a plastic molding technology of blanks containing a substantial amount of silica/sand; (2) to develop a technology of low-temperature synthesis of ceramics whose color ranges from black to gray from high-siliceous clays by analogy with the technology developed in [1]; (3) to evaluate the properties of the synthesized material from the viewpoint of its application as building bricks or a filler in the case of increased contents of sand and cullet, and, hence, an increased amount of the glass phase in the newly formed materials.

To realize objective 1, namely, plastic molding of blanks, it is intended to determine the limits of decrease of the content of the clay component in the mixtures because exactly the total content of montmorillonite in clay and sand determine the plastic properties of the mixtures at a certain content of introduced water. To realize objective 2, black sand containing hematite (Fe$_2$O$_3$) was chosen (see Table I) because it is known that the presence of
iron oxide in clays under certain sintering conditions (reduction firing of clay) provides a decrease in the sintering temperature and the transformation \(\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4\), thus stimulating the appearance of black color in the ceramics [27-29]. To realize objective 3, it is necessary to carry out a complex analysis of the properties of the synthesized ceramics, particularly from the viewpoint of the evaluation of the compressive strength, fracture strength, pore formation, and water absorption.

2. Materials and Experimental Procedures

For study the effect of the composition of the gaseous medium on the low-temperature sintering process of highly siliceous clays, in this work a double and triple mixtures consisting of yellow clay, black sand, and milled cullet from brown, green, and colorless bottles with low temperatures of melting were used. In the binary clay–sand and clay–glass mixtures, the clay content was varied from 100 wt% to 10 wt%. In the ternary mixtures, the contents of clay, sand, and glass were (wt%): 40:30:30, 29:25:50, and 15:25:50. Blanks were prepared by the plastic molding method from the initial mixtures with 100 g of the dry component per 40 or 30 ml of water. After natural drying in air for 8 days, blanks were carried into a hermetic draught cupboard. Then the chamber was blown by argon. Inside the chamber, blanks were placed in hermetically closable steel capsules. Capsules containing blanks were transferred into a Carbolite CWF 1300 electric furnace. Sintering was carried out at 800 °C for 8 h. The temperature was raised from room temperature up to 800 °C at a rate of 14.1 °C/min. Then heating was turned off, and the furnace was cooled down to room temperature. The sizes of the experimental specimens were 80 mm × 20 mm × 15 mm.

For the research of the initial components, mixtures, and ceramics, we used the following analytical methods: X-ray diffraction (XRD) analysis (a Siemens D-500 diffractometer in Cu \(K_α\) radiation). An electron microscopy study and electron-probe microanalysis were performed with a SU 5000 Hitachi scanning electron microscope. Infrared spectra were obtained on a Frontier FT-IR 101804 spectrometer. The contents of oxides in specimens were determined with use of an S8 TIGER X-ray fluorescence spectrometer (XRF) (Bruker).

The linear shrinkage of specimens was determined as \(\Sigma, \% = \left[\frac{(l_0 - l_1)}{l_0}\right] \cdot 100\), where \(l_0\) is the initial length of blanks and \(l_1\) is the length of blanks after sintering (ceramics). The water absorption was determined by the formula: \(W, \% = \left[\frac{(P_1 - P_0)}{P_0}\right] \cdot 100\), where \(P_0\) is the initial weight of a specimen and \(P_1\) is the weight of the specimen after water absorption. The mechanical properties of the ceramics were investigated by standard techniques [30] on electromechanical universal tester, Model 312.31, Load Frame 250 kN, Serial 1088 machine. The compression strength was calculated by the formula: \(C = \frac{W}{A}\) (kg/cm²), where \(C\) is the compression strength, \(W\) is the maximum load (kg) indicated by the test machine, and \(A\) is the average of the gross areas of the upper and lower bearing surfaces of the specimen (cm²). The flexural strength was calculated by the formula: \(R_{\text{flex}} = \frac{3FL}{2bd^2}\) (kg/cm²), where \(F\) is the maximum load indicated by the test machine (kg), \(L\) is the length of the support section (cm), \(b\) and \(d\) are the width and thickness of specimen (cm) [31].

To determine the average value of experimental data for clay and the obtained ceramics, measurements were performed on 10 specimens.

3. Results and Discussion
3.1. Characterization of the initial materials

According to the XRF data, in all components used in the present work, iron oxide is present (Table II). In temperature treatment of the given materials, with increase in the
treatment temperature, under conditions of oxygen deficiency, their color gradually changes (see Fig. 1). Already at $T_{tr.} = (500-600) \, ^\circ C$, clay turns dark brown, and, at $T_{tr.} \geq 700 \, ^\circ C$, becomes dark gray. Sand gradually turns darker and becomes black $T_{tr.} \geq 500 \, ^\circ C$. Glass begins to melt at $T_{tr.} > 600 \, ^\circ C$ and gets a gray color. In the range $T_{tr.} \sim (800-1000) \, ^\circ C$, intensive melting of glass occurs. Due to a decrease in the viscosity, the melt of glass spreads over the substrate surface, and, in cooling, as a result of the generation of microstresses on the “substrate–glass mass layer” boundary, cracking of glass occurs.

**Tab. II** Chemical composition of used components.

| Component    | SiO$_2$ | Fe$_2$O$_3$ | Al$_2$O$_3$ | K$_2$O | CaO | Na$_2$O | TiO$_2$ | P$_2$O$_5$ | MgO | MnO | Σ |
|--------------|---------|-------------|-------------|--------|-----|---------|---------|-----------|-----|-----|---|
| Clay         | 97.30   | 1.13        | 0.81        | 0.34   | 0.16| –       | 0.13    | 0.05      | 0.04| 0.01| 0.13 |
| Sand black   | 68.9    | 4.29        | 14.19       | 2.6    | 1.62| 3.74    | 0.86    | 0.19      | 1.33| 0.05| 2.23 |
| Glass        | 72.81   | 1.08        | 0.29        | 0.45   | 11.29| 13.25   | 0.14    | 0.03      | 0.5 | 0.02| 0.15 |

Note: powder glass consists of cullet of green, brown, and transparent bottle cullet.

![Fig. 1](image-url)  
**Fig. 1.** Temperature treatment of initial materials under conditions of oxygen deficiency, $t_{tr.} = 30 \, \text{min.}$

The change in the color of the used materials indicates the possibility of the partial reduction of hematite, which is present in clay, sand black, and glass (see Tables I and II). The transfer of Fe$^{2+}$ ions into plagioclases, silica (SiO$_2$), and glass is not improbable. The formation of new phases of dark ferrosilicate compounds is also possible [32-35].

3.2. Preparation of blanks.

In preparation of blanks by the plastic molding method (see Fig. 2), 40 or 30 ml of water were introduced into mixtures, and wooden molds were filled by plastic mass. For the binary mixtures containing from 10 to 100 wt.% clay, the extrusion method of obtaining blanks can be used. After drying for 8 days, only on the surface of blanks containing 90 wt% sand, “down” appears. It consists of evaporation products of water soluble salts, which are present in clay and sand (see Table II) [36]. A characteristic feature of these blanks is the bad cohesion of sand particles due to the small content of montmorillonite in the composition.
3.3. Characterization of ceramic specimens.
3.3.1. Appearance of ceramic specimens

Note that ceramic specimens sintered at 800 °C differ in color, which, depending on the composition of the initial mixtures, varies from light gray, to gray and black (Fig. 3). This means that, by changing the composition of the initial mixtures in the same sintering regime (temperature, time, composition of the gas atmosphere in the firing furnace), it is possible to obtain bricks with dark color of different intensity in contrast to reddish brown bricks obtained by firing in air. Specimens obtained with a large sand content (≥60 wt%) swell, in the volume of the ceramics, porosity increases. The cause of pore formation in sintering is dehydration processes, dehydroxilation of phyllosilicates, and release of gas/vapor bubbles through melt [2, 3, 37-40]. The surface of such specimens has signs of “vitrification”. In the ceramics obtained for the clay–glass mixtures, vitrification signs occur more intensively. The preparation of specimens from the clay–glass mixtures is possible only at a glass content no greater than 50 wt%.

![Fig. 2](image-url) Preparation of blanks by the plastic molding method. The content of water introduced into mixtures is 40 ml/100 g solid.

![Fig. 3](image-url) Change in the color of ceramics depending on the composition of the initial mixtures. $T_{\text{sint.}} = 800 \, ^\circ\text{C}, t_{\text{sint.}} = 8 \, \text{h}$. Comment: c denotes clay; g denotes glass; s denotes sand.
3.3.2. Shrinkage of blanks at sintering

In sintering, the sizes of blanks change. Their changes depend on the composition of the initial mixtures (Fig. 4).

![Fig. 4](image)

**Fig. 4.** Change in the shrinkage of ceramic specimens obtained from different mixtures.

Sintering at \( T_{\text{sint.}} = 800 \, ^\circ\text{C}, \ t_{\text{sint.}} = 8 \, \text{h} \) under conditions of oxygen deficiency.

For specimens obtained from the clay–sand mixtures, at a sand content \( \geq 50 \, \text{wt} \% \), the shrinkage gradually decreases due to the increase in the silica (quartz) content in the mixtures. However, at \( C_{\text{sand}} > 50 \, \text{wt} \% \), as a result of the formation of pores in the ceramics (see also Fig. 3), the process of deformation/"swelling" of ceramic specimens occurs. The linear sizes of the specimens increase. In Fig. 4a, these changes are as negative values of the shrinkage. As noted, the “swelling” of specimens depends on the content of phyllosilicates in the mixtures and the content of eutectic melt, in the formation of which plagioclases play a significant role.

According to Table I, with increase in the sand content in the mixtures, the content of plagioclases rises, and the content of phyllosilicates decreases. This must lead to a decrease in pore formation and partial “healing” of pores by melt.

For the ceramics obtained from the clay–glass mixtures, the shrinkage gradually decreases with increase the glass content up to \( C_{\text{glass}} = 50 \, \text{wt} \% \) (Fig. 4b). However, at \( C_{\text{glass}} > 50 \, \text{wt} \% \), due to the large content of eutectic melt, blanks lose their shape, take the form of glass mass, and, in cooling, split into fragments/debris.

The shrinkage of the ceramic specimens obtained from the ternary mixtures (Fig. 4c), as in the previous cases, depends on the silica content in billets, the amount of formed melt, and evidently depends on the porosity of specimens. This character of the shrinkage of ceramic specimens is radically different from the character of the shrinkage of similar blanks in firing in air. According to [1], with increase in the content of sand and/or glass in mixtures, the shrinkage of ceramic specimens increases, whereas in this case, it decreases. To understand this difference, it is necessary to analyze the phase composition and porosity of specimens.

3.3.3. X-ray data

The results of the investigation of the phase composition of specimens by the XRD method show (Fig. 5) that quartz and feldspars are the main crystalline phases [41-43]. With increase in the contents of sand glass in the initial compositions, the contribution of the amorphous phase to the ceramics, which is recorded as a diffuse halo in XRD patterns, increases. The data of the semi quantitative analysis of the content of these phases indicate that, depending on the composition of the initial mixtures, in the ceramics, the quartz content changes, new feldspars appear, and the content of the amorphous phase changes (Fig. 6). It can be concluded that, in sintering, the interaction processes of the components with the
participation of quartz actively proceed in the formed eutectic melt. In cooling, a material consisting of quartz, feldspars, and the amorphous phase forms.

Fig. 5. X-ray diffraction patterns of ceramics obtained from different mixtures under conditions of oxygen deficiency (a–d). \( T_{\text{sint.}} = 800 \, ^\circ\text{C}, t_{\text{sint.}} = 8 \, \text{h} \).

3.3.4. IR data

IR spectra of ceramic specimens are a superposition (Fig. 7) of the spectra of quartz, feldspars, and glass [41, 42, 44-46]. Depending on the individual contribution of one or another phase, the observed shift of the intensive absorption band ranges from \( \nu \sim 1090 \, \text{cm}^{-1} \) to \( \nu \sim 850 \, \text{cm}^{-1} \), which indicates that the content of the glass phase in specimens rises with increase in the contents of sand and glass in the initial mixtures. At the same time, in the frequency range \( \nu \sim (800–600) \, \text{cm}^{-1} \), the shape of the absorption band changes substantially. For the ceramics obtained from the initial mixtures consisting of clay and sand, the shape of the absorption band corresponds to a greater extent to that of sodium feldspar, whereas, as the content of the cullet introduced into the initial mixtures increases, it corresponds to that of potassium feldspar (see the upper right part in Fig. 7). In the case where large amounts of glass are introduced into binary and ternary initial mixtures, the IR spectra of specimens are most similar to that of the glass phase.

Thus, the IR spectroscopy data agree with the XRD data, indicating that, in sintering of blanks, interaction processes of components, which lead to both the formation of both new feldspars and the glass phase, occur.
Fig. 6. Change in the intensity of peaks of the main ceramic phases with the clay content in initial mixtures (a, a’–c, c’). (a) for the clay–sand system; (b) for the clay–glass system; (c) for the clay–sand–glass system. (1) for quartz ($2\Theta = 26.7^\circ$), (2) for feldspar 1 ($2\Theta = 28.1^\circ$), (3) for halo, (4) for feldspar 2 ($2\Theta = 21.9^\circ$), (5) for feldspar 3 ($2\Theta = 29.9^\circ$). Sintering under conditions of oxygen deficiency at $T_{sint.} = 800^\circ$C, $t_{sint.} = 8$ h.

Fig. 7. IR absorption spectra in ceramic materials obtained by sintering of mixtures: (a) clay–sand; (b) clay–glass; (c) clay–sand–glass. $T_{sint.} = 800^\circ$C, $t_{sint.} = 8$ h. Sintering under conditions of oxygen deficiency.
3.3.5. SEM and EDS results

The SEM data indicate that, after introduction of sand and cullet into ceramic specimens, the sizes of areas joined by melt increase. This is most clearly recorded in specimens obtained from the clay–glass mixtures (Fig. 8). The X-ray microanalysis data demonstrate (Fig. 9-11) that, on fractures of all specimens, predominantly Si, Al, and O are present. The amount of Ca, Mn, Mg, K, Na, and Fe is much smaller, but their distribution is relatively homogeneous, which is explained by the spread of formed melt over the whole volume of the specimen. It follows from the data of Table III that the sand and glass additives influence the change in the contents of the elements in the ceramics. Though the evaluation of the content of the elements was performed in small areas of specimens (20 ×10 μm) and is not exact for the whole specimen, we, nevertheless, can arrive at the conclusion that the Fe content depends to a substantial extent on the amount of the introduced sand, which contains the largest amount of iron oxide (see Table II). At the same time, with increase in the content of glass introduced into the initial mixtures, the iron content in the ceramics decreases because, in the used glass powder, the Fe₂O₃ content is small (see Table II).

Fig. 8. Micrographs of fractures of specimens obtained from different mixtures: (a) clay; (b) 70 wt% clay + 30 wt% sand; (c) 70 wt% clay + 30 wt% glass. \( T_{\text{sint.}} = 800 \, ^\circ\text{C}, \ t_{\text{sint.}} = 8 \, \text{h} \).
Fig. 9. Distribution of elements over the fracture surface of ceramics in the map mode. Ceramics obtained from clay. $T_{sint} = 800 \, ^{\circ}\text{C}, t_{sint} = 8 \, \text{h}$.

Fig. 10. Distribution of elements over the fracture surface of ceramics in the map mode. Ceramics obtained from the 50 wt% clay + 50 wt% sand mixture. $T_{sint} = 800 \, ^{\circ}\text{C}, t_{sint} = 8 \, \text{h}$.

Fig. 11. Distribution of elements over the fracture surface of ceramics in the map mode. Ceramics obtained from mixture 50 wt% clay + 50 wt% glass. $T_{sint} = 800 \, ^{\circ}\text{C}, t_{sint} = 8 \, \text{h}$. 

The study of the porous structure of specimens indicates (Fig. 12 a) that, at \( C_{\text{sand}} \geq 50 \text{ wt\%} \), for the binary clay–sand mixture, an increase in the porosity of the ceramics is observed. Taking into account that, in sintering, new feldspars and the glass phase are formed (as evidenced by the XRD data, IR spectroscopy data, and the vitrified appearance of specimens), we can conclude that precisely the interaction processes of the components are the source of pore formation. Exactly these processes lead to an increase in the volume of specimens (see Fig. 4 a). The ceramics sintered from the clay–sand mixtures with \( C_{\text{sand}} \geq 60 \text{ wt\%} \) can be classified with foamed ceramics. Similar results on the low-temperature synthesis (850 °C for 2 h) of mesoporous ceramics were obtained in [47].

![Fig. 12. Change in the porous structure of ceramic specimens with a large content of sand (a), glass (b), and sand + glass (c) in the initial mixtures. \( T_{\text{sint}} = 800 \text{ °C}, t_{\text{sint}} = 8 \text{ h.} \)]

In the ceramics obtained from the binary clay–glass mixtures with \( C_{\text{glass}} > 50 \text{ wt\%} \), (see Fig. 12 b), a decrease in the porosity due to a substantial increase in the content of eutectic melt and filling of a large part of open and interconnecting pores by it was noted. This ceramics is similar in properties to glass, has a low toughness, loses its shape, and readily fractures in a fast cooling regime (see also Fig. 3). Thus, it is possible to add at most 50 wt% of low-melting glass to this high-silica clay.

The character of changes in the porous structure of the ceramics obtained from the ternary clay–sand–glass mixtures is also caused by the interaction processes of the components, the evolution of vaporous and gaseous products, the increase in the content of the glass phase, and the filling of a part of formed pores by melt (see Figs. 12 c, 4 c). Undoubtedly, it is possible to extend substantially the composite composition of the initial mixtures that provide the preservation of the shape of specimens, but, in sintering, the glass phase with a low toughness must not dominate.

The appearance of the dark color of different tints of the ceramic specimens in the stationary sintering regime of different mixtures arouses particular interest (Fig. 3). As it follows from Table II, in all used initial components, the content of iron oxide is not so high.
Only in sand, the Fe$_2$O$_3$ content is ~4.3 wt%. However, the XRF method shows that the total content of iron oxide in the mixtures can attain required values. Black ceramics is usually obtained in the reduction-firing regime of clay at iron oxide content in it above 5 wt% [27]. The basis of the appearance of the dark color is a number of processes, namely, the incomplete reduction Fe$_2$O$_3$ to FeO and formation of magnetite Fe$^{3+}$Fe$_2$$^{3+}$ (Fe$_3$O$_4$), fayalite Fe$_2$SiO$_4$, and hematite α–Fe$_2$O$_3$ in bricks, and the presence of [Fe$^{3+}$O$_4$]$^{4-}$ and [Fe$^{3+}$O$_4$]$^{9-}$ anions in the composition of the glass phase and in metakaolin. According to the EDS analysis data, iron is present in all ceramic specimens (see Table III). It can be noted that the larger the total content of Fe/Fe$_2$O$_3$ in the initial mixtures, the darker the color that of the sintered brick products. This concerns the clay–sand mixtures. Correspondingly, the smaller the content of Fe/Fe$_2$O$_3$ in the initial mixtures, the lighter the color of the ceramics. This concerns the clay–glass and clay–sand–glass mixtures (see Fig. 3) because, in glass, the content of iron oxide is smallest.

Tab. III Contents of elements in ceramic specimens on an area 20 x10 $\mu$m according to EDS data.

| Components                  | Si   | Al   | O    | Ca  | Mg  | Fe   | Mn  | K    | Na  |
|-----------------------------|------|------|------|-----|-----|------|-----|------|-----|
| Clay 100%c                   | 34.99| 10.46| 42.53| 0.70| 0.80| 6.53 | 0.38| 1.82 | 1.79|
| Clay + sand 80%c+20%s        | 34.00| 10.86| 45.35| 1.26| 1.12| 3.18 | 0.56| 1.88 | 1.64|
| Clay + sand 60%c+40%s        | 36.28| 10.00| 42.49| 0.74| 0.68| 4.47 | –   | 3.15 | 2.21|
| Clay + sand 20%c+80%s        | 39.72| 7.45 | 42.40| 0.63| –   | 5.02 | –   | 2.49 | 2.28|
| Clay + sand 10%c+90%s        | 32.40| 8.80 | 42.44| 2.42| 0.75| 6.70 | –   | 2.54 | 3.94|
| Clay + glass 90%c + 10%g     | 35.09| 9.95 | 39.90| 1.18| 1.13| 6.92 | 0.56| 3.29 | 1.91|
| Clay + glass 70%c + 30%g     | 41.06| 7.26 | 37.99| 3.22| –   | 6.43 | –   | 1.36 | 2.67|
| Clay + glass 50%c+70%g       | 39.72| 7.45 | 42.40| 0.63| –   | 5.02 | –   | 2.49 | 2.28|
| Clay + glass 20%c+80%g       | 38.25| 2.06 | 43.47| 7.69| –   | 2.15 | –   | 0.55 | 5.82|
| Clay + glass 10%c+90%g       | 34.72| 2.75 | 47.83| 8.84| –   | –   | –   | 0.79 | 5.08|
| Clay + sand + glass 40%c+30%s+30%g | 42.03| 10.49| 34.60| –   | 1.85| 8.31 | –   | –   | 2.71|
| Clay + sand + glass 25%c+25%s+50%g | 43.29| 7.38 | 40.24| 4.71| –   | –   | –   | –   | 4.39|
| Clay + sand + glass 15%c+25%s+60%g | 33.37| 9.83 | 45.44| 1.18| 0.56| 5.71 | 0.40| 1.94 | 1.56|

Note: c denotes clay; g denotes glass; s denotes sand.

The question arises as to what dominant process provides dark color of specimens. In view of the fact that, at $T_{sint} = 800 ^\circ$C, a large amount of the liquid phase appears, the active reconstruction of feldspars with the participation of silica occurs, and phyllosilicates are absent, it can be concluded that the main sources of the appearance of dark color are the formation of [Fe$^{3+}$O$_4$]$^{4-}$ and [Fe$^{3+}$O$_4$]$^{9-}$ anions in the composition of the glass phase and feldspars, and the formation of Fe$_2$SiO$_4$. Since the fayalite phase was not detected in the X-ray diffraction patterns, the source of the appearance of the dark color is predominantly the glass phase and feldspars alloyed with iron ions. This is confirmed by the X-ray diffraction patterns of specimens synthesized from the mixtures with large contents of sand and/or glass (see Fig. 5).
3.3.6. Water absorption in ceramic specimens

Depending on the field of application of building ceramics (materials for external and internal walls, facing and roofing materials, etc.), different requirements on water absorption are imposed upon brick products. In the present work, it was established that, for the ceramics obtained from the binary clay–sand mixtures, the water absorption \((W)\) is about 23-25% (Fig. 13 a) at a sand content of at most 50 wt\%, which differs from the standard value for wall ceramics, for which \(W \approx (6-16)\%\). For the ceramics obtained from the binary clay–glass mixtures, with increase in the glass content up to 50 wt\%, \(W\) decreases from 8 down to 5% (Fig. 13 b). For the ceramics obtained from the ternary mixtures, as the total content of sand and glass decreases down to 50 wt\%, \(W\) decreases from 15 down to 3% (Fig. 13 c). It is possible to assume that by selection of the sand-to-glass ratio, it is possible to reduce the value of the water absorption. The water absorption of this ceramics must approach that for stone products, which will provide its application for the brickwork of the lower stories of buildings. According to the XRD and IR spectroscopy data (see Figs. 5-7, 12), these changes in \(W\) depend on the content of the amorphous (vitreous) phase in specimens. The larger the content of the amorphous phase, the smaller the water absorption because open pores are filled by liquid melt.

Fig. 13. Change in the water absorption capacity in ceramic specimens of different composition. The ceramics was obtained at \(T_{\text{sint.}} = 800^\circ\text{C}\) for \(t_{\text{sint.}} = 8\) h under conditions of oxygen deficiency.

3.3.7. Mechanical properties of ceramics

Since the compressive strength and fracture strength of building bricks depend on the content, composition, and morphology of the binder, the function of which is fulfilled by low-melting eutectic and/or the glass phase [1-3, 48], the observed changes in the compressive strength of the ceramics obtained from the clay–sand mixtures at \(C_{\text{clay}} \leq 80\) wt\% (Fig. 14 a) can be associated with the increasing deficiency of the binder (namely, the glass phase), though the fracture strength begins to decrease only at \(C_{\text{clay}} \leq 60\) wt\% (Fig. 14 a’), when quartz begins to precipitate from the eutectic melt (see Fig. 6 a), and the porosity of the ceramics increases (see Fig. 13 a). At \(C_{\text{clay}} \leq 50\) wt\%, when porous ceramics are formed (see Fig. 12 a), the compressive strength and fracture are reduced. However, such samples can be used as heat-insulating aggregates (analogue of expanded clay) [2-3].

For the clay–glass mixture, with increase in the glass content in the initial mixtures, the compressive strength increases (see Fig. 14 b) as a result of the increase in the content of melt (see Fig. 6 b) and filling the pore space by it (Fig. 13 b). However, the fracture strength decreases at \(C_{\text{clay}} \leq 80\) wt\% due to the brittleness of the glass phase (Fig. 14 b’). The ceramics obtained from the ternary mixtures is characterized by the highest strength properties (see Fig. 14 c, c’). In it, a smaller amount of quartz is contained, different feldspars form, and a sufficient amount of the glass phase, which joins quartz and feldspars and partially fills the
pore space formed in sintering, is preserved (see Figs. 5 c, 6 c, 13 c). Note that the strength properties of bricks sintered under the conditions of oxygen deficiency at \( T_{\text{sint}} = 800 \, ^\circ \text{C} \) for \( t_{\text{sint}} = 8 \, \text{h} \) do not have a standard. In [50], strength data for bricks obtained after firing in air by the traditional technology \( (T_{\text{sint}} = 1000 \, ^\circ \text{C}, t_{\text{sint}} = 24 \, \text{h}) \) are presented. The compressive strength and flexural strength are 110 kg/cm\(^2\) and 57 kg/cm\(^2\), respectively. These values are higher than those for black bricks obtained from the binary mixtures in the present work. However, as seen in Figs. 14 c, c’, by varying the composition of the ternary mixtures (clay, sand, and glass), black ceramics with high strength properties is easily obtained in the energy-saving sintering regime.

**Fig. 14.** Change in the compression (a–c) and fracture strength (a’–c’) of specimens with the composition of the initial mixtures. Sintering at \( T_{\text{sint}} = 800 \, ^\circ \text{C}, t_{\text{sint}} = 8 \, \text{h} \) in conditions of oxygen deficiency. Column 1 corresponds to standard of Guerrero State in Mexico [49], column 2 corresponds to experimental data.

4. Conclusion

The performed investigations have shown that by using high-siliceous clay and sand similar in mineralogical composition with additives of low-melting glass, it is possible to realize plastic molding of blanks.

The sintering of mixture with a total content of iron oxide of about 5 wt\% under reducing conditions at \( T_{\text{sint}} = 800 \, ^\circ \text{C} \) for 8 h leads to the formation of glass ceramics consisting of quartz, feldspars, and the glass phase. The basis of preparation of ceramics of different color spectrum (from gray to black) is diffusion of iron ions into eutectic melt.
By changing the contents of clay, sand, and glass in sintering, it is possible to obtain two types of ceramic materials: (a) in the form of building bricks; (b) in the form of porous fillers (expanded clay). To obtain products of type a, it is necessary to use the binary mixtures $x$ wt% clay + $y$ wt% sand, where $x \geq 80$ wt%; $x$ wt% clay + $z$ wt% glass, where $x \leq 50$ wt%; and ternary mixtures $x$ wt% clay + $y$ wt% sand + $z$ wt% glass, where $y + z \geq 60$ wt%. To obtain products of type b, it is necessary to use binary mixtures $x$ wt% clay + $y$ wt% sand, where $x \leq 40$ wt%.

5. References

1. M. Flores Nicolas, M. Vlasova, P. A. Márquez Aguilar, M. Kakazey, M. M. Chávez Cano, R. Arroyo Matus, T. Pi Puig, Constr. Build. Mater. 242 (2020) 118142.
2. G. S. Upadhyaya, Sci. Sintering, 50(4) (2018) 501-508.
3. P. P. Budnikov, A. S. Berezhnoy, I. A. Bulavin, G. P. Kalliga, G. V. Kukolev, D. N. Poluboyarinov, Technology of Ceramics and Refractories, State Publishing House of Literature on Construction and Architecture, Moscow, 1955.
4. A. I. Ivanov, Wall ceramic materials of compression molding from dispersed high-siliceous rocks, Dis. Ph.D., Novokuznetsk, Russia, 2018.
5. J. G. Song, F. Wang, X.B. Bai, J. Ceram. Process. Res. 12(2011) 357-360.
6. Mei Hua Chen, Yan Yang, Wang Chen, Jie Guang Song, Yue Liu, Xin Shuang Guo, Lin Chen, Song Lin Guo, Yue Ning Qin, Effect of Molding Method on the Properties of Prepared Quartz Sand Sintered Brick Using the River Sand, Solid State Phenomena Metallurgy Technology and Materials VI, Edited by: Nor Sabirin Mohamed, 261-265, 2018. https://doi.org/10.4028/www.scientific.net/SSP.279.261
7. W. D. Nesse, Introduction to Mineralogy, 2nd Edition. Oxford University Press, 2011.
8. W. A. Deer, R.A. Howie, J. Zussman, An Introduction to the Rock-Forming Minerals, 2nd Edition. Prentice Hall, 1996.
9. J. Ajala Amkpa, N. Azam Badarulzaman, A. Bakar Aramjat, Intern. J. Engineer. Techn. (IJET), 8(6) (2016) 2588-2593.
10. S. Kitouni, A. Harabi, Cerâmica. 57(344) (2011) 453-460.
11. J. Ajala Amkpa, A. Edogbo Aye, F. Enefola Omagu, Traektoriâ Nauki = Path of Science, 3(4) (2017) 6.15-6.20.
12. P. H. Ribbe, Feldspar. In: McGraw Hill Encyclopedia of Science & Technology, 10th Edition. McGraw-Hill, v. 7. 45-49, 2007.
13. H. J. Alves, F.G. Melchiades, A.O. Boschi, J. Europ. Ceram. Soc., 32 (10) (2012) 2095-2102.
14. F. Burat, O. Kokkilic, O. Kangal, V. Gurkan, M.S. Celik, Min. Metall. Process. 24 (2) (2007) 75-79. ABI/INFORM Trade & Industry.
15. Kr. D. Swapans Das, D. Kausik, Thermochim. Acta, 406 (1-2) (2003) 199-206.
16. R. Sokolârâ, L. Keršnerovâ, M. Šveda, J. Asian Ceram. Soc. 5 (3) (2018) 290-294.
17. D. Gouvêa, Taisa Tisse Kaneko, H. Kahn, E. de Souza Conceição, J. L. Antoniassi, J. Ceram. Intern. 41(2015) 487-496.
18. K. Belhoucuet, A. Bayadi, H. Belhoucuet, M. Romero, Cerâmica y vidrio, 58 (2019) 28-37.
19. S. Yuruyen, H. O. Toplan, J. Ceram. Int. (35) (2009) 2427-2433.
20. F. Matteucci, M. Dondi, G. Guarini, J. Ceram. Int. 28 (2002) 873-880.
21. R. G. Eromasov, Fundamental research. 8 (part 6) (2013) 1312-1316.
22. P. Muñoz-Velasco, M. P. Morales-Ortíz, M. A. Mendívil-Giro, L. Muñoz-Velasco, Constr. Build. Mater. 63 (2014) 97-107.
23. V. Mymrin, M. J. J. S. Ponte, H. A. Ponte, N. M. S. Kaminari, U. Pawlowsky, G. J. P. Solyon, Constr. Build. Mater. 41 (2013) 360-364.
24. A. A. Shakir, S. Naganathan, K. N. Bin Mustapha, Australian J. Basic and Appl. Sci., 7(8) (2013) 812-818.
25. A. A. Shakir, S. Naganathan, K. N. Mustapha, Constr. Build. Mater. 41 (2013) 131-138.
26. Y. Pontikes, C. Rathossi, P. Nikolopoulos, G. N. Angelopoulos, D. D. Jayaseelan W. E. Lee, J. Ceram. Intern. 35 (1) (2009) 401-407.
27. K. A. Verevkin, Ceramic facing brick based on highly iron clays of reduction firing, Ceramic facing brick based on highly iron clays of reduction firing, Ph.D. Thesis, Rostov-on-Don, Russia, 2011.
28. Reduction and Ceramic Firing by Smart Conseil. https://smart2000.pagesperso-orange.fr/reduction_eng.htm
29. G. Conway, Pottery Reduction Firing with a Fuel-Burning Kiln, LEONARDO, 9 (2) (Spring, 1976) 89-93. 10.2307/1573113. https://www.jstor.org/stable/1573113
30. ASTM C773-88. Standard test method for compressive (crushing) strength of fired whitewares materials. West Conshohocken, PA: ASTM International; 2002.
31. ASTM C161-02c(2008)e1. Standard Test Method for Flexural Strength of Advanced Ceramics at Ambient Temperature, ASTM International, West Conshohocken, PA.
32. C. Klein, C. S. Hurlbut, Jr., Manual of Mineralogy, New York, John Wiley & Sons, 1999.
33. A. M. Hofmeister, G. R. Rossman, Color infeldspars. In: Feldspar Mineralogy (P.H. Ribbe, editor). Mineralogical Society of America, Washington, D.C. 1983.
34. A. Putnis, R. Hinrichs, C. V. Putnis, U. Golla-Schindler, L. G. Collins, Lithos, 95 (2007) 1018.
35. W. L. Roberts, T. J. Campbell, and G. R. Rapp, Encyclopedia of Minerals (Second edition) Van Nostrand, Reinhold, New York, 1990.
36. A. Mizune, R. Rehamnia, Phosphorus Research Bulletin, 27 (2012) 018-022.
37. M. Dondi, M. Raimondo, C. Zanelli, Appl. Clay Sci., 96 (2014) 91-109.
38. M. P. Groover, Fundamentals of modern manufacturing: materials processes, and systems. John Wiley & Sons, 2010.
39. A. Parra Parra, M. Vlasova, P. A. Márquez Aguilar, T. Tomila, Sci. Sinter. 49 (2017) 207-224.
40. F. Wang, J. G. Song, M. H. Xu, Key Eng. Mater. 697 (2016) 423-426.
41. Weiqing Wang, Jinyao Cong, Jie Deng, Xiaqing Weng, Yiming Lin, Yang Huang, Tiefeng Peng, Minerals, 8 (149) (2018).
42. S. Shakhatreh, J. Mater. Sci. Res. 4 (2) (2015) 22-33.
43. D. Moore, R. C. Reynolds, Jr., X-Ray Diffraction and the Identification and Analysis of Clay Minerals, 2nd ed., Oxford University, 1997.
44. I. I. Plyusnina, Infrared spectra of silicates, Moscow University Publishing House, Moscow, 1957 (in Russian).
45. F. Bosch-Reig, J. V. Gimeno-Adelantado, F. Bosch-Mossi, A. Doménech-Carbó, Spectrochimica Acta. Part A: Molecular and Biomolecular Spectroscopy, 181 (2017) 7-12.
46. W. R. Taylor, Proceed. Indian Acad. Sci. - Earth and Planetary Sciences, 99 (1) (1990) 99-117.
47. N. Kamoun, F. Jamoussi, M.A. Rodríguez, Cerámica y Vidrio, 59 (2020) 25-30.
48. Pallan Nur Fadilah Baharuddin, Matori Khamirul Amin, Hashim Mansor, Azis Raba’ah Syahidah, Zainuddin Norhaizlin, Pallan Nor Faizah Baharuddin, Idris Fadzidah Mohd, Ibrahim Idza Riati, Wah Loy Chee, Rusly Siti Nor Ain, Adnin Noorfauzana, Khiri Mohammad Zulhasif Ahmad, Alssan Zarifah Nadakkavil, Mohamed Nurzilla, Zaid Mohd Hafiz Mohd, Sci. Sinter. 51(4) (2019) 377-387.
49. J. C. Adame, Comparacion de la calidad de ladrillos de arcilla y el tabicón de concreto, que utiliza para la mamposteria en el Municipio de Chilpancingo, Guerrero, 2008.
50. Standard specification for building brick. Norma Mexicana NMX-C404-ONNCCE-2012.

Саметак: У овом раду проучавани су фазна реконструкција и својства керамике добијене из смеша глина-песак, глина-стакло и глина-песак-стакло. Могуће је спровести пластично обликовање датих смеша услед присуства монтморилонита у глини и песку при синтеровању на 800 °C током 8 h уз одсуство кисеоника. У зависности од састава почетне смеше, узорци варирају у боји од сиве до црне. Реногено-структурна анализа, инфра-црвена спектроскопија и електронска микроскопија синтетисаних материјала су утврдиле да се керамика састоји из кварца, гелдспара и стакласте фазе. У зависности од садржаја почетних компоненти у смешама, могуће је добити стакласту керамику високе чврстости или грубо-порозне стакласте керамике чија су својства слична са својствима пенасте керамике.

Клучне речи: глина, песак, стакло, синтеровање, керамичка својства.