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Research Article

ANALYSIS OF CERAMIC WALL MATERIALS BASED ON FUSIBLE CLAYS WITH THE ADDITION OF ZEOLITE-CONTAINING ROCKS

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Abstract

At present day a high level of power consumption of manufacturing says an actual problem of Russian economic and industry in general. Furthermore, in residential construction, along with requirements of power effectiveness of ceramic items, are mandatory stated requirements for high values of their strength characteristics. Combination of such properties anticipates the application of fusible clays as a basis for production of energy-effective ceramic bricks with addition of modifiers creating pore space. In this article the impact of ZCR of Tatar-Shatrashanskoe deposit on fusible clay of Sakharovskoe deposit is researched. The following methods were applied in course of research: roentgen-phase analysis (diffractometer XRD-7000S (Shimadzu, Japan); diffractometer D2 Phaser (Brucker, Germany)), electronic-microscopical analysis (microscope EVO-50XVP), thermal analysis (derivatograph Q-1500D), measuring of physical characteristics (press ПМГ – 500 МГК 4 СКБ, Stroypribor, Russia, etc.) Behavior of fusible clay of Sakharovskoe deposit with increase of burning temperature up to 1050°C was researched. At burning temperature of 1050°C was observed growth of share of quartz, hematite and significant increase of share of amorphous phase from 35 to 45% in burned samples. According to thermal researches on derivatograph Q-1500D is established that in temperature interval of 25 - 200°C, the loss of mass of ZCR of Tatar-Shatrashanskoe deposit is 2.9 %, in temperature interval of 200 - 600°C – 2.88 %, in temperature interval of 600 - 850°C – 12.0 %, general mass loss in temperature interval of 50 - 100°C is 17.86 %. For samples received on basis of clay of Sakharovskoe deposit with addition of ZCR of Tatar-Shatrashanskoe deposit is detected that at burning temperature of 1050°C the 5% addition of SCR causes a slight growth of strength by comparison with a pure clay sample at comparatively low density. At studying of phase composition of samples burned at temperature of 1050°C was recorded a 2 times growth of share of amorphous phase with increasing of addition of ZCR of Tatar-Shatrashanskoe deposit from 5 to 10%. Correlation of strength characteristic from composition of mineral phases formed in result of burning is

established. The received data can be used in production of energy effective ceramic items.

Key words: ceramic; zeolite-containing rock; clay; strength; highly effective ceramic materials

Introduction

Every year the attention of global energetics to issues of energy resources saving and energy effectiveness is growing. In spite of RF taking of necessary measures on energy saving, the power consumption of Russia economic is significantly higher than respective indexes in states - members of Organization for Economic Co-operation and Development at high level of power consumption per person, manufacturing of production and provision of comfort services (heating, lighting etc.). The general technological potential of energy saving is conservatively estimated as 350 million tons of reference fuel, in which approximately 80 million tons - at consumption of energy by industrial branches. One of the tasks for elimination of energetic barriers of social-economic development of Russian Federation till 2020 and use of energy saving potential is the increase of energy effectiveness of residential-communal complex [1].

One of priority directions in energy resources saving is a reduction of power costs in costs of production. The development and implementation of respective energy saving technologies at industrial enterprises is necessary for realization of this direction. Furthermore, in contemporary construction, beside the energy effectiveness requirements, the requirements to high indexes of strength value are set for ceramic wall materials. In order to combine these properties at production of energy effective ceramic wall materials, fusible clays characterized by fast fusibility at comparatively low burning temperatures are used as a basis. Due to this fusible clays require a serious and often costly modification for creation of pore space in burned item. Optimal selection of necessary addition represents a significant problem for engineers. One of the most widespread methods of this problem solution is the introduction of burning additions into initiate batch. However, application of this method frequently leads to formation of large pores (more than 2 mm), irregularly dispersed over sample's volume of the sample. The most effective decision is the introduction of natural additions creating a homogeneous pore space into initial batch.

On territory of Privolzhskii region are located large reserves of zeolite-containing rocks of Tatar-Shatrashanskoe deposit.

Zeolites are framework aluminosilicates , in which structure there are connected cavities occupied by cations of diverse elements (most frequently alkali and alkali-earthy) and molecules of water, capable to be both removed and adsorbed by structure; by virtue of this occurs ion exchange and reversible degradation without structure destruction

[2].

Dependently on natural conditions of formation, zeolite-containing rocks can contain other minerals too, beside zeolites. Many domestic and foreign scientists had written about the unique properties of ZCR, namely about their high porosity, small volume weight, selective permeability, connected to specific frame structure [2-6]. Zeolite-containing rocks find a wide practical use in practically all branches of national economic.

Detection of specific features and studying of phase transformations at thermal procession of ZCR of Tatar-Shatrashanskoe deposit would allow to expand the field of application of the given raw material type.

The following methods were applied in course of research: electronic-microscopic analysis, roentgen-phase analysis, thermal analysis, measuring of major physical characteristics.

Mineral composition of ZCR of Tatar-Shatrashanskoe deposit and fusible clays of Alexeevskoe deposit was studied, change of phase composition of given raw material types is researched. The impact of ZCR of Tatar-Shatrashanskoe deposit on fusible clay of Alexeevskoe deposit is estimated. Correlation of strength characteristic from composition of mineral phases formed in result of burning is detected. Data can be applied in production of energy effective ceramic items.

Methods

Selected raw materials (Alexeevskoe clay, ZCR of Tatar-Shatrashanskoe deposit) was thoroughly dispersed and riddled through a sieve with apertures diameter of 0.5 mm. Samples of cylindrical form with addition of ZCR in amount of 0-20% with step of 5% were formed from sieved mass. Samples were prepared by method of compression forming of semi-dried masses at pressure of 15 MPa, after that they underwent thermal procession at burning temperatures of 1000 - 1150℃ with step of 50 °C in muffle furnace LOIP LF-7/13-G2, burning time - 4 hours.

Roentgen-phase analysis of burned samples was conducted on diffractometers XRD-7000S (Shimadzu, Japan) and D2 Phaser (Brucker, Germany). Electronic-microscopic researches were conducted on microscope EVO-50XVP, and thermal analysis – on derivatograph Q-1500D. In strength tests the hydraulic press ПМГ – 500 МГК 4 СКБ (Stroypribor, Russia) was used.

Results and Discussion

ZCR of Tatar-Shatrashanskoe deposit are characterized by high content of carbonates. Raw materials with high content of carbonates have the important distinguishing characteristics; particularly, in process of its burning are synthesized silicates of calcium [7]. Another peculiarity of ZCR of Tatar-Shatrashanskoe deposit is the presence of amorphous phase, presented by silicon earth. Silicon earth's structure pre-determines high hydraulic activity of silicious raw material. Peculiarities of behavior of such raw materials are stated by domestic and foreign authors in detail [8, 9].

In researched rock zeolite is presented by clinoptilolite mineral, for which a high Si/Al proportion is characteristic. In our researches the proportion of silicon and aluminum is 20:1. According to classification this rock is related to low-zeolitized (less than50% of clinoptitolite) with low degree of silicification; this allow to make a suggestion: addition of ZCR of Tatar-Shatrashanskoe deposit would not cause a significant impact on contraction and water absorption of samples.

Electronic-microscope researches of ZCR detected that zeolites in rock are presented by extremely finely-dispersed formations. In order to detect peculiarities of ZCR of Tatar-Shatrashanskoe deposit was conducted research of its behavior in course of temperature increase (Fig. 1).

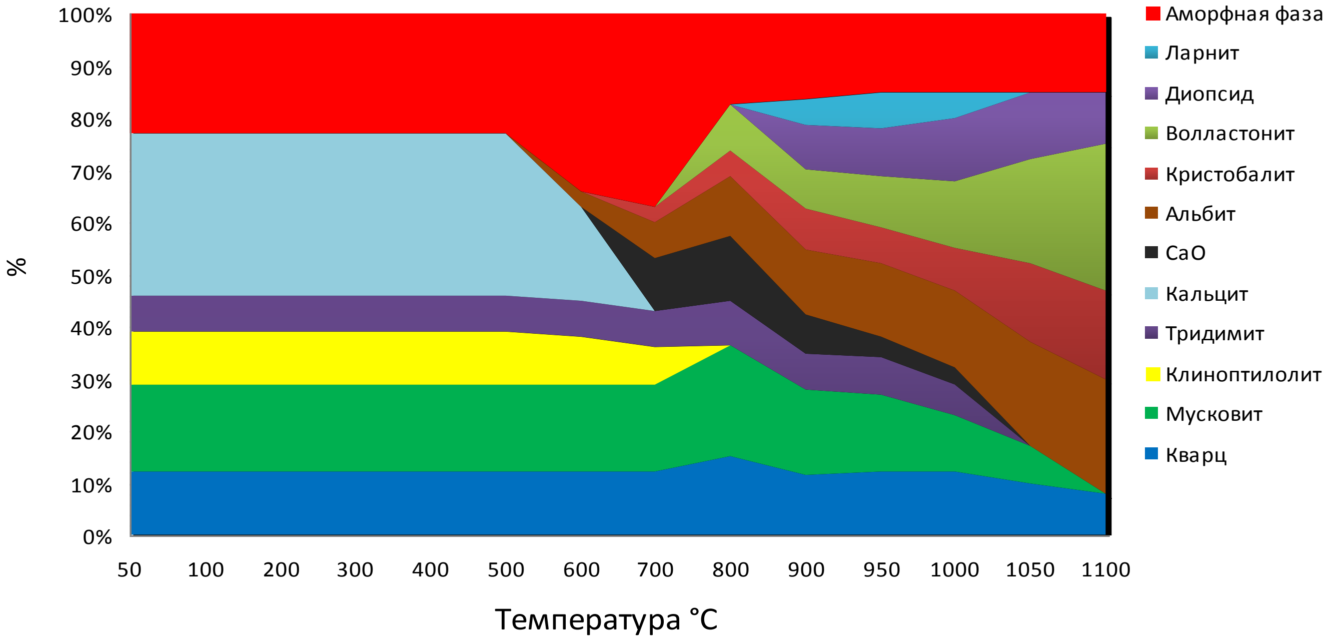

Fig. 1. Diagram of changing the phase composition of zeolite rocks Tatar-Shatrashanskoe field [10]

Temperature °C

Amorphous phase

Larnite

Diopside

Vollastonite

Cristobalite

Albite

CaO

Calcite

Tridimite

Clinoptilolite

Muscovite

Quartz

Diagram analysis allows to suppose that degradation of lime spar starting at temperature of 500°C leads to release of carbon dioxide and formation of calcium oxide. At temperature of 800°C clinoptitolite degrades, forming amorphous silicon dioxide in finely dispersed condition, which actively enters into interaction with calcium oxide, promoting synthesis of albite and calcium silicates at comparatively low burning temperatures. Namely this circumstance allowed to consider zeolite-containing rock as rather effective addition that would allow to reduce the power consumption of ceramic industry. Probably the presence of amorphous silicon earth interferes into interaction of calcium oxide and its complete disappearance occurs only at temperature of 1050 °C.

By thermal researches on derivatograph Q-1500D is established that in temperature interval of 25 - 200°C, the loss of mass is 2,9 %, in temperature interval of 200 - 600°C – 2.88 %, in temperature interval of 600 - 850°C – 12.0 %, general mass loss in temperature interval of 50 - 100°C is 17.86 %.

Fusible clay of Sakharovskoe deposit is presented by the following minerals: quartz, albite, muscovite and microcline. In course of burning it does not form new mineral phases, except for hematite, which share is less than 1%, at temperatures up to 1000°C [10]. In order to study clay behavior at higher temperatures was conducted phase analysis and this clay sample burned at 1050°C on diffractometer D2 Phaser (see Table 1). Growth of quartz, hematite share and significant increase of amorphous phase from 35 to 45% were observed. Shards of completely degraded muscovite and partly degraded mineral albite passed into amorphous phase, from which was synthesized mineral helenite of silicates' class, group of melilite with tetragonal syngony.

Table 1. Phase composition of sample from clay of Sakarovskoe deposit. T_{burn} = 1050°C.

Amorphous phase	Quartz	Albite	Microcline	Helenite	Hematite
45	36	7	8	2	2

Introduction of ZRC of Tatar-Shatrashanskoe depost anticipated its complex action, because this rock contains quartz, calcite, clinoptilotite and tridimite. Beside the thinning action of quartz and calcite caking that shorten the interval, the caking action of clinoptitolite capable of amplification at interaction with feldspatic constituents of fusible clay was anticipated.

Determination of major physical-mechanical characteristics of receiver ceramic samples had shown that samples changed linear dimensions insignificantly, and increase of water absorption and reduction of density at increase of content of ZCR of Tatar-Shatrashanskoe deposit are the evidence of significant content of carbonates in ZCR; they are degrading and promote intensive pore formation (see Table 2).

Table 2. Characteristics of samples from Sakharovskoe clays with ZCR of Tatar-Shatrashanskoe deposit. T_{burn} = 1050°C.

ZCR content, %	0	5	10	15	20
Density, g/cm3	1.78	1.74	1.68	1.56	1.58
Water absorption, %	16.1	16.74	18.32	22.5	23.16
Linear fire construction, %	-0.9	-0.8	-0.8	-1.1	-1.0
Strength, MPa	23	24.5	17	8.5	9

It was established that at burning temperature of 1050°C, addition of 5% of ZCR of Tatar-Shatrashanskoe deposit leads to slight growth of strength by comparison to sample of pure clay at comparatively low density. The result received is explained by activation of processes accompanied by phase transformations. By cost of significant share of amorphous phase crystallizing a stable mineral diopside is synthesized and share of crystalline phase is increased (see Table 3).

Table 3. Phase composition of sample from clay of Sakharovskoe deposit with 5% of ZCR of Tatar-Shatrashanskoe deposit. $T_{burn.}$ = 1050°C.

Amorphous phase	Quartz	Albite	Microcline	Diopside	Hematite
24	47	14	9	4	2

At studying of phase composition of samples burned at temperature of 1150°C was recorded the growth of amorphous phase 2 time growth with increase of addition of ZCR of Tatar-Shatrashanskoe deposit from 5 to 10% (see Table 4) which is connected to activation of process of liquid phase caking in result of optimal proportion of clay and ZCR of Tatar-Shartrashanskoe deposit.

Table 4. Phase composition of sample from clay of Sakharovskoe deposit with 5 and 10 % of ZCR of Tatar-Shatrashanskoe deposit. T_{burn} = 1150°C.

ZCR content, %	Tburn, ℃	Amorphous phase	Quartz	Albite	Microcline	Vollastonite	Diopside	Hematite
5	1150	40	32	20	1	2	2	3
10	1150	81	11.4	5.5	0.6	0.5	0	1

Therefore, at reduced burning temperatures (900-1050°C) the combination of such mineral phases as quartz, albite and diopside is impacting ceramic material's strength characteristics in the most significant manner. Alternately, at increased burning temperatures (1100-1150°C) strength characteristics depend on formed amorphous phase to more degree.

By thermal researches of clay of Sakharovskoe deposit with addition of 10% of ZCR of Tatar-Shatrashanskoe deposit is established that in temperature interval of 25 - 200°C, the loss of mass is 2.13 %, in temperature interval of 200 - 600°C – 2.23 %, in temperature interval of 600 - 850°C – 5.39 %, general mass loss in temperature interval of 50 - 100°C is 9.84 %.

It should be noted that addition of ZCR of Tatar-Shantrashanskoe deposit lends light tones to ceramic items by virtue of high content of calcite in composition of ZCR. At this the share of hematite decreases (see Table 4).

Results of conducted researches can be used in technology of effective ceramic materials creation.

Acknowledgements

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