Modern methods of studying the phase composition of clay raw material at kiln process

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Abstract. It was developed methods for study of change clay rocks mineral phase composition at kiln process. The object of study was clay feed which is used to produce of ceramic materials. The main method of investigation was X-ray diffraction analysis. An additional method was synchronous thermal analysis (STA).

At work was used X-ray diffractometer Shimadzu XRD-7000S (Japan) with a high-temperature furnace. Such equipment allows carrying out research of samples composition from 25°C to 1200°C. Experimentally established optimal temperatures of research: 20, 100, 200, 300, 400, 500, 600, 700, 750, 800, 850, 900, 950, 1000, 1050, 1100, 1150 and 1200°C. Data at these temperatures were processed in the DIFFRAC.EVA software. The result was quantitative information and graphs of the change in clay phase mineral composition during (burning?) firing process. At the same time was a studied quantitative change of the amorphous phase at different temperatures.

The STA was used as an additional method of investigation. Sample analysis was carried on Netzsch STA 449 F3 Jupiter device (Germany), which allowing measurements of mass changes and thermal effects at temperatures up to 1200°C. We fixed changes using thermogravimetric measurements (TG) and curves of differential thermal analysis (DTA).

The integration of methods allowed to obtain obtaining important information about the qualitative and quantitative changes of clays samples composition during firing process. Also results of our study showed reactions of minerals transformation due exothermic and endothermic processes. The overall result is a diagram of phase and quantitative transformations of minerals at temperatures from 20 to 1200°C including amorphous phase.

1. Introduction

The study of the clay raw materials clinkering process often involves the study of the initial material and the final product of burning. However, such studies do not carry information about the actual sintering processes. First of all, changes in samples phase composition at different temperatures. Therefore, it is not possible to understand how the clinkering process itself realized and it is not possible to reveal the raw materials sintering mechanisms. Most often they have to be guessed. Therefore, study of clay phase composition changes during their firing will allow us to understand the mechanism of their sintering and also to make changes in the technology of raw materials preparation and its burning conditions.

Analysis of modern literature about clay raw materials sintering process shows that in the production of ceramic materials the synergetic approach is very important [1]. The preparation of raw materials needs increased attention. Such an approach can greatly increases the physico-mechanical properties of the resulting materials. In the foreign literature [2, 3], also much attention is paid to the...
study of the sintering process. For this purpose, used studies are carried out of change in the clay raw material phase during its burning.

2. Methods
The method of ceramic materials thermal X-ray analysis was developed to study clay rocks phase (mineral) composition changes during the process of their burning. The object of the study was clay batch, which is used to produce ceramic products. The main method of investigation was X-ray analysis. An additional method of investigation was the method of synchronous thermal analysis.

At work was used X-ray diffractometer Shimadzu XRD-7000S (Japan) with a high-temperature furnace (Figure 1). Such equipment allows carrying out research of samples composition from 25°C to 1200°C. Experimentally established optimal temperatures of research: 20, 100, 200, 300, 400, 500, 600, 700, 750, 800, 850, 900, 950, 1000, 1050, 1100, 1150 and 1200°C. Data at these temperatures were processed in the DIFFRAC.EVA software. It was possible to obtain information about mineral composition of each sample at different temperatures. The result was quantitative information and graphs of the change in clay phase mineral composition during burning process. At the same time was a studied quantitative change of the amorphous phase at different temperatures. Qualitative and quantitative analyzes were taken using a computer international database PDF-2.

The used diffractometer is designed for a wide range of studies: X-ray diffraction analysis of any crystalline materials. It has a high-temperature chamber for monitoring changes of phase temperature transitions. It can be done with specific software.

The optimal diffractometer mode for prepared clay samples and ceramic materials was selected experimentally. It was based on the instrumental characteristics of the equipment used, type of sample, the expected phase content and the research task at hand. Registration was carried out at the following conditions of X-ray diffractometer: angular range from 3 to 40° at 2θ; exposition 1° per minute; scanning step 0.02° at 2θ; current 20 mA, voltage 30 kV.

The selected modes allow reliably fixing the minerals diffraction maxima composing clay and ceramic materials. Research objects were Quaternary clays, used as raw materials at ceramic-brick factories of the Middle Volga region. It was various by mineral composition clay material. The clays main difference was at carbonates content. Quite often the batch of clays was modified by various additives.

Figure 1. X-ray diffractometer Shimadzu XRD-7000S (Japan). General view (left), goniometer with a high-temperature furnace (right)

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thermal effects at temperatures up to 1200°C. We fixed changes using thermogravimetric measurements (TG) and curves of differential thermal analysis (DTA).

The integration of methods allowed obtaining important information about the qualitative and quantitative changes of clays samples composition during firing process. Also results of our study showed reactions of minerals transformation due exothermic and endothermic processes. The overall result is a diagram of phase and quantitative transformations of minerals at temperatures from 20 to 1200°C including amorphous phase.

3. Results and Discussion

The thermal X-ray analysis results of some clay raw material, as well as modified clays.

The polymineral clay of the Sakharov deposit during the heating process up to 1000°C does not form new mineral phases (Figure 2). It can be seen that some minerals disappear at certain temperatures: montmorillonite (up to 200°C), dolomite (up to 600°C), chlorite and calcite (up to 700°C). The temperatures of their thermal destruction different from their monomineral phases decomposition temperatures. This may be due with amorphous phase presence. It plays role as flux agent. At the same time with the decomposition of these minerals an amorphous phase forms. It also plays the role as glass rim, which gives to samples a mechanical strength.

It should be noted that the same clay with mechanical activation behaves differently. During the firing process, it is also thermal destruction of montmorillonite, chlorite, calcite, dolomite occurs, increased percentage amount of the amorphous phase (glass rim). But also we can see processes of new phase of minerals formed: metastable silicon oxide (lime) and larnite, as well as stable akermanite, wollastonite and diopside. X-ray analysis data indicate that the last three minerals are formed from the amorphous phase.

The reasons for such significantly different at phase diagrams (Figure 2 and 3) are the mechanical activation processes of the Sakharov deposit polymineral clay samples. This leads to an increase in the reactivity of the thermo active components of clay raw materials.
Quite significant changes in the phase composition of clays also occur with calcite high content in the initial raw material (Figure 4). At the same time, during the firing process, the appearance of newly formed metastable calcium oxide (lime) and larnite, as well as stable akermanite and diopside, is observed.

**Figure 3.** The diagram of phase composition changes of mechanical activation clays of the Sakharov deposit

**Figure 4.** The diagram of clays phase composition changes of the Sakharov deposit
There is an appearance of an amorphous phase (glass rim). The glass phase appearance maximum is observed at temperatures of 600-700°C and more than 1050°C. At temperatures of 600-700°C fixed high mechanical strength appears of samples. And at temperatures over 1050°C, the sample is partial melting and its geometric shape is lost.

The data obtained during thermal X-ray studies are confirmed and supplemented by the results of synchronous thermal analysis [4]. In Figure 5, the DSC (differential scanning calorimetry) and TG (thermogravimetric) curves in the temperature range up to 200°C show losses sample hygroscopic and interlayer water by montmorillonite. At temperatures just over 400°C, the endoefect due to the decomposition of chlorite is detected. Thermal destruction of calcite is detected by the endothermic effect at 720°C. And three exothermic effects in the temperature range of 850-1000°C are caused by the appearance of new minerals - akermanite, diopside, larnite. The decrease in the DSC curve after 1000°C is due to the increase amount of amorphous phase (glass rim) in the sample.

![Figure 5. Synchronous thermal analysis data of the Salmanovsk clay deposit. The solid line is the differential scanning calorimetry (DSC) curve, the dotted line is the mass loss curve (TG)](image)

Changes close to those described also occur with the mechanically activated clay of the Salmanovsk deposit (Figure 6). An important difference is that in mechanically activated clay, mineral composition changes observed at earlier temperature. Therefore, burning clay achieves strength characteristics at lower temperatures.
Figure 6. The diagram of phase composition changes of mechanical activation clays of the Salmanovsk deposit

The results obtained during the research also show that the presence of calcite in clay does not impair the physical and mechanical properties of ceramic materials [5]. However, the high dispersion of calcite, which can be obtained by mechanical activation of clay raw material, is a necessary condition. It should also be said that the presence of calcite in burning initial raw materials does not impair the properties of the final products. It gives them a lighter color and increases the cost.

4. Conclusions
Based on our research and obtained diagrams the following conclusions about change in the phase composition of clay raw material during its burning:

- Methodic of thermal X-ray analysis for the clay raw materials phase composition study in the burning process was developed and introduced.
- It is established that mechanical activation of clay raw material leads to complication of clay raw material phase transformations of during its firing.
- The study of the clay raw materials phase composition during the firing process shows that its mechanical activation leads to an increase in the rate of phase transformations and minerals transformation takes place at lower temperatures.
- It is shown that the integration of thermal X-ray and synchronous thermal analysis data allows better understanding of the mechanisms clay raw materials sintering and making changes in technological schemes for ceramic materials production.
- The presence of finely dispersed calcite in clay raw materials generally does not impair the physical and mechanical properties of ceramic materials. In this case, the products acquire a lighter color and are characterized by higher consumer properties.
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References
[1] Bakunov V S and Belyakov A V 2005 Synergistic aspect of ceramic technology Glass and Ceramic Vol 3 pp 10-13
[2] Emiliani G P. and Corbata F 2001 Tecnologia ceramica Le materie prime (Faenza Editrice) p 198
[3] Liop J, Stoyanova L, Barrachina E, Nebot I and Carda J B 2014 The Ceramic Industry in Spain Ceramic forum international Vol 6 pp 43-46
[4] Salakhov A M and Tagirov L R 2015 Structure formation in ceramics with clays which form various phases at burning Stroitel’nye Materialy Vol 8 pp 68-74
[5] Salakhov A, Ashmarin G, Morozov V and Salachova R 2014 Baukeramische Erzeugnisst aus Rohstoffen mit hohem Karbonatgehalt Keramische zeitschrift Vol 1 pp 35-38