Bochkarihinskoe clay as raw material to building ceramics production

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Abstract. The possibility of using clay from Bochkarihinskoe deposit (Sverdlovskaya oblast, Russia) in the ceramic building production has been considered. The chemical, mineral and granulometric composition of clay was determined. The basic technological properties of clay were studied: plasticity, sensitivity to drying, sintering. The frost resistance and mechanical properties of ceramic brick samples were determined. The clay studied with introduction of organic additives also may be used in ceramic production.

1. Introduction

The present work is devoted to expanding the raw materials resources for the production of building materials, specifically an investigation of Bochkarihinskoe clay in order to determine the possibility of using it in the production of ceramics. Along with refractory clays in the area of the Bogdanovich town in the Sverdlovsk region there are types of red-burning clay [1]. These clays are not utilized in the production of refractories, but they can be used in the production of other, cheaper types of ceramics. The Bochkarihinskoe clay is one of the varieties of such clays [2].

Red-burning clay is most often used in the manufacture of ceramic bricks [3–12]. In connection with this, it is of interest to study the properties of Bochkarihinskoe clay in the production of ceramic bricks and other types of building ceramics [13-14].

2. Experimental procedure

The chemical composition and the mineral composition of the clays was studied by means of differential scanning calorimetry using an STA 449 F3 Jupiter calorimeter (Netzsch G. GmbH, Germany) and by means of XPA using a Miniflex 600 diffractometer (rotating anode; CuKα radiation; λ = 1.541862 Å; measurement interval 3.00-90.00°; scan step 0.02°) Rigaku – Carl Zeiss (Japan) with MiniFlex guidance software for control and data collection and a PDXL Basic package for data processing. The JSPDS database was used to identify the diffraction peaks. To determine the chemical analysis, we used emission spectral analysis with inductively coupled plasma on the Optima 4300 DV (PerkinElmer, USA).

The plasticity number of the clays according to the Vasil’ev method [15], coefficient of sensitivity of the clays to drying according to Nosova’s method are tested in this study. The water absorption, porosity and apparent density were determined in accordance with [16], the density – in accordance with [17], the compressive strength – [18]. Frost resistance was determined by an indirect method using the formula: \( G = B_1/B_2 \), where \( B_1 \) – water absorption of samples determined according to [19];
B2 – water absorption determined after boiling for 4 hours with further cooling to room temperature. Frost-resistant brick is when the value of the coefficient G is less than 0.85.

3. Results and discussion
The chemical composition of clay is presented in Table 1.

| Material          | LOI   | SiO₂  | Al₂O₃ | Fe₂O₃ | CaO   | MgO   | Na₂O  | K₂O  | TiO₂ |
|-------------------|-------|-------|-------|-------|-------|-------|-------|------|------|
| Dry matter        | 9.03  | 64.84 | 11.65 | 7.16  | 2.70  | 1.23  | 0.82  | 1.54 | 0.72 |
| Calcined matter   | –     | 71.30 | 12.81 | 7.87  | 2.97  | 1.35  | 0.90  | 1.69 | 0.79 |

The Al₂O₃ content of the clay shows the Bochkarikhinskoe clay to be acidic raw material. In terms of the content of coloring oxides the clay is raw material with high content of coloring oxides.

The granulometric composition of clay of the Bochkarikhinskoe deposit is presented in Table 2. According to the fracture content of size < 0.01 mm the clay studied is a medium-disperse raw material, and according to the fracture content of size < 0.001 mm it is a low-disperse raw material.

| Parameter          | Weight content (mm) |
|--------------------|---------------------|
| 0.25–0.06          | 0.06–0.01           |
| 0.01–0.005         | 0.005–0.001         |
| < 0.001            |                     |
| Weight content of fraction (%) |           |
| 15.96              | 22.59               |
| 12.73              | 14.54               |
| 34.18              |                     |

According to the content of coarse-grained (> 0.5 mm) inclusions (14.9%) the clay from Bochkarikhinskoe deposit is a raw material with a high content of coarse-grain inclusions (Table 3). In terms of the size of the inclusions the clay belongs to a class of raw materials with small inclusions (62.4% particles of size 1–0.5 mm).

The inclusions in clay are represented predominately by quartz sand with rare carbonate inclusions of dolomite.

| Parameter          | Weight content of fraction (%) of size (mm) |
|--------------------|-------------------------------------------|
| 1–0.5              | 2–1                                       |
| 3–2                | 5–3                                       |
| > 5                | Total                                     |
| with particles of size < 0.5 mm | 9.3  | 2.2  | 1.8  | 0.5  | 1.1  | 14.9 |
| without particles of size < 0.5 mm | 62.4 | 14.8 | 12.1 | 3.4  | 7.4  | 100.0 |

According to the DTA data the clay contains montmorillonite, dolomite and quartz. Total weight loss under firing up to 1200°C is 16.3 wt%. X-ray phase analysis was conducted mainly to determine the composition of the impurity mineral phases. The presence of calcium-containing minerals – dolomite and anorthite is established. However, both mineral phases are crystalline. They form highly porous granules within which other impurities are located, for example, quartzite. Both calcium-containing phases are approximately equal.

According to the plasticity number (P = 13), air shrinkage (Sₐ = 9.8%) and coefficient of sensitivity to drying (Kₐ = 3.5), the clay under study is medium plastic, poorly drying and low-sensitive to drying.
The relation of Bochkarikhinskoe clay to sintering is studied under firing in temperature range of 850–1050°C. The clay was ground to a grain size of less than 3 mm. The body with optimal molding moisture (W = 27%) has been prepared and 35×30 mm 15 samples were molded. The properties of fired samples are presented in Table 4.

### Table 4. Post-firing properties of the samples.

| Firing temperature (°C) | Shrinkage (%) | Water absorption (%) | Open porosity (%) | Apparent density (kg·m⁻³) | Frost resistance | Compressive strength (MPa) |
|-------------------------|----------------|----------------------|-------------------|-----------------------------|-----------------|-----------------------------|
|                         | total          | fire                 |                   |                             |                 |                             |
| 850                     | 7.4            | 0.8                  | 10.5              | 20.9                        | 1990            | 1.17                        | 41.2                        |
| 900                     | 8.2            | 1.6                  | 10.5              | 21.1                        | 2020            | 1.15                        | 47.2                        |
| 950                     | 9.0            | 2.5                  | 7.2               | 14.9                        | 2150            | 1.05                        | 52.1                        |
| 1000                    | 9.0            | 2.5                  | 8.1               | 16.7                        | 2080            | 0.96                        | 26.9                        |
| 1050                    | 8.9            | 2.4                  | 7.4               | 15.2                        | 2050            | 0.97                        | 21.4                        |

As the temperature increases up to 950°C the density of the samples increases from 1.99 to 2.15 g/cm³, the compressive strength increases from 41.2 to 52.1 MPa, at the same time water absorption decreases from 10.5 to 7.2% and porosity decreases from 20.9 to 14.9%.

A further increase in the firing temperature leads to structure loosening, which is confirmed by a decrease in density from 2.15 to 2.05 g/cm³ during firing in the temperature range of 950–1050°C. It also decreases the strength from 52.1 to 21.4 MPa. The shrinkage of the samples increases with firing in the range of 850–950°C, with a further increase in temperature no shrinkage of the samples is observed. All samples calcined in the range of 850–950°C are non-frost-resistant, although an increase in the frost resistance of the samples with an increase in the calcination temperature is observed.

All clay samples have white inclusions – “blowing” associated with dolomite decomposition and formation of both magnesium oxide and calcium oxide. “Blowing” because of interaction with water, increases in volume and destroy the structure of the ceramic product. All samples after firing have a bright orange color.

All samples have a black core. As the temperature increases the black core becomes more pronounced. This is associated with the burning of organic impurities from clay, as well as the decomposition of carbonate inclusions. The access of oxygen to the central part of the samples during firing becomes complicated with the appearance on the surface of the samples of an impermeable layer resulting from the sintering process. In this regard, a reducing atmosphere and carbon deposition in the pores of the samples occurs inside the sample. Even though sufficiently durable samples were obtained, in accordance with [20] grade M 200 and higher, the production of ceramic bricks based on clay from the Bochkarikhinskoe deposit is complicated by a high content of carbonates and the formation of “blowing”, as well as black core.

To eliminate such a defect, it was proposed to carry out more fine grinding of clay to a size of < 0.5 mm. Samples of this clay were molded and fired in the temperature range of 900–1000°C. The properties of Bochkarikhinskoe clay samples are presented in Table 5.

As the temperature increases in temperature range of 900–1000°C the fire shrinkage increases from 1.5 to 3.2%, total shrinkage increases from 8.1 to 9.6%, the density increases from 2.00 to 2.06 g/cm³, the compressive strength increases from 19.0 to 42.7 MPa, at the same time the water absorption decreases from 10.3 to 8.5% and open porosity decreases from 20.6 to 17.5%. All samples are not frost-resistant, although as the firing temperature increases the frost resistance increases.
Table 5. Post-firing properties of the samples of Bochkariikhinskoe clay.

| Firing temperature (°C) | Shrinkage (%) | Water absorption (%) | Open porosity (%) | Apparent density (kg·m⁻³) | Frost resistance | Compressive strength (MPa) |
|-------------------------|---------------|----------------------|------------------|--------------------------|-----------------|---------------------------|
|                         | total         | fire                 |                  |                          |                 |                           |
| 900                     | 8.1           | 1.5                  | 10.3             | 20.6                     | 2000            | 0.99                      | 19.0                      |
| 950                     | 8.9           | 2.4                  | 10.4             | 17.1                     | 2040            | 0.95                      | 34.7                      |
| 1000                    | 9.6           | 3.2                  | 8.5              | 17.5                     | 2060            | 0.92                      | 42.7                      |

No “blowing” defects of samples is observed. Small grains of calcium and magnesium oxides after dolomite decomposition are transferred to the glass phase, which improves the quality of the samples. All samples have a black core.

In addition, the clay studied can be recommended to produce expanded clay since when it is fired, a black core is formed. To increase the coefficient of expansion, it is necessary to introduce organic materials in the form of, for example, technical oil [1].

Conclusion
In summary, clay from Bochkariikhinskoe deposit is suitable for obtaining ceramic brick with a compressive strength of more than 10 up to 40 MPa. To eliminate the appearance of “blowing”, the clay must be thoroughly ground to a grain size of < 0.5 mm to turn calcium and magnesium oxides after the dolomite decomposition into the glass phase. Even though the black core does not affect the strength and appearance of the brick, its presence is still undesirable in finished products. To eliminate it, it is necessary to introduce additional components into the composition of masses to produce bricks. The obtained brick samples have low frost resistance, and therefore it is necessary to conduct additional studies on the compliance of frost resistance with the requirements of national standard.

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