Resource-saving technology of ceramic brick production with nickel slags of Orenburg Region

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Abstract. The paper considers the problem of using technogenic products in the production of construction materials thus obtaining ceramic products with specified properties both in Russia and abroad. It provides data on chemical and mineralogical composition of initial raw materials, defines pre-calcination and calcination properties of clay and nickel slag. Compositions with different percentage of clay/slag are developed and two-factor experiment is carried out, where the first factor is the percentage of slag in a sample, while the second factor is the sintering temperature of samples. The diagrams show the influence of material composition of clay/slag charge mixture on compression strength, water absorption and density of test samples after firing at a temperature of 900, 950, 1000 and 1050 °C. The obtained results allowed identifying the need for sintering of masses from clay of Khalilovsky deposit with nickel slags of OAO Yuzhuralnickel of Orenburg Region in the production of ceramic brick.

1. Introduction

Every day, huge amounts of raw materials are extracted worldwide and are used for processing and construction of industrial and residential buildings and structures thus spending kilowatts of electricity and non-renewable resources. Resource saving in all areas of human activity was one of the most key tasks of the modern industry. The construction industry, as one of the most material-intensive, needs resource-saving technologies. The paper studies the development of basic compositions of charge with nickel slags of Orenburg Region in the technology of ceramic brick production. These developments are necessary for the production of quality materials thus reducing the costs of extraction, transportation, processing of primary mineral raw materials, regulating their properties by introducing additives – various by-products (wastes) of industry.

Orenburg Region has the richest mineral reserves and fertile lands. The region has large deposits of gas, oil, ores, ferrous and non-ferrous metals, construction and decorative stone, ceramic clays, carbonate and silica rocks, brick and refractory clays, etc. Considerable reserves of mineral raw materials and fuel resources triggered the development of mining and processing industries [1]. Most of all non-ferrous metals in Russia are extracted in the Urals. The geographical location of Orenburg Region links it with developed non-ferrous metallurgy having large deposits of copper, nickel, aluminum, etc. The enterprises that develop such deposits besides non-ferrous metals produce tons of waste that are stored occupying huge areas and causing damage to the environment. Therefore, the problem of developing methods of recycling and reutilization of industrial waste is relevant for Orenburg Region. As a result of the processing of unused slags of nonferrous metallurgy into the
production of construction materials the development of waste disposal technologies will increase the profitability of processing plants and provide the construction industry of Orenburg Region with affordable quality materials. The disposal of these wastes will minimize the impact of slag deposits on the environment, solve social and economic problems. The use of non-ferrous metallurgy wastes is one of the efficient ways of saving natural materials.

The lack of primary resources such as high-quality clays forces scientists around the world to develop ceramic brick production technologies using accumulated waste. The reduction of high-quality natural raw material reserves at the accumulation of technogenic products makes the problem of using wastes as secondary raw materials in production of construction ceramics relevant [2]. Scientists of different countries studied the use of copper-nickel ores, copper-nickel production slags, etc. as additives to ferro-chromium slag charge mixture, zeolite of apatite-nepheline ores mill tailings [3–10].

A great contribution to the development of technological principles for improving the quality of ceramic products was made by the following domestic scientists: A.I. Avgustinik, P.P. Budnikov, I.I. Moroz, R.Z. Rakhimov, L.L. Maslennikova, I.F. Schlegel, P.I. Bozhenov, etc.

V.Z. Abduraev and his co-authors described the technology of ceramic brick production with the addition of phosphorus slag to the charge [3, 4].

Turkish researchers from Bartin University [5] studied the influence of ferro-chromium slag and zeolite and their various combinations on physical, mechanical properties and microstructure of bricks.

2. Methods and materials
Clays of Khalilovsky deposit and slags of OAO Yuzhuralnickel Plant (Kempirsaisky massif, Orenburg Region) were selected for the study.

The experiments were based on the standard methods to study compositions and technological properties of raw materials. Mineralogical and chemical analyses were performed to study compositions of clay raw materials and slag wastes. The reparation of raw materials, development of prepared mixtures, drying and burning of samples were carried out according to standard enterprise methods.

3. Results
Earlier studies on the production of ceramic bricks from clays of Alimsaisky deposit and nickel slags showed the prospect of using this kind of slag for the production of ceramic bricks [11].

Based on the results of the study the clay of Khalilovsky deposit was chosen for this experiment [11]. At the same time, the condition of haulage was assumed. The Alimsaisky clay deposit is located at a distance of 300 km from the dumps of nickel slags, in turn the distance to Khalilovsky deposit is only 40 km. Closer territorial location to slag dumps in case of good technological properties of clays will make it possible to significantly reduce the transportation costs for the delivery of raw materials in the future.

The Khalilovsky group of iron ore deposits is located in Orenburg Region on the eastern slopes of the Southern Urals (Figure 1). The total reserves of iron ores with 30–40 % Fe content exceed 310 million tons. Khalilovsky deposit is characterized by quite thick capping and adjacent rocks represented by clay rocks. Khalilovsky clay deposit is promising for use in ceramic brick production.

Until now, clay is the main component in the raw material charge for the production of ceramic products, so it is extremely important to assess its compositions and processing properties. The assessment of clay quality and its suitability for ceramic production in the course of the study was carried out on the basis of laboratory tests. At the first stage, chemical and mineralogical compositions of Khalilovsky clay deposit were analyzed. Figure 2 shows the chemical composition.

In terms of alumina content (Al₂O₃) the clay of Khalilovsky deposit belongs to the group of acid argillous raw materials. According to the content of iron oxides (Fe₂O₃ > 3 %) – to a group with high content of coloring oxides. The largest component in the clay under study is quartz, which is present in clay in bound and free form. SiO₂ share – 49.5 %.
The Okhotin diagram was used to define the type of clay of Khalilovsky deposit – loam (Figure 3).

**Figure 1.** Khalilovsky group of deposits, Gaisky district, Orenburg Region, Southern Ural, Russia

**Figure 2.** Chemical composition of Khalilovsky clay deposit

**Figure 3.** Okhotin diagram for clay of Khalilovsky deposit
The mineral composition of clay rocks was defined via X-ray diffraction method. The X-ray phase analysis of clay test samples of Khalilovsky deposit allowed establishing that the clay is polymineral, chlorite-illite-kaolinite with admixed quartz.

The samples were made from the clay of Khalilovsky deposit, and pre-calcination and calcination properties were studied [12]. The results are shown in Table 1.

| Pre-calcination properties of clay raw material | Relative molding-moisture content, % | Plasticity | Drying sensibility factor |
|-----------------------------------------------|-------------------------------------|------------|--------------------------|
|                                               | 6.25                                | II=27 (high plasticity) | 0.23 (low plasticity) |
| Calcination properties of clay raw material   | Water absorption, % | Potsherd density, g/cm³ | Compression strength, MPa |
|                                               | 9.5                                 | 1.73       | 10.5                     |

The use of technogenic dumps – unused non-crystalline nickel-containing slags of the South Ural Nickel Plant (OAO Yuzhuralnickel Plant) was studied as the second component of the charge. It is a large Russian non-ferrous metallurgy enterprise, whose share in the world nickel production is more than 1 %. It is located in Orsk, Orenburg Region.

Figure 3 shows the chemical composition of slag samples taken at OAO Yuzhuralnickel Plant.

![Figure 4. Chemical composition of slags of OAO Yuzhuralnickel Plant](image)

The method of mathematical multi-factor analysis was used in the planning of the experiment. Clay composition from Alimsaisky deposit and nickel slags of OAO Yuzhuralnickel Plant were used as samples. At the first stage, the main factors influencing the properties of ceramic item are selected: \( X_1 \) – slag content in a two-component charge in the amount of 5–40 % and \( X_2 \) – firing temperature, 900–1050 °C.

Based on clay plasticity (\( P = 27 \)) the method of sample forming was adopted – plastic (Figure 4).

According to the design matrix 4 compositions were developed: composition 1 (slag – 5 %, clay – 95 %, burning temperature – 900 °C), composition 2 (slag – 40 %, clay – 60 %, burning temperature – 900 °C), composition 3 (slag – 5 %, clay – 95 %, burning temperature – 1050 °C) composition 4 (slag – 40 %, clay – 60 %, burning temperature – 1050 °C).

The tests were carried out on samples measuring 2x2 cm, 6 samples of each composition in a series of tests.

In order to carry out the experiment and process the obtained data, a mathematical model was obtained in the form of a second order polynomial for each characteristic of an item.
where \( a_0; a_1; a_2; a_3; a_4; a_5 \) – beta coefficients; \( X_1 \) – slag content in charge, \%; \( X_2 \) – firing temperature, °C.

\[
Y = a_0 + a_1 X_1 + a_2 X_2 + a_3 X_1^2 + a_4 X_2^2 + a_5 X_1 X_2.
\]  

(1)

**Figure 5**: a) as-formed samples; b) samples dried for 48 hours at 20 % relative humidity and 22 °C

Compression strength, MPa, water absorption, %, average density, g/cm³ are used as optimization parameters. The selection of these parameters is based on their significant influence on structure formation of ceramic products and operational properties, which ensures the duration of ceramic operation under fixed conditions [13].

After processing the results, the beta coefficients were determined (Formulas 2–4) and the mathematical models of the optimization parameters were constructed (Figures 6–8).

\[
W = 17.4 - 1.43X_1 - 0.94X_2.
\]  

(2)

**Figure 6.** Change of water content depending on clay/slag ratio

When calculating the compression strength of the samples by the volume of standard size brick, we took 60 % of the volume specified on the diagram (Figure 8).

4. Conclusion

The analysis of data in the diagrams (Figures 6–8) shows that the increase in the slag content of the charge leads to the increase in water absorption. At the lowest studied temperature equal to 900 °C, water absorption increases with the growth of slag fraction in a charge from 16.9 to 20.24 %.

At a temperature equal to 1050 °C the slag content in a charge increases from 15.04 to 18.38 %. In general, water absorption in experimental samples exceeds the recommended technological interval, which for common brick makes 12–14 %, for ashlar brick – 8–10 %. 
Besides, the increase of slag content in a charge contributes to the reduction of the following parameters: compression strength, average density. This is caused by the fact that at a firing temperature of 900–1050 °C the fracture density of slag increases thus increasing its effective porosity. Structural changes in slag composition lead to the fact that with the increase in the amount of technogenic raw material (nickel slag) in a charge regardless of the clay component properties the effective porosity and water absorption of a ceramic product as a whole increase.

\[ p = 1.69 + 0.08x_1 + 0.06x_2 \] (3)

**Figure 7.** Change in average density depending on clay/slag ratio

\[ R_s = 24.67 + 4.4x_1 + 2.6x_2 \] (4)

**Figure 8.** Change in compression strength depending on clay/slag ratio

These studies serve as the basis for further development of ceramic brick production technology with the use of clay raw materials and technogenic wastes – nickel slag, and ensure the production of a rational charge with directional structure formation of ceramic brick.

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