To issue of studying mechanism of increasing strength of porous ceramic crock

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Abstract. In our country at the modern stage of the development of constructional industry the necessity arises in qualitative ceramic wall materials. The use of this items provides durability, comfort and architectural expressiveness for constructions. In connection with what is an acute problem of use of "low-grade" clay raw material for production of high-quality wall ceramic products. The solution of problem is to activate clay raw materials in various ways. One of relatively simple, effective and economically expedient methods of the activation of clay raw material is mechanical activation. It is used to improve the quality of dense metamorphized clay raw materials. But it is not enough, therefore it is offered to hold extra chemical activation by adding chemical additives in raw mixtures. The purpose of present research is to study mechanism of increasing the strength of the ceramic crock affected by the fluxing additive, imputed in raw mixtures proportion based on medium-plastic clay raw materials. To achieve the given purpose, it is necessary to solve the following tasks: a) to investigate influence of fluxing additives on rheological raw mix behavior; b) to study modification mechanism of changing the properties of ceramic crock by adding fluxing additive into the raw mixtures.

1. Introduction
At the present time, due to the rapid growth of individual low-rise construction the interest in effective ceramic wall materials is increasing, the use of which provides durability, comfort and architectural expressiveness for constructions [1-5]. Abroad, in a constructive attitude at buildings construction dominate frame construction by which walls carry out basically functions of a heat-protection fencing [4-9].

In our country at the modern stage of the development of manufacture ceramic wall building materials, there is a tendency of priority production of effective wall materials with an average density of 600-1000 kg/m3 and thermal conductivity up to 0,14 W/(m*°С).

High-quality easily-melted clay materials must be used in order to obtain qualitative wall ceramics. The granular composition should be as follows. Content of fractions less than 0,2 mcm not less than 24 %, and for improvement of drying properties of a raw material not above 50 %. In clay raw materials the content of particle fractions 2-20 mcm should be 30-47 %, and fractions 20 mcm size 6-34 %. The contents of clay particles (size less than 5 mcm) must be at least 30%. To sum it up, raw materials for the production of high-quality wall ceramics should provide drying and roasting of semi-finished items without deformations and cracks, have air shrinkage no more than 6% for sandy clay, 6-10 % - for medium-plastic and more than 10 % for high-plastic and have good molding capacity with the plasticity number not less than 7.
Nowadays, there is a shortage of high-quality clay. In this regard, there is an acute need to use low-grade, widespread in many regions of our country clay raw materials without compromising the quality of the final products of the ceramic industry. The solution of this problem is possible by modification of clay raw materials with various additives and activation which promote its quality. To the "low-grade" it is possible to attribute the raw material, which does not provide at least one of the technological stages (forming, drying or firing) of the production of ceramic products. One of relatively simple, effective and economically ways of processing of clay raw material is dry its grinding, which is used to improve the quality of dense metamorphised clay raw materials.

Mechanical activation of clay raw materials is a set of phenomena, which are not only quantitative accumulation of defects, but also leading to radical transformation of the structure, accompanied by a significant change in composition and chemical properties. From two thermodynamic parameters - temperature and pressure, the last one plays a decisive role as the reason for activation. Field of stresses is created as a result of high pressures and pressures with shear in certain areas of solid substance, the relaxation of which takes place in different channels: heat excretion, formation of new surface and short-lived active centers, formation of plastic waves, interaction of which leads to formation in structure of various kind of defect and metastable conditions.

The use of decontaminators, rotary, centrifugal, inkjet, ball and mine mills, runners, hole and differential rollers is offered for fine comminuting, which allows increasing the strength of ceramic crock.

In the process of mechanical activation the mineral raw material is subjected to intensive mechanical influence in the milling-activators of various types. Mineral particles are not only crushed, but also undergo complex structural changes, namely, the crystalline structure of the surface layer (amorphization) with the change of the function of the existing active centers and the occurrence of new ones, as well as the plastic deformation of the inner layers of crystals with deep disturbance of the crystalline structure, is disturbed. As a result of these changes the raw material accumulates a significant part of the applied mechanical energy and becomes more reactionary in various technological processes.

However, only mechanical activation is not enough to produce ceramic products with durability that provides high-grade wall materials. This requires additional activities such as chemical activation of clay raw materials.

Chemical activation of "low-grade" clay raw materials allows to regulate the parameters of finished ceramic products, such as durability, frost resistance, water absorption, thermal conductivity, and also to reduce the temperature of sintering. Fluoding additives, such as liquid glass, dolomites and iron ore, which have different oxides, are used most often in practice.

Introduced chemical additives to activate clay raw materials in the composition of raw mixtures lead to the appearance of roasting at the early stages, easy-melting components, causing the emergence of neoplastic in the formation of ceramic crock. The nourishing additives give a high increase in the strength of the products due to the sufficient formation of the glass, obtained from the molten components of the additive.

Decrease the average density and thermal conductivity of products may achieved by porosity of the crock and increasing the voidness of products. However, reducing the average density and thermal conductivity of products by introducing burning additives we reduce their strength characteristics [10-13]. Therefore, adding organic burnout additives in the mix proportion it is necessary to take measures conducting the strength of the crock. This can be achieved, for example, by mechanical activation of clay raw material [14-17] or by introduction a chemical additive in the form of spent-soap lye. In works [18-20] the increase of crock durability of a wall ceramics after adding fluxing additive – spent-soap lye (further SSL) were experimentally proved.

The purpose of present research is to study mechanism of increasing the strength of the ceramic crock effected by the fluxing additive, imputed in raw mixtures proportion based on medium-plastic clay raw materials.
2. Research methods

To execute given purposes, control cubes-samples from the mix proportion with different content of the spent-soap lye (SSL) additives were made and were exposed to roasting. Selected test samples were investigated by methods of X-ray analysis and electron microscopy. Analysis of dependence of X-ray analysis (XRA) allowed to explain the mechanism of increasing the strength of porous crock with SSL additive.

For neat clay first endoeffect connected with the removal of free water is registered at 1800 °C, and with the adding SSL in the mix proportion in the amount of 1.5% of raw materials weight, the peak of this endoeffect is shifted by 10% and equals 1700 °C. Subsequent increasing the amount to 3% is contributed to the displacement of the first endoeffect to the area of lower temperatures to 1600 °C. A similar pattern is observed for the endoeffect peculiar for the removal of constitutional water. If for neat clay this endoeffect has a peak at 5150 °C, then with increasing of SSL from 1.5 to 3%, this endoeffect shifts up to 510 and 4850 °C. The utmost importance, from a point of explanation the reasons of crock strength change, the endoeffects observed in the high-temperature region. Thus, in neat clay (Fig.1 curve 1) there is an endoeffect at 8300, connected with the end of removal of group OH-, and also destruction of a lattice of deplete minerals and Hydromicas. With the adding SSL in the mix proportion in the amount of 1.5% (Figure 1, Curve 2) and 3% (Figure.1 Curve 3), this endoeffect is shifted to the lower temperatures, respectively 825 and 8100 °C. Displacement of mentioned endoeffects in the area of lower temperatures is explained reduction of glass phase formation temperature at the adding of the spent-soap lye, which, as already mentioned above, plays the role of the flux.

Therefore, increasing the strength of the crock with the adding of the SSL from 0 to 1.5% is mainly related with increase the quantity of glass phase. The strength is not enough with zero composition (SSL = 0%), and at 1.5% more dense packing of particles of quartz and crystalline neoplasms is shaped, and the optimum quantity of a molten mass or a roasting coalescence is formed around them. The ratio of the roasting coalescence (RC)/solid phase (SF) is optimal.

Further increase of SSL contributes increasing liquid phase, which intensifies the melting process of insoluble components, contributes more intensive roasting of quartz grains in the mix proportion, increases amorphous phase and reduces the crystalline phase of melt, which entails strength decline of the crock. The RS/SF relationship is not optimal. TDA data are confirmed by results of X-ray analysis.

Comparing the diffraction of XRA for neat clay and clay with additives of SSL (Figure 2, Figure 3, Figure 4) it may be noted, that adding of SSL entails the formation of new crystalline phases of the primary mullite, for which the reflexes 3,482; 3,386; 2,694; 2,193; 2,129; 1,690; 1,543 are characteristic. It is necessary to note, that some reflexes are obscured by other reflexities imposed from effects of other neoplasms. So, reflexes 3,482 and 3,386 mullite, the reflexes of albita (3,482) and quartz 3,342 are superimposed. The most clear presence of mullite is declare at 2,129. The blurring of the mullite is occurred by reflexes appropriate of hematitit at 1,689 and for quartz at 1,543.

So, analyzing results of XRA and TDA with adding in the mix proportion fluxing additive in the form of SSL, it is possible to make a conclusion, that with increasing of a SSL there is also increasing of a fluxing sodium containing component concentration which helps to decrease the temperature of the glass phase formation in the area of lower temperatures, and consequently the increase melt to the optimum values in the firing of the crock at 950 °C. This is the main reason of increasing the strength of material by increase contact area of non-melted quartz particles, feldspar, amorphous components by the formation of a large volume of sodium-chloride glass phase, which with optimum quantity contributes intensive cementation of the crock. Furthermore, the angles and faces of the grains of crystalline silica are melted (corroded), but entirely in the reactions of the liquid phase formation aren’t existed, staying together with the crystalline neoplasms skeleton frame elements of the roasted material.
Figure 1. Curves TDA (thermal differential analysis) of roasted pattern: 1- clay 100%; 2- clay 98.5 % + SSL 1.5%; 3 – clay 97%+ SSL 3%

Figure 2. Diffraction of fired patterns clay + SSL.
3. Conclusions

1. Increasing the strength of the ceramic crock with the adding of spent-soap lye in raw mixtures proportion is related with increasing the quantity of liquid glass melt.
2. Liquid glass melt is bound rough components by partial melting of conglomerate edge that contributes increasing the strength of the ceramic crock.
3. There are mullite needles at the crystal phase of roasting crock based of stiff clay with adding waste products of electroplating industry. They reinforce liquid glass melt of crock and increase its strength.

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