

Study of ceramics color development on the basis of Nizhnevelsky Kaolin clay

Kristina A. Ariskina, Renas R. Mukhametzyanov, Al'mir M. Salakhov,
Farit G. Vagizov, Anatoly G. Nikolaev

Center of Quantum Technologies, Kazan Federal University, Kazan, 420008, Russia

Abstract

Aim: They analyzed the influence of iron-containing phases on the ceramics color development made of Kaolin clay of Nizhnevelsky deposit. **Materials and Methods:** The result of the complex application of modern study methods - thermal, electron microscopic, radiographic, Mossbauer, optical - it was established that the change of kaolin clay calcination temperature from 1000°C to 1200°C leads to the increase of L* luminance from 75 to 79 NBS units (National Bureau of Standards, USA), which correlates with the analysis of Mössbauer spectra, reflecting the decrease of the strongly staining phase of hematite. The crystallization of the mullite mineral is the consequence of ceramics clarification process based on Kaolin clay with the calcination temperature increase from 1000°C to 1200°C. **Results:** It was found that the absorption bands in the calcined clay of the Nizhnevelsky deposit with the wavelengths of 432 and 480 nm, baked at 1000°C, are associated with spin-forbidden transitions ${}^6A_1({}^6S) \rightarrow {}^4A_1({}^4E)$ in Fe^{3+} ions that have an octahedral environment. **Conclusion:** It was found that Fe^{3+} ions could produce the absorption lines at the wavelengths of 432 and 480 nm, only being in the structure of mullite. At 1200°C, the partial amorphization of the mineral composition of clay takes place, which leads to the averaging and broadening of the absorption band in the area of 400–550 nm.

Key words: Ceramics color, hematite, Kaolin clay, kaolinite, Mossbauer spectrum, mullite, optical spectrum

INTRODUCTION

The experts from the Federal State Unitary Enterprise “TsNIIgeolnerud” note the following:^[1] “Clay rocks, in which kaolinite is the dominant or one of the dominant mineral components, constantly attract human attention and have been studied since the time of ancient civilizations.” In the last few years, there has been a steady trend of light tone ceramic brick production increase in Russia. In the technology of facing brick production producers use white clays more and more often, that are understood as the clays,^[2] which contain a minimum number of coloring oxides, especially iron oxides. However, the study of a number of clays, both kaolinic and polymineral, with inclusions of carbonates, shows that, despite the substantial content of iron oxides in raw material, these clays give a crock of light tones during roasting, and with the increase of roasting temperatures, ceramics samples acquire even lighter shades.

As is known, color is one of the material characteristics, depending on optical absorption spectrum and the reflection of its surface.

Absorbing and reflecting properties are conditioned by surface properties and allowed and forbidden bands of electronic transitions of elements and minerals that make up the material. Nobel prize winner in physics Frank Wilczek, pointing to the most important role of color, notes the following:^[3] “In simple terms, the color of objects encrypts information about their composition.”

When they analyze raw materials for the production of ceramics, a primary attention is paid to the presence of silicon and aluminum oxides as the main components of clay minerals. A significant amount of works is devoted to the influence of calcium-containing components on the behavior of ceramic masses during roasting. Color formation issues have been discussed in many special publications.^[4-9] Iron oxide (hematite) is the most important chromophore of ceramic materials due to the wide prevalence of this element

Address for correspondence:

Kristina A. Ariskina, Center of Quantum Technologies, Kazan Federal University, S. Saydashev Street, Kazan, 420008, Russia. E-mail: kristina.ariskina.95@mail.ru

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in raw materials. However, they studied the effect of iron compounds on the optical characteristics of ceramic materials and the regularity of ceramic material color change during the firing process. In our view, these studies were completely insufficient. When they analyzed ceramic raw materials, its chemical composition is given, in which the content of Fe_2O_3 and FeO is fixed, but the question remains: Which minerals contain iron and it is not predicted what changes will occur with iron after the roasting of raw materials.

In the works by Bulatov,^[10,11] the Mossbauer method was used to analyze in detail the crystal-chemical characteristics of iron ions in the structure of layered silicates. However, his studies were limited to the analysis of natural minerals. In this work, the authors, using Mossbauer spectroscopy and a number of other methods, have studied the structural-phase transformations in the process of Kaolin clay calcination from Nizhneuvelsky deposit to establish the patterns of color changes in ceramic materials.

Objects and Methods of the Study

The Kaolin clay of Nizhneuvelsky deposit was provided for research by its large consumer - the Ufa Tile Production Plant LLC "Lasselsberger."

At the first stage of the work, thermal characteristics, mineral composition of clay, its structure, and elemental composition were studied. During the next stage, the clay was subjected to thorough grinding before its passing through a sieve with a hole of 0.5 mm. The samples were prepared by compression (15 MPa) molding, and then, they were fired in the temperature range of 1000°C–1200°C with 50°C increments in LOIP LF-7/13 muffle furnace with the heating rate of 400°C/h, an isothermal holding time made 2 h. The obtained samples were sent for spectrophotometric and Mossbauer studies.

The work was carried out using a synchronous thermal analysis instrument STA 443 F3 Jupiter (Netzsch GmbH, Germany) with the Netzsch Proteus Thermal Analysis software running by Windows XP to record thermogravimetry curves and differential scanning calorimetry in the temperature range of 30–1250°C.

The radiographic studies of clay at room temperature were carried out on D2 Phaser diffractometer (Bruker GmbH, Germany). The processing of the diffractograms was carried out using DIFFRAC-plus Evaluation Package - EVA software.

The micromorphology of the clay samples and the elemental analysis of the selected fragments were established using Philips EVO-50XVP scanning electron microscope with the Energy 350 Oxford INCA characteristic X-ray spectrometer. The elemental analysis was carried out in a low-vacuum mode at the probe-electron energy of 20 keV. For a given electron energy, the sounding depth was 1 μm .

Mossbauer spectroscopy on ^{57}Fe nuclei was carried out on WissEl (Germany) spectrometer in the transmission geometry. The source of the resonance radiation was ^{57}Co nuclei in the rhodium matrix. The measurements were made at room temperature. The values of the isomeric shift are indicated relative to the metallic iron. Mathematical processing of Mossbauer spectra was carried out using the SpectrRelax program, which allows to take into account the distribution of hyperfine fields on resonance atom nuclei and relaxation processes.^[12] The identification of the obtained Mossbauer spectra was carried out according to the literature data.^[13]

Photometric studies in reflected light were performed on MSFU-K (Lomo, Russia) microscope-spectrophotometer at room temperature in the visible region of 380–800 nm, and scattered daylight was selected as the radiation source. The analysis of reflection spectra was carried out in spectra program. The widely used CIELab model was adopted as a color model for quantitative color estimation, approved by the International Lighting Commission of 1964.

STUDY RESULTS AND THEIR DISCUSSION

An essential content of iron atoms was revealed in separate fragments of the studied clay sample from Nizhneuvelsky deposit [Figure 1], which corresponds to the chemical analysis results [Table 1].

According to the results of X-ray studies, hematite was not detected in the phase composition of the raw material sample [Figure 2 and Table 2].

A distinctive feature of the studied Kaolin clay is a significant content of rock-forming mineral kaolinite. An ideal lattice of kaolinite has an equal number of aluminum and silicon atoms (1:1), but there are no iron atoms there. In real clay minerals, isomorphic substitutions occur inevitably both in the tetrahedral layer (silicon atoms by aluminum atoms) and

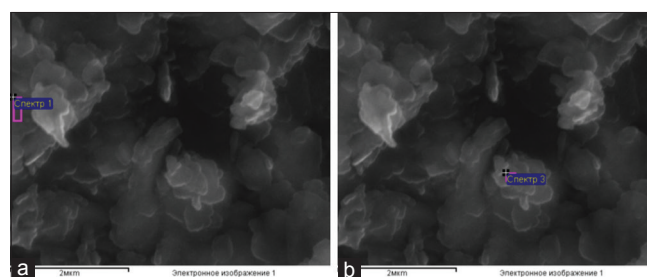


Figure 1: (a and b) Scanning electron microscope image of Nizhneuvelsky deposit clay fragment. The elemental composition of the X-ray spectra of the sites designated "Spectrum 1:" O - 64.79, Mg -- 0.44, Al - 12.68, Si - 16.90, K - 0.20, Ca - 0.14, Ti - 0.27, Fe - 4.57 %; "СПЕКТР 3:" O - 61.43, Mg - 0.21, Al - 12.99, Si - 16.58, K - 0.19, Ca - 0.13, Ti - 0.76, Cr - 0.06, Fe - 7.64%

octahedral layer (aluminum atoms by iron or magnesium atoms), which leads to the fluctuations in the quantitative ratios of aluminum, silicon, and iron atoms.

Similar isomorphous substitutions occur in other clay minerals, including micaceous minerals and montmorillonite. However, the absorption of electromagnetic radiation in chromophore-containing minerals is not the same, because of different structures of a crystal lattice, its symmetry, and bond types.

To determine the iron-containing phases and the crystallographic positions of the iron atoms in clay, the Mossbauer spectroscopy method was used. The Mossbauer spectrum of the Nizhneuvsk clay [Figure 3 and Table 3] was decomposed into two sextets and a doublet.

Magnetically ordered components of the spectrum are characterized by broad and asymmetric absorption lines. The mathematical processing of the spectrum showed that the

sextets are well described under the assumption of hyperfine magnetic field Gaussian distribution on the nuclei of resonant atoms. The distribution of fields for a sextet with a large hyperfine magnetic field corresponded to an asymmetric Gaussian function with different half-widths toward small and large fields from the most probable value ($H = 513$ kE). The half-width toward the small fields was much wider ($\Delta H_{LF} = 28$ kE) than toward larger fields, which is manifested by a noticeable asymmetric broadening of the external lines of this sextet into the inner part of the spectrum. The ultrafine parameters of this sextet were equal: $IS = 0.37$ mm/s and $QS = -0.21$ mm/s. These values are characteristic for hematite crystals. The broadening and the asymmetry of lines are probably related to the scatter of crystallite sizes and the heterogeneity of iron ion environment in the structure of natural hematite. The content of this component was about 31%.

Broad lines are also characteristic for another magnetic component [it is marked as the sextet 2 in Table 3]. The best fit

Table 1: Chemical composition of Nizhneuvsky deposit clay according to the input control of the clay consumer LLC “Lasselsberger” on February 26, 2016 (content in % by weight on an absolutely dry sample)

| SiO ₂ | Al ₂ O ₃ | Fe ₂ O ₃ | TiO ₂ | CaO | MgO | K ₂ O | Na ₂ O | PPP | Sum |
|------------------|--------------------------------|--------------------------------|------------------|------|------|------------------|-------------------|------|-------|
| 57.00 | 25.78 | 4.86 | 1.27 | 0.20 | 0.46 | 0.88 | 0.0 | 9.56 | 100.0 |

Table 2: Mineral composition of Nizhneuvsky deposit clay, %

| Quartz | Montmorillonite | Mixed-layer mineral | Mica minerals | Chlorite | Kaolinite |
|--------|-----------------|---------------------|---------------|----------|-----------|
| 37.4 | 13.1 | | 8.9 | 0.4 | 40.1 |

It was not possible to strictly determine the content of montmorillonite and the mixed-layer mineral

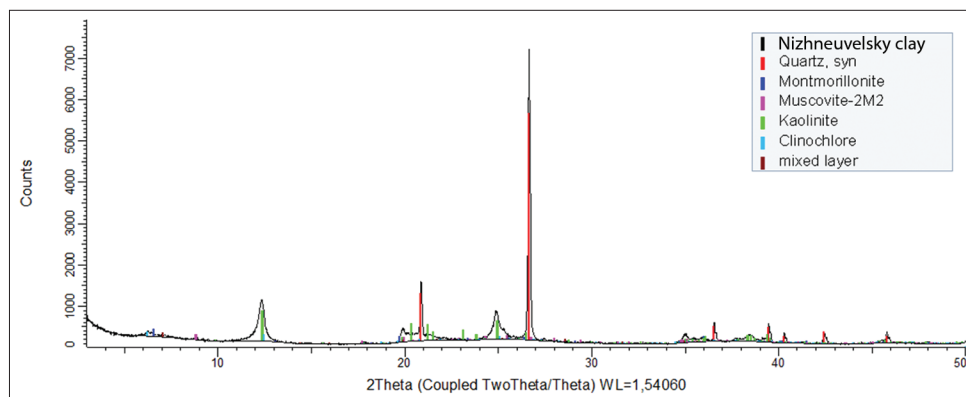


Figure 2: Diffractogram of Nizhneuvsky deposit clay of grade NUPK

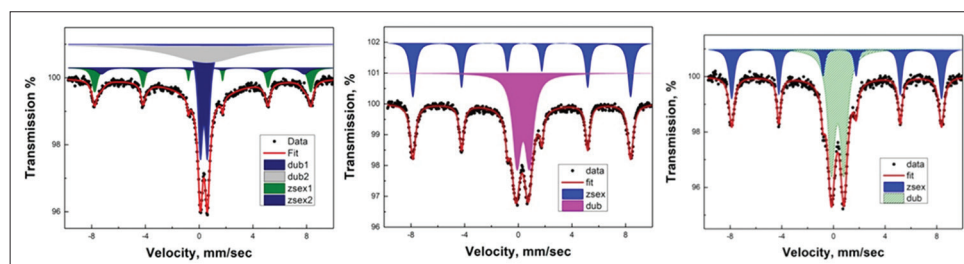


Figure 3: Mossbauer spectra (from left to right): Nizhneuvsky deposit clay, ceramics from Nizhneuvsky deposit clay ($T_{bur} = 1000^{\circ}\text{C}$ and $T_{bur} = 1200^{\circ}\text{C}$)

Table 3: Hyperfine parameters, crystallographic coordination of iron atoms, and the percentage of components corresponding to different phases of iron in Nizhneuvelsky deposit clay and ceramics after firing at 1000°C and 1200°C

| T _{bur} , °C | Component of the model spectrum | Hyperfine parameters | | | Crystallographic coordination of Fe | Relative area, % |
|-----------------------|---------------------------------|----------------------|----------|--------|-------------------------------------|------------------|
| | | IS, mm/c | QS, mm/c | H, kOe | | |
| Clay | Doublet | 0.35 | 0.53 | - | [6]Fe ³⁺ | 54 |
| | Sextet 1 | 0.37 | -0.21 | 492 | [6]Fe ³⁺ | 31 |
| | Sextet 2 | 0.49 | -0.35 | 152 | [6]Fe ³⁺ | 15 |
| 1000 | Doublet | 0.29 | 0.93 | - | [4.6]Fe ³⁺ | 54 |
| | Sextet | 0.36 | -0.22 | 502.6 | [6]Fe ³⁺ | 46 |
| 1200 | Doublet | 0.33 | 0.97 | - | [4.6]Fe ³⁺ | 60 |
| | Sextet | 0.36 | -0.22 | 502.9 | [6]Fe ³⁺ | 40 |

for this sextet was obtained under the assumption of a symmetric Gaussian distribution of hyperfine magnetic fields with the most probable value equal to 152 kOe and the half-width of the distribution function of the order 35 kOe. The ultrafine parameters of this sextet were equal: IS = 0.49 mm/s and QS = -0.35 mm/s. Such values correspond to the parameters of Fe³⁺ in the octahedral environment. The observed broadening is probably also related to the inhomogeneity of the environment of iron atoms and the distribution of crystallite sizes. The area under the spectrum of this component was about 15%.

The largest area (54% of the total area of the spectrum) in the Mössbauer spectrum of the original sample was represented by the doublet with the following parameters: IS = 0.35 mm/s and QS = 0.54 mm/s. According to the literature data, such values of hyperfine parameters can correspond to Fe³⁺ ions in octahedral sites of the kaolinite mineral. For example, in Jefferson *et al.* study,^[14] according to Mossbauer studies of kaolinite, they showed that the parameters IS = 0.36 mm/s and QS = 0.53 mm/s correspond to Fe³⁺ ions in the octahedron.

During the firing process at 1000°C, clay minerals collapsed, and the local environment of iron ions changed, which led to a qualitative change in the Mossbauer spectrum [Figure 3 and Table 3]. This spectrum was decomposed into a doublet and a sextet. The sextet was also referred to hematite. It should be noted that its area is noticeably increasing (from 31% to 46%). The values of the hyperfine doublet parameters are close to the values of the mullite studied earlier.^[13]

The formation of the mullite mineral is confirmed by X-ray studies of the Kaolin clay from Nizhneuvelsky deposit. This clay was baked at the temperature of 1100°C [Figure 4].

The processes of mullite synthesis during the firing of Kaolin clays are described in detail by the domestic literature^[15] and foreign literature.^[16]

During thermal studies of the clay from the Nizhneuvelsky deposit, it was found that the exothermic peak at 968°C is caused by the formation of new crystalline phases [Figure 5].

It has been established that the calcination temperature change from 1000°C to 1200°C in the clay of Nizhneuvelsky deposit leads to the increase of L* luminance value from 75 to 79 of NBS units (National Bureau of Standards, USA), which correlates with the analysis of Mössbauer spectra reflecting the decrease of the strongly staining phase of hematite. The crystallization of the mullite mineral is the consequence of ceramics clarification process based on Kaolin clay with the calcination temperature increase from 1000°C to 1200°C.^[17]

Figure 6 shows the optical spectra of ceramic samples obtained by Kaolin clay firing to the temperatures of 1000°C and 1200°C. An intense absorption band is observed in the region of 400–530 nm with the peaks at wavelengths of 432 and 480 nm in the optical spectrum of Nizhneuvelsk clay surface reflection, burned at 1000°C [Figure 6, Spectrum 1]. According to the results of chemical analysis and Mossbauer studies, it was revealed that the main chromophore in the represented raw material is Fe³⁺ ions located in different coordination positions.

The result of literature data and precursor work analysis, according to the optical spectroscopy of minerals and their synthetic analogs, showed that absorption bands in ceramics at the wavelengths of 432 and 480 nm are associated with spin-forbidden transitions ${}^6A_1({}^6S) \rightarrow {}^4A_1({}^4G)$ in Fe³⁺ ions with an octahedral environment.^[18,19] According to the results of X-ray structural analysis, the mineral composition of the clay from the Nizhneuvelsky deposit, calcined at the temperature of 1100°C, is represented by quartz, mullite, pseudowollastonite, and hematite [Table 4]. The study of the mineral composition and the isomorphism of the iron group elements established that Fe³⁺ ions could give absorption lines at the wavelengths of 432 and 480 nm only being in the structure of mullite. The crystalline structure of mullite is close to the structure of sillimanite, but mullite is characterized by considerable disorder in Si and Al atoms. The analysis of the literature data on the color of yellow and orange sillimanites confirmed the interpretation of electronic transitions in Fe³⁺ ions, which are located in octahedral positions within the structure of newly formed mullite, which was developed during the calcination of Nizhneuvelsk clay [Table 5].^[20]

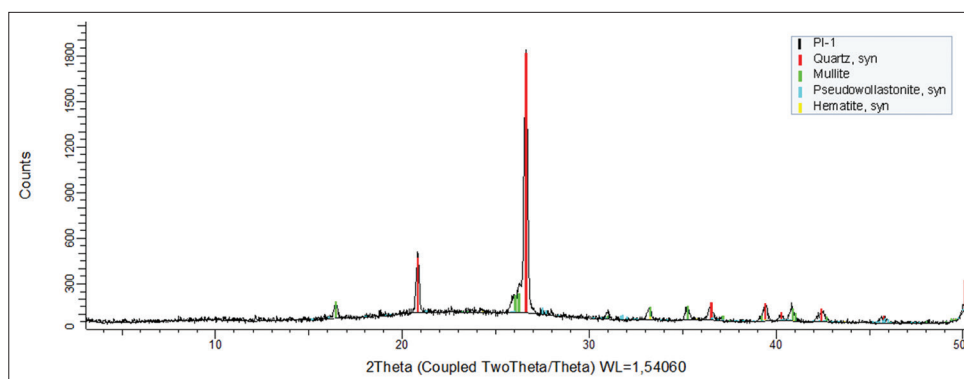


Figure 4: Diffractogram of Nizhneuvsky deposit clay. $T_{bur} = 1100^{\circ}\text{C}$

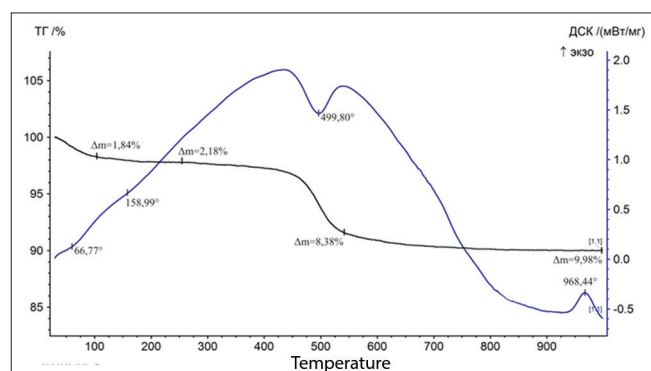


Figure 5: Curves of DTA and thermogravimetry. Nizhneuvsky deposit clay, grade NUPK. The maxima of thermal effects and mass loss at the end of each of them are indicated

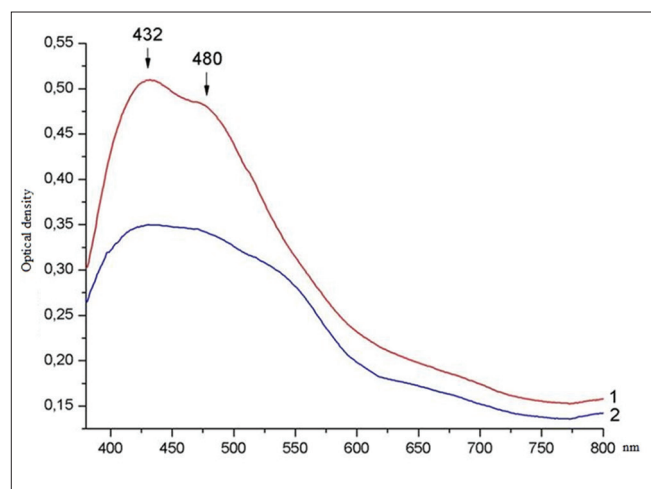


Figure 6: Dependence of the optical density on the wavelength of the reflected spectra of samples based on the Nizhneuvsky clay (1 - $T_{bur} = 1000^{\circ}\text{C}$ and 2 - $T_{bur} = 1200^{\circ}\text{C}$)

Table 4: Mineral composition of Nizhneuvsky deposit clay. $T_{bur} = 1100^{\circ}\text{C}$, %

| Quartz | Mullite | Pseudowollastonite | Hematite |
|--------|---------|--------------------|----------|
| 68.0 | 22.9 | 8.3 | 0.8 |

At higher temperatures, partial amorphization of the mineral composition of clay takes place, which leads to the averaging and the broadening of the absorption band in the region of 400–550 nm [Figure 6, Spectrum 2].

CONCLUSION

(1) The essential content of iron oxide ($>3\%$) is characteristic not only of polymineral clays, forming a red crock during roasting, but also for Kaolin clays belonging to the category of whitened. A distinctive feature of kaolin clay is its clarification in the firing process. (2) The hematite content decreases in the kaolin clay with a significant iron content ($>3\%$) at roasting temperature increase from 1000°C to 1200°C , and iron is introduced into the structure of the newly formed mullite mineral, which helps to neutralize the staining effect of hematite. (3) It has been revealed that absorption bands in ceramics based on kaolin clay calcined at 1000°C with the wavelengths of 432 and 480 nm are associated with spin-forbidden ${}^6\text{A}_1({}^6\text{S}) \rightarrow {}^4\text{A}_1({}^4\text{G})$ transitions in Fe^{3+} ions that have an octahedral environment. (4) At 1200°C , partial amorphization of the mineral composition of clay takes place, which leads to the averaging and broadening of the absorption band in the range of 400–550 nm. (5) A popular opinion that the whitened clay is the clay with a minimum amount of coloring oxides requires some clarification. There can be different amounts of chromophores (coloring oxides). To design the color of the ceramics, it is necessary to find out how the coordination of iron ions varies, which makes it possible to reveal Mössbauer spectroscopy. Of course, along with iron, there are other chromophores (chromium, titanium, manganese, etc.), but their content in kaolin clay is insignificant and, accordingly, it almost does not affect the formation of ceramic material color. (6) The ceramic materials of light colors can be obtained from the clays with a high content of coloring oxides (according to GOST 9169–75, the clays with a high content of coloring oxides are the clays in which the Fe_2O_3 content exceeds 3%).

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Table 5: Thermal effects and weight loss of sample Nizhneuvelsky deposit clay grade NUPK

| Thermal effect | Maximum temperature, °C | Loss of mass by the sample at the end of the effect, % | Interpretation |
|----------------|-------------------------|--|--|
| Endo | 66.77 | 1.84 | Removal of adsorbed water |
| Endo | 158.99 | 2.18 | Removal of interlayer water from montmorillonite |
| Endo | 499.80 | 8.38 | Removal of OH groups from kaolinite |
| Exo | 968.44 | - | Formation of new crystalline phases |

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