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Procedia Chemistry 15 (2015) 120 – 126

Procedia Chemistry

16th International Scientific Conference "Chemistry and Chemical Engineering in XXI century" dedicated to Professor L.P. Kulyov, CCE 2015

Influence of Stony Rocks Additives on Strengthening of Aluminosilicate Ceramics from Fusible Clays

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Abstract

The paper presents the results of the research, connected with the granulometric and mineralogical compositions of fusible clay raw materials of Krasnoyarsk region - argillic and loose clay varieties. The influence of granitoid and diabase rocks stony additives on the sinterability and strength characteristics of the ceramic materials based on fusible clays is evaluated. It is found that the introduction of sintering additives into the loose fusible clay leads to the significant increase of samples strength – 50-100 MPa, while the introduction of the similar additives in the argillic clay does not influence positively on samples strength.

Peer-review under responsibility of Tomsk Polytechnic University
Keywords: clay, fusible, granitoid, diabase, aluminosilicate ceramics, sintering, hardening.

1. Introduction

Recently, the problem of increasing the mechanical and thermomechanical properties of the aluminosilicate ceramics has obtained a special significance, which will expand the field of its use in modern science and technology [1].

One of the main ways to improve the competitiveness of aluminosilicate ceramics is to reduce the consumption of expensive raw materials and decrease the temperature of its burning. This necessity forces to search for new sources of raw materials and technological solutions for activating the process of mullite-containing ceramic materials sintering.

A feature of a modern domestic base of ceramic raw materials is the depletion of the total reserves of high-quality

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Peer-review under responsibility of Tomsk Polytechnic University
doi:10.1016/j.proche.2015.10.019

clays and kaolins, which causes the forced involvement of more available, but less quality fusible clay rocks in the production. The issues of broadening the use of nonplastic natural silicate raw materials and technogenic wastes in the production of ceramic materials, including painted shard become of key importance [2].

Traditionally, the formation of the desired properties in ceramic products predetermines the proper selection of raw materials, mass recipes and ceramic technologies, what is impossible without comprehensive investigations of clay-containing raw materials as a main component of aluminosilicate ceramics.

Earlier complex studies of the mineralogical composition, mechanical and technological properties of kaolin and refractory clays have shown [3-5] that the main reason for the low strength of the samples on their basis after firing up to the full sintering temperature is the polymorphism of their siliceous component, both in the form of a natural impurity and a released one in the mullitization process of a main clay-formed mineral - kaolinite. This feature makes this raw material unsatisfactory in terms of using it as the main clay raw material for producing high strength aluminosilicate ceramics. Therefore, one of the ways to improve the strength characteristics of ceramic products based on fusible clays as well as to reduce their short melting is their additional charging with natural alumina-containing and technogenic additives. Additives doping will bind a siliceous component into the secondary mullite [6-9].

2. Special Features of Granulometric and Mineralogical Composition of Fusible Clay Raw Materials

The objects of the investigation were two samples of fusible clay raw materials of Krasnoyarsk region - a loose type (sample P5) and an argillic sample (sample A).

In order to strengthen the samples from low-melting red-burning clays the additives of natural stony materials (diabase and granitoid rocks) were tested.

The comparative analysis of the results of a granulometric composition, using a pipette method (Table 1), showed that the sample of the loose clay raw material according to the content of a fine fraction (less than 1 micron) belonged to the group of particulate clay and represented silty clay (by Okhotin) with the content of sand particles up to 15 % wt. (14.36 % wt.) and clay particles - up to 60 % wt. (58.01 % wt.).

The argillic raw clay material represented a transitional type between silty clay and plastic clay with virtual absence of a sand fraction (1.65 % wt.) and with the content of a clay fraction more than 60 % wt. (64.49 % wt.).

Table 1. Granulometric composition of clay raw materials

Sample code	Content (% wt.) of fraction (mm)				
	1-0.25	0.25-0.06	0.06-0.01	0.01-0.005	0.005-0.001
loose clay rock					
P5	4.24	10.12	16.31	11.22	27.11
argillic clay rock					
A	0.46	1.19	17.83	16.03	34.22

The mineralogical composition of the investigated samples of clay and non-plastic materials was established by the X-ray and thermal methods of analysis. Radiographic studies were carried out at the diffractometer DRON-3.0 in CuKα-radiation at the tube voltage of 40 kV and the current of 25 mA, the goniometer rotational speed was 4 degrees per minute, the measuring range (shooting sensitivity) - from $2 \cdot 10^3$ to $1 \cdot 10^4$ pulses / sec.

It was found that the tested sample of loose clay was a polymineral clay rock, folded as a mixture of such clay minerals as kaolinite $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$, as it was evidenced by the well-defined characteristic reflections with interplanar spacings at 0.717 – 0.72; 0.356 and 0.247 nm, and hydromica of the illite type $0.2 \cdot K_2O \cdot Al_2O_3 \cdot 3SiO_2 \cdot 1.5H_2O$ (0.992; 0.444 nm) (Fig. 1). The presence of illite was determined by the conditions of formation of kaolinite clays as the products of feldspars weathering, because illite was a clay mineral, which was a product of feldspars change. In the non-plastic part of loose clay quartz and feldspar in the form of orthoclase were present.

The fine (clay) part of argillic clay was qualitatively represented by a mixture of clay minerals – kaolinite ($Al_2O_3 \cdot 2SiO \cdot 2H_2O$), montmorillonite ($Al_2O_3 \cdot 4SiO_2 \cdot H_2O \cdot mH_2O$) and hydromica in the form of illite ($0.2 \cdot K_2O \cdot Al_2O_3 \cdot 3SiO_2 \cdot 1.5H_2O$). The X-ray reflections of these compounds were well defined and sufficiently intensive, what proved the high content and good crystallinity of these clay minerals (Fig. 2).

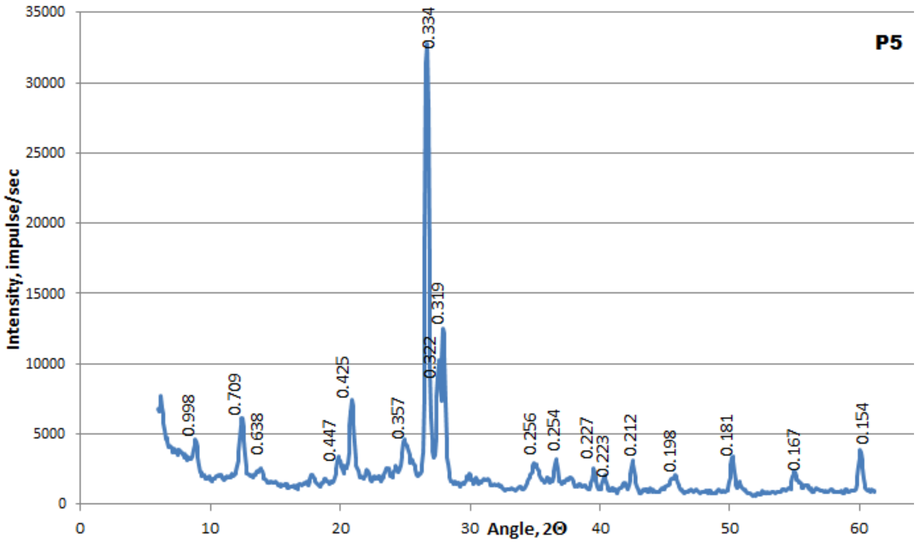

Fig. 1. X-ray diffraction pattern of loose fusible clay

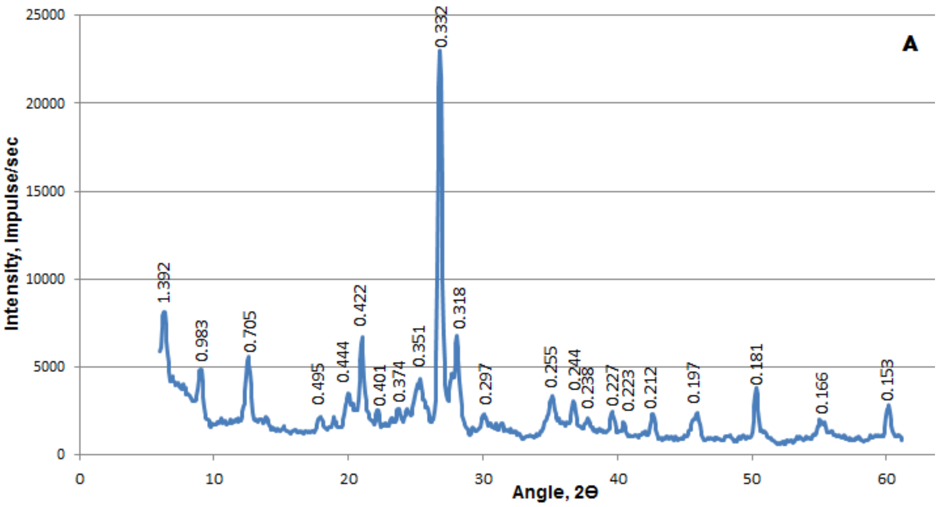

Fig. 2. X-ray diffraction pattern of argillic fusible clay

In the impurity (non-clay) part of the given argillic clay the presence of quartz was diagnosed. However, judging by the dispersion analysis, for the analyzed clay almost complete absence of the sand fraction (ranging in the size from 1 to 0.06 mm) was typical. This fact allowed confirming that in this clay rock the quartz component was concentrated in the finer fractions (in silt and, possibly, in clay fractions). Thus, the presence of montmorillonite clay in the part of this clay would provide its high ductility, and the absence of a sand fraction would complicate drying the products on its basis.

The specificity of grain and chemical-mineralogical compositions determined the technological properties of the investigated clays: in the case of loose clay - high ductility (a plasticity index – 26), increased air shrinkage (more than 7%), full sintering at the temperature of 1050 ^{o}C with the formation of strong structures with mechanical characteristics (compression strength) at 118 MPa. Argillic clay is a superplastic (a plasticity index – 28) and a low-temperature sintering clay with the sintering temperature of 1000^{o}C, forming high-strength structures – 122 MPa at 1050 ^{o}C.

3. Special Features of Mineralogical Composition of Natural Stony Materials – Diabase and Granitoid Rocks

The analysis of the X-ray diffraction pattern (Fig. 3) indicated that the investigated granitoid comprised a mixture of quartz and feldspar minerals in the form of potassium feldspar (orthoclase, microcline) with sodium feldspar (albite) and a mica mineral in the form of biotite-potassium-magnesium-aluminum-iron-containing mica, the presence of which determined the prospects of granitoid use as a fluxing agent in the compositions of ceramic materials.

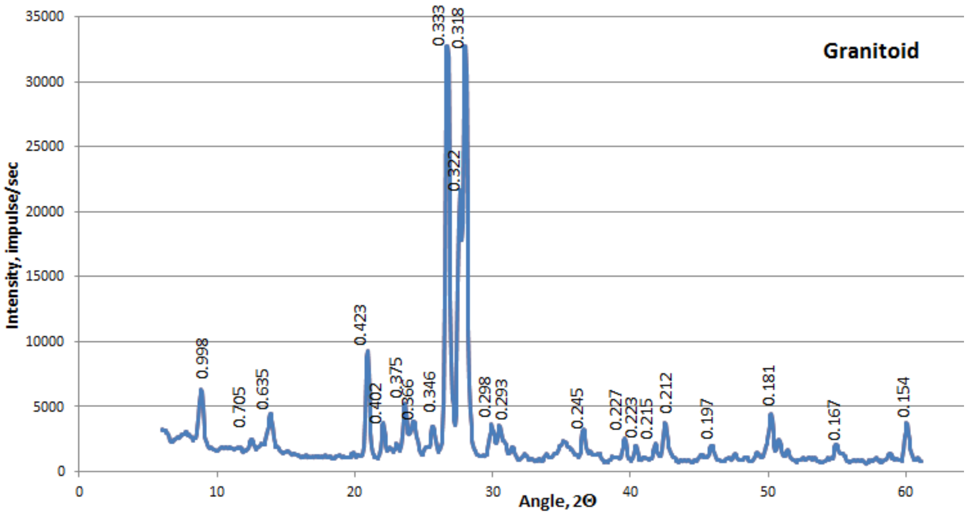

Fig. 3. X-ray diffraction pattern of the granitoid rock sample

The X-ray diffraction revealed that the diabase rock (Fig. 4) was a polymineral rock composed of a mixture of oligoclase (the isomorphic mixture, containing 10-30% of anorthite $CaAl_2Si_2O_8$ and 70-90% of albite $NaAlSi_3O_8$), anorthite, augite (magnesium-iron silicate, pyroxene), potassium (albite) and calcium (anorthite), feldspar, magnetite and serpentine.

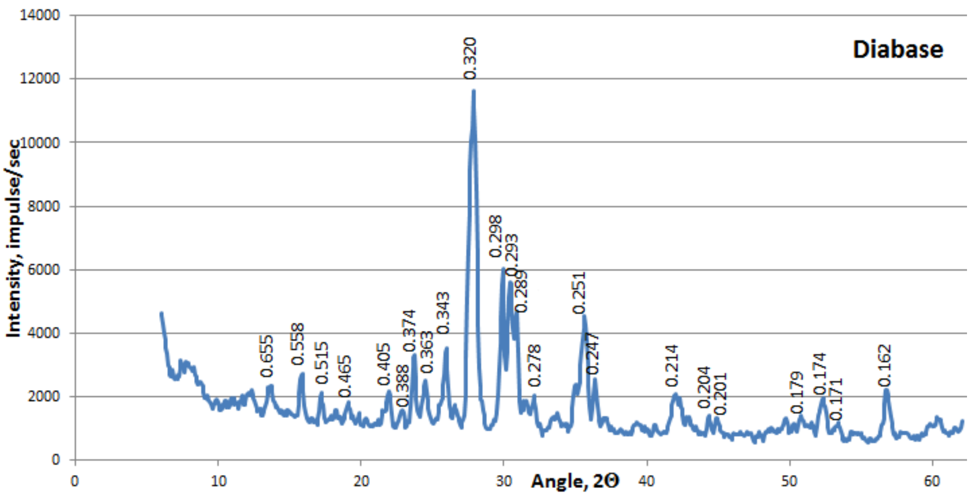

Fig. 4. X-ray diffraction pattern of the diabase rock sample

4. Influence of Stony Additives on Ceramic Materials Strength Characteristics

To evaluate the effect of stony additives on the strength characteristics of the ceramic materials, based on clay rocks, granitoid and diabase rocks were used in the amount of 20 - 30 wt.%.

Additives of stony rocks were finely milled in a ball mill until complete passing through the sieve 0063.

The samples in the form of tablets or cylinders were molded by semidry pressing in a hydraulic press under the pressure of 15 MPa.

Calcination of the samples was carried out in the temperature range from 1000 to 1100°C with an exposure at the final temperature for 2 hour.

Sintering character was investigated by the degree of samples compaction characterized by the following indicators: total shrinkage, water absorption, bulk density and compression strength of the fired samples.

Studies showed that the introduction of granitoids and diabase additives in sample P5 had a positive effect on the sinterability of the ceramic mass (Fig. 5).

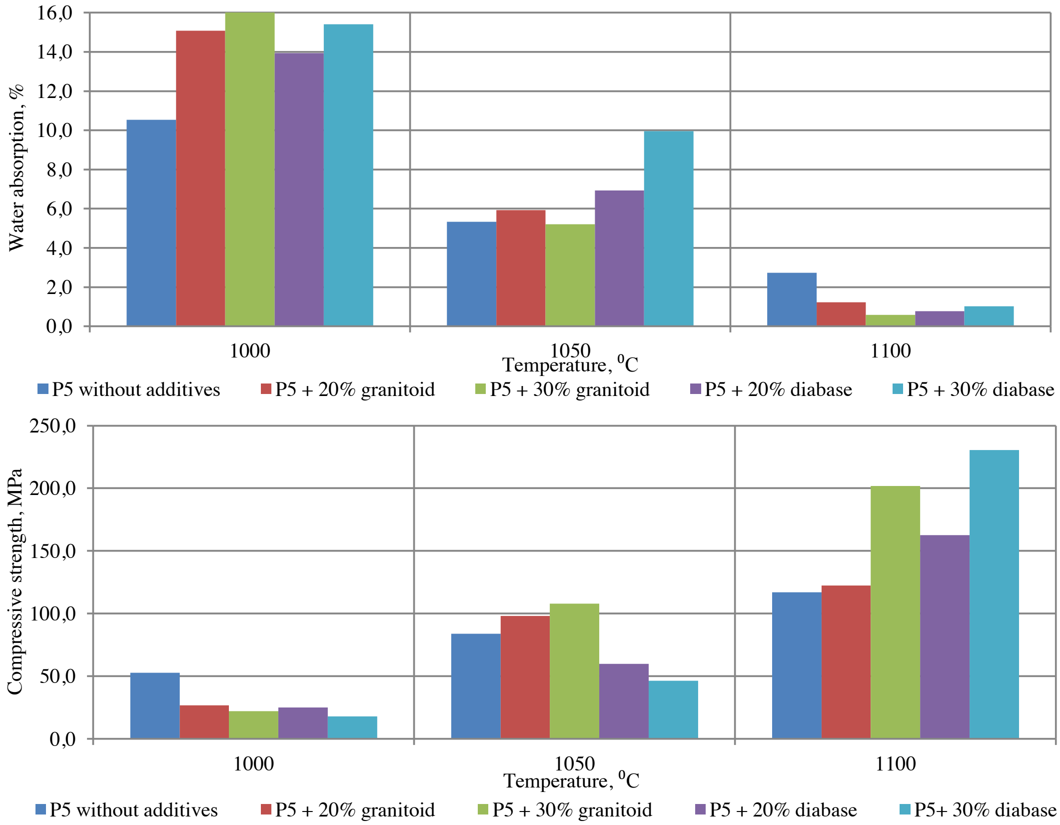

Fig. 5. The influence of granitoid and diabase rocks additives on the strength characteristics and the sinterability of the investigated loose clay (sample P5) in the temperature range from 1000 to 1100 ° C

The comparative analysis of the obtained data by the type of stony additives influence on the sintering of loose fusible clay (sample P5) indicated as follows: at firing up to 1050°C the samples of semidry pressing from P5 the additives of granitoids as well as diabase in amounts of 20-30% had a decompact effect, it was accompanied by increased water absorption values of the samples calcined at 1000-1050°C, compared with the samples without any additives. Increasing the firing temperature up to 1100°C led to rapid activation of the sintering process, which was accompanied by the processes of burnout, showing themselves in surface vitrification of the molded specimens. Thus, both additives used in combinations with the investigated loose fusible clay during firing in the temperature range 1050-1100°C acted as a fluxing agent, reducing the interval of the particular clay sintering. It should be noted that the additives of granitoid and diabase in the amount of 30% had the greatest positive effect on the strength characteristics of the samples: the strength of these samples was 200 and 230 MPa, respectively.

In the case of argillic clay (sample A) the introduction of the specified additives did not influence positively on its hardening (Fig. 6). At the firing temperatures of 1000 - 1050°C the strength of the samples with the additives was lower than that of the pure samples (without any additives) of sample A. The further temperature increase, also, did not have a positive strengthening effect, except the samples with the addition of 20% diabase, but even in this case, the strengthening effect was insignificant.

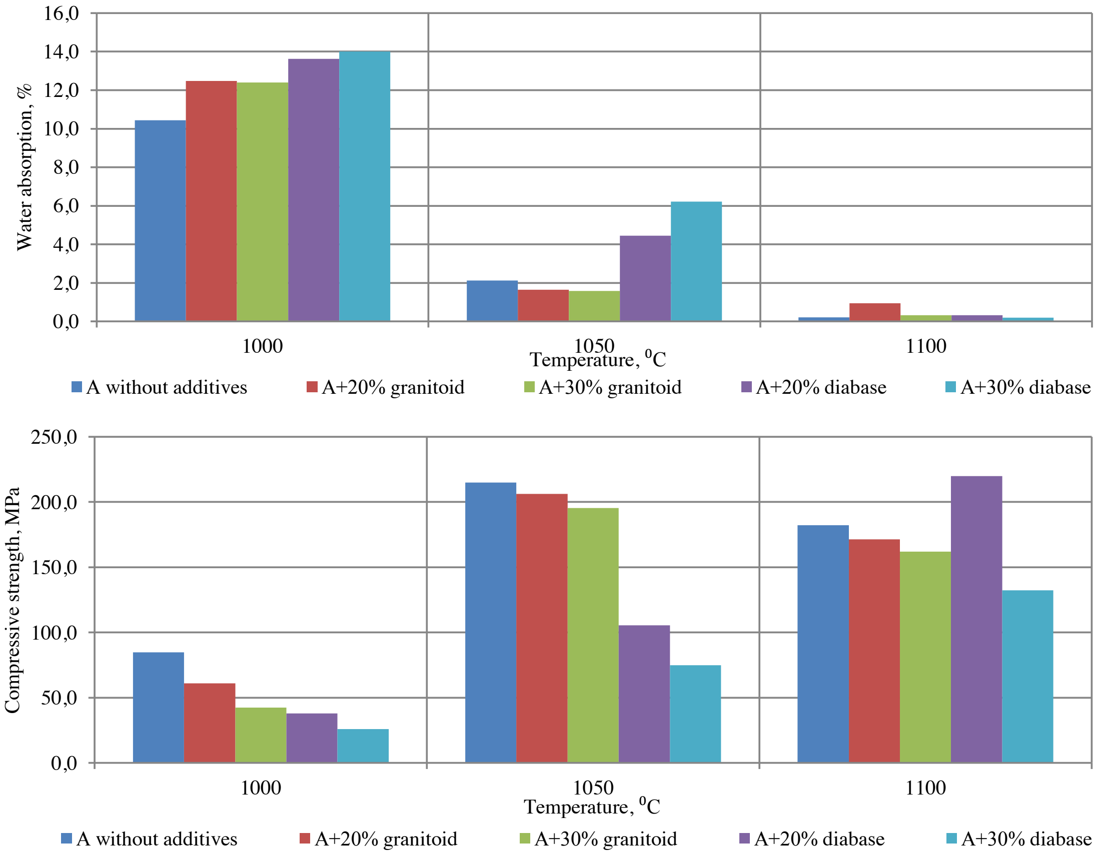

Fig. 6. The influence of granitoid and diabase rocks additives on the strength characteristics and the sinterability of the investigated argillic clay (sample A) in the temperature range of 1000 - 1100 ° C

4. Conclusions

1. The increased strength of plastic molding samples (118.6 MPa at 1050ºC) from the loose fusible clay (sample P5) and argillic clay rock (121.8 MPa at 1050ºC) determines their prospects in the technology of aluminosilicate ceramics with a painted shard.

2. Granitoid and diabase rocks in the amount of 20-30 wt.% in the combination with fusible loose and argillic clays at firing above 1050 ºC operate as active fluxing agents, reducing the interval of sintering (increasing short melting behavior) of the given clays.

3. Short melting behavior of the investigated red-burning clays represents a threat of spalls formation in the case of firing in rotary kilns.

4. To expand the sintered state interval of the given clays the additional charging with the aluminous component

is suitable. This operation, also, will influence positively on the hardening of the compositions, if the binding process of additional charging alumina in the crystalline aluminosilicate compound is provided.

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