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Evaluation of Siliceous Opal-Cristobalite Rocks for the Production of Wall Ceramics

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Abstract. To ensure the development of the industry of wall ceramic materials, it is necessary to expand the raw material base by involving siliceous opal-cristobalite rocks - gaize, diatomites and tripoli, which are an almost ready-made raw mix for the production of ceramic products. To select a production technology and form the structure and quality indicators of finished products, a comprehensive methodology for assessing both the natural properties of these rocks and the technological ones that determine the choice of technology for preparing raw materials and molding products, as well as the properties of future products. This article discusses the main criteria for evaluating siliceous opal-cristobalite rocks as raw materials for the production of various types of building ceramics and presents the dependences of the types of opoka-like rocks, molding methods and the range of wall ceramic products. Ceramic materials obtained on the basis of gaize rocks are presented both in laboratory conditions and in brick factories.

Keywords: Brick · Raw materials · Technology · Methodology · Evaluation · Classification · Siliceous opal-cristobalite rocks · Structure · Properties

1 Introduction

The development of the wall ceramics industry in Russia has led to the fact that a wide range of products is now on the market - from ordinary solid bricks to elite hand-molded bricks, product formats from European WDF (clinker brick) to 15.6NF (ceramic block). The presented products meet the requirements of regulatory and design documentation for compressive and bending strength, density, frost resistance, water absorption, acid resistance, thermal conductivity and appearance [1–5]. Wall ceramic materials are used both for private low-rise construction and for complex development of districts and quarters, as well as industrial and cultural facilities.

As a raw material for the production of bricks, blocks, crossbars, enterprises use clays, loams, mudstones, slates, various industrial wastes and additional materials. The main volume of products is produced using plastic molding technology, but at the same time, products manufactured using compression molding and soft molding (“hand molding” technology) do not lose their positions”) [6–9].

Increasing production volumes and improving product quality, expanding the range of wall ceramic materials, tightening legislation in the field of subsoil use in terms of

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transferring agricultural land to industrial use, the logistics component of raw materials in the cost of production, have led to the fact that plants are already conducting advanced research and checking previously received scientific results on the expansion of the raw material base while maintaining the properties of products and using existing production capacities [10, 11].

Siliceous opal-cristobalite rocks are widespread in the European part of Russia and Western Siberia. Explored reserves and predicted resources amount to several billion cubic meters [12]. Their feature is the presence of opal or opal-cristobalite silica in the composition and a finely porous structure, which predetermines a low density - on average from 800 to 1400 kg/m3. According to structural features, diatomites, tripoli, gaize, siliceous clays, spongolites, radiolarites are distinguished among siliceous rocks, among which, in turn, clayey, carbonate and other varieties are distinguished according to the features of the material composition. Spongolites and radiolarites are much less common [13]. The chemical composition is characterized by a high content of silica, but basically it is similar to the chemical composition of loams - the main raw material for the production of ceramic products (Table 1).

Molding boxes are distinguished by the widest distribution and wide diversity associated with the presence of clay minerals and finely dispersed calcium carbonate in various amounts [14, 15]. A distinctive feature of gaize from tripoli and diatomites is their higher density (1100–1800 кг/м^3), strength and, which is important for ceramic technology, non-wetting or poor soakability in water.

In the 70s of the last century, scientists from All-Union Scientific Research Institute of Building Materials and Structures, and at the beginning of this century, scientists from the Rostov State University of Civil Engineering and Don State Technical University carried out a lot of work to obtain various types of building ceramics based on siliceous rocks and, above all, gaize, as their most common type [16]. However, gaize and their varieties in the production of building ceramics, despite the positive laboratory, technological and factory results, have not yet been widely used.

The main factors are:

- lack of classification of rocks according to technological properties, which are determined by the chemical and mineralogical composition and structural features;
- lack of generally accepted methods for evaluating rocks as a raw material base for the production of certain types of wall ceramic products;
- lack of fields prepared for development;
- lack of technological developments and recommendations for the production of certain types of wall ceramic products.

According to the results of a literature review, opal-cristobalite rocks were previously used more widely, in particular for obtaining lightweight bricks. Back in 1932, industry standard (IS) 4728 was introduced for lightweight solid bricks. According to this document, a lightweight solid building brick was "an artificial solid stone of fixed shapes and sizes, made by molding and firing from mixtures of clay with varieties of tripolite and other diatomaceous earths, or only from varieties of diatomaceous earths". Brick with a density of 600 to 1200 kg/m^3 was produced. The quality of bricks for individual characteristics should have corresponded to the indicators indicated in Table. 2.

Table 1. Average chemical composition of siliceous rocks and loams

Breeds	Ignition losses	SiO2	AI2O3	Fe2O3 +FeO	CaO	MgO	SO3 cum	K_2O	Na_2O
Diatomites	2.6–13.0	62.2–93.6	2.1–21.8	0.4–6.7	0.2–6.8	0.2–2.4	0.1–1.9	0.1–1.5	0.2–1.8
Berg-meals	1.8–22.6	66.2–84.7	2.7–18.6	0.2–5.6	0.3–22.1	0.1–1.8	0.01–1.6	0.4–1.5	0.12–0.9
Gaize	2.3–22.5	52.1–89.8	3.2–14.5	1.0–6.6	0.4–25.2	0.03–5.6	0.1–1.2	0.6–3.08	0.2–1.79
Siliceous clays	3.5–18.4	51.2–69.7	9.6–17.3	2.7–5.2	0.6–14.3	0.4–3.8	0.1–1.2	1.6–3.5	0.8–2.2
Loams	4.3–12.9	58.6–79.0	5.8–18.1	3.2–9.9	1.4–24.2	0.02–3.3	0.1–1.2	1.2–3.9	1.2–3.4

Table 2. Requirements for lightweight solid brick according to IS 4728

Name of quality or lack	Grade 1	Grade 2	Grade 3	Grade 4
Average brick weight, no more	2.4 kg	2.0 kg	1.5 kg	1.2 kg
Average temporary compressive strength (kg/cm^2), not less than	A100 B70 V50 G35	A60 B60 V40 G30	A60 B50 V35 G22	A40 B30 V23 G15
Frost resistance	Depending on working conditions			

There was also a separate state standard (SS) 648–73 "Brick and building stones from tripoli and diatomites." In SS 530 "Brick and ceramic stones. Specifications" editions of 1980, 1995, 2007 and 2012 expressly state that siliceous sedimentary rocks can be used as raw materials for the production of bricks.

After analyzing the situation, we decided to consider the existing methods for evaluating raw materials for the ceramic industry, choose siliceous opal-cristobalite rocks - gaize as raw materials and determine the conditions for developing a methodology for evaluating siliceous opal-cristobalite rocks for the production of wall ceramics.

2 Methods and Materials

The gaize are distinguished by a variety of chemical and mineralogical composition, which determines the properties of the resulting products and the choice of the optimal production technology. At one time, according to the material composition and technological features, we identified 8 varieties of siliceous rocks - gaize: low-clay; medium clay; clay; low-clay carbonate; medium clay carbonate; clayey carbonate; low-clay high-carbonate; medium clay high carbonate. The classification features in this classification are the content of opal silica, the content of clay minerals and the content of carbonates. Low-clay, non-carbonate gaize are considered classic. The composition naturally affects the physical and mechanical properties and the properties of the resulting products, the variety of which has significantly expanded in recent decades. On Fig. 1 shows a view of the deposit of carbonate molding boxes.

We proposed to consider the properties of gaize for the production of wall ceramics at 3 levels: natural, technological, aesthetic. Table 3 discusses the main criteria for evaluating siliceous rocks as raw materials for the production of various types of building ceramics.

Fig. 1. Deposit of carbonate clay. Rostov region

3 Results

As can be seen from Table 3, there are currently no comprehensive methods for assessing siliceous opal-cristobalite rocks, including the assessment of the natural properties of raw materials, technological properties and aesthetic indicators.

According to the pre-calcination technological properties, which are determined by the material composition and structure, all siliceous rocks can be conditionally divided into several groups according to the selected classification features.

So, according to the degree of soaking in water, three groups can be distinguished: soaked, difficult to soak (soaked with mechanical activation) and not soaked. The former mainly include diatomites, tripoli and siliceous clays. To the second, clay and medium clay gaize. To the third, low-clay silicified gaize. Soakable and difficult to soak opal-cristobalite rocks can be used without additives as the main raw material according to the traditional extrusion technology for the production of ceramic products. For non-soakable varieties, mechanical activation is required, which consists in the "release" of clay minerals from the opal mass and the introduction of water reducing admix.

The amount of aluminum oxide characterizes the amount of clay minerals. For diatomites and tripoli, kaolinite and montmorillonite are more characteristic, and for gaize and opoka-like rocks, hydromica. For the production of ceramic products, rocks with an Al2O3 content of more than 8% can be considered suitable. This corresponds to an approximate content of clay minerals of more than 20–30%. Significant technological factors affecting the strength and density of the ceramic material are the firing temperature and the degree of mechanical activation of the original rock. Opal is a significantly more reactive variety of silica compared to quartz, which is mainly found in loams, and already at low temperatures begins to actively interact with clay minerals, which contributes to sintering and increasing the strength of the material.

The composition and properties of gaize, as well as the desired types of manufactured products, determine the choice of the method of molding products and the choice of the optimal technological scheme of production. So for the extrusion molding process, clay gaize after preliminary grinding are more suitable. For the compression molding method, low-clay gaize are more suitable. For the soft molding method, medium-clay gaize are more acceptable. The content of the carbonate component affects the color of the products - for molding boxes, the color of fired samples varies from red-brown to yellow and beige, and high-carbonate rocks give a pink color. In order to choose the optimal technological solutions when designing enterprises for the production of wall

Table 3. Main evaluation criteria

Level	Types of work and defined indicators	What conclusions are drawn from the results	Test Methods
Natural properties	Macroscopic characteristic and basic physical properties	The color, the presence of inclusions (gypsum, glandular, etc.) is determined. The density in various types, porosity, water absorption, rock strength are determined. The results are necessary for technological calculations and the choice of mass preparation equipment	There are no methods. It is necessary to develop
	Chemical and mineral composition	The content of sulfur as a harmful component, the content of clay and carbonate components that affect the method of molding and the color of products	SS 21216–2014, SS 8269.1–97

(*continued*)

Table 3. (*continued*)

Level	Types of work and defined indicators	What conclusions are drawn from the results	Test Methods
Technological properties	Pre-fired properties for plastic (extrusion) molding: plasticity, cohesion, air shrinkage, drying sensitivity, structural strength	These properties depend both on the properties of the rock itself and on the grain composition of the crushed rockThe results are necessary for technological calculations, determining the optimal grain composition of the raw mass, determining the technological parameters of production, conclusions and the suitability of this type of raw material for the production of certain types of products using the plastic (extrusion) molding method	There are no methods. It is necessary to develop

(*continued*)

Table 3. (*continued*)

Level	Types of work and defined indicators	What conclusions are drawn from the results	Test Methods
	Pre-fired properties according to the soft molding method: cohesiveness, air shrinkage, stickiness, drying sensitivity, structural strength	These properties depend both on the properties of the rock itself and on the grain composition of the crushed rock. The results are necessary for technological calculations, determining the optimal grain composition of raw materials, determining the technological parameters of production, determining the type of surface of products, conclusions and the suitability of this type of raw material for the production of certain types of products using a soft molding method	There are no methods. It is necessary to develop

(*continued*)

Table 3. (*continued*)

Level	Types of work and defined indicators	What conclusions are drawn from the results	Test Methods
	Pre-fired properties according to the compression molding method: air shrinkage, strength, density of compacts, sensitivity to drying	These properties depend both on the properties of the rock itself and on the grain composition of the crushed rock. Tests are carried out at different moisture content of granular molding compound and molding pressure. The results are necessary for technological calculations, determining the optimal grain composition of the raw mass, determining the optimal technological parameters of production (moisture content of the press powder, molding pressure), conclusions and suitability of this type of raw material for the production of certain types of products using the compression molding method	There are no methods. It is necessary to develop

(*continued*)

Table 3. *(continued)*

Level	Types of work and defined indicators	What conclusions are drawn from the results	Test Methods
	Firing properties, taking into account the peculiarities of the molding method. The strength of products, density, porosity, water absorption, fire shrinkage, frost resistance are determined.	These properties depend both on the properties of the rock itself, the grain composition of the crushed rock, the features of the method of molding products and the firing temperature. The results are necessary for technological calculations, determining the optimal firing temperature. The appearance of the products is also determined. The color of products, the presence of dutiks, efflorescence, water absorption by the supporting surface are taken into account. Conclusions are drawn about the suitability of this type of raw material for the production of certain types of products using the compression molding method	There are no methods. It is necessary to develop
	Conducting semi-factory tests	Final conclusions are drawn about the suitability of this type of raw material for the production of certain types of products using a particular molding method	There are no methods. It is necessary to develop

(continued)

Table 3. *(continued)*

Level	Types of work and defined indicators	What conclusions are drawn from the results	Test Methods
Aesthetic properties	Color of fired products. The presence of efflorescence and spalling from lime inclusions. The ability of raw materials to bulk staining. Interaction with engobes, glazes and polymer dyes	The possibility of producing facial products, products for special orders with high aesthetic value is evaluated	There are no methods. It is necessary to develop

products based on gaize and not make strategic mistakes, it is necessary to take into account the following interrelated factors, shown schematically in Fig. 2.

For each group of siliceous opal-cristobalite rocks, it is possible to establish the dependences of natural, technological and aesthetic factors after conducting research and evaluating their properties.

Our experiments have shown that on the basis of opal-cristobalite rocks at firing temperatures of 950–1050 °C and appropriate preparation of the raw mass, a ceramic shard with a density of 1100–1500 kg / m3, with a strength of 20–40 MPa and reduced thermal conductivity due to the microporous structure is obtained. This allows, at 50–55% voidness, to obtain products with a density of 600–800 kg / m3, thermal conductivity less than 0.16–0.18 W / (m°C) and a compressive strength of more than 10 MPa. At the same time, the cost of products is lower due to the simplified technology (direct loading of molded products on kiln cars) and lower firing costs.

Preliminary results of testing the methodology for a comprehensive assessment of the properties of our rocks made it possible to obtain bricks of various colors and shapes, various sizes, with a huge variety of textures of the front surface. For example, Figs.3, 4 and 5 show photographs of ceramic bricks produced using various technologies based on various types of gaize.

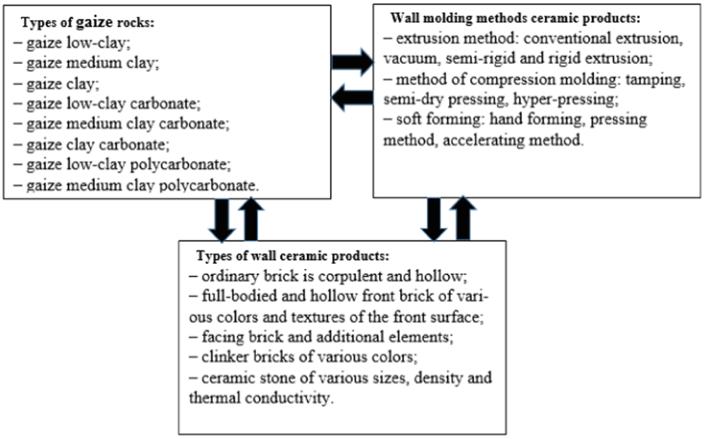

Fig. 2. Block diagram of the relationship between the types of slab-like rocks, moulding methods and types of wall ceramic articles

4 Discussion

As can be seen, for the widespread introduction of opoka-like raw materials in the production of building ceramics, it is necessary to develop specific generally accepted test methods, taking into account the accepted methods of molding. The algorithm of actions proposed by us and the methods proposed earlier were tested at several dozen flask deposits and at several basic enterprises. At present, it is necessary to formalize

Fig. 3. Face ceramic brick based on medium-clay and clayey supports obtained by soft molding technology

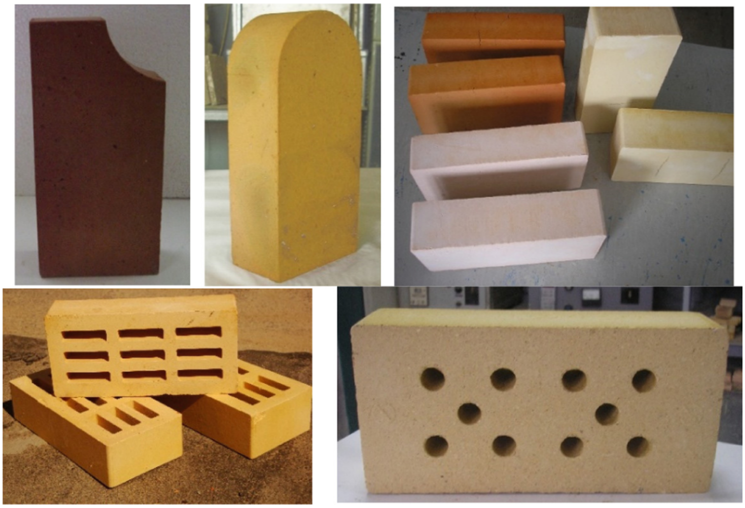

Fig. 4. Ceramic brick produced by compression method moulding based on different types of supports

our developments, together with other specialized organizations, into generally accepted methods, generally accepted recommendations and specific technological schemes for production with specific equipment of domestic and foreign production. The set of measures proposed by us will significantly expand the raw material base of building ceramics in Russia and will contribute to its successful development.

Fig. 5. Ceramic brick produced by compression method moulds based on clay types of supports

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