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Optimization of technological parameters for obtaining mineral additives based on calcined clays and carbonate rocks for cement systems

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ABSTRACT: Introduction. The management of physical and chemical processes of structure formation of high performance cement composites can be provided at several scale levels through the use of modifiers of various nature and mechanism of action, in particular, micro- and nanoscale mineral additives of natural and technogenic origin. It is known that clays and carbonate rocks are promising raw materials to obtain mineral modifiers for cement systems. The purpose of this study was to establish the influence regularities of the prescription and technological parameters (material and granulometric compositions, temperature calcination) to obtain mineral additives based on calcined clays and carbonate rocks on their activity in cement systems. **Methods and materials.** Polymineral clays and carbonate rocks (dolomite and chalk) from several deposits of the Republic of Mordovia were used as raw materials for obtaining mineral additives. The specific surface area of modifiers was determined on the PSX-12 dispersion analysis device using the Kozeny-Carman method. The study of the granulometric composition of sedimentary rock powders was carried out by laser diffraction method. The research of physical-chemical processes occurring during the heat treatment of polymineral clays and carbonate rocks was carried out using the synchronous thermal analysis method. Optimization of calcination temperature of clay-carbonate mixtures was carried out based on the research results on the effect of their additives on the cement binder activity with the determination of the modifier activity index in accordance with the methodology of the Russian State Standard GOST R 56178-2014. **Results and discussion.** The optimum calcination temperature, located for polymineral clays in the area of 500–800°C, was established according to the study results of dehydration processes of clay minerals using the synchronous thermal analysis. This temperature range corresponds to the initial restructuring processes in the crystal structure of minerals of the kaolinite and illite groups, associated with their dehydroxylation, which contributes to the transition of these phases to the active form. The study results of influence of additives of calcined clay-carbonate mixtures on the cement binder activity proved the thermal analysis data. It was found that calcination of clays and clay-carbonate mixtures at 700°C contributes to obtaining of the most effective mineral modifiers. **Conclusions.** On the totality of studies, regularities were revealed in the system "modifier composition – calcination temperature of sedimentary rocks – mixed binder activity", which allow optimizing the prescription and technological parameters for obtaining mineral additives to achieve the required level of strength characteristics of cement composites.

KEYWORDS: cement system, nanomodifier, calcined clay, carbonate rock, granulometric composition, calcination temperature, thermogravimetric analysis, dehydration, activity, optimization.

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INTRODUCTION

The development of energy-efficient high performance cement concretes is topical direction of modern building materials science [1, 2, 3, 4, 5]. The management of physical and chemical processes of structure formation of such composites can be provided at several scale levels through the use of modifiers of various nature and mechanism of action, in particular, micro- and nanoscale mineral additives of natural and technogenic origin, which contribute to solving problems of resource and energy saving, as well as environmental protection environment by reducing the clinker capacity of compositions [6, 7, 8, 9, 10, 11, 12].

It is known that aluminosilicate rocks, in particular monomineral kaolinite clays ($Al_2(OH)_4[Si_2O_5]$ or $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$) [13], are promising raw materials for obtaining mineral additives. Thermal activation of these clayey rocks within the range of 650–800°C, which contributes to the removal of about 14 wt. % of chemically bounded water, leads to the destruction of their initial crystalline structure and formation of the amorphous phase, called metakaolinite (metakaolin). Metakaolin is sufficiently effective pozzolanic additive [14, 15, 16], however, its degree of application in the cement industry remains low due to a number of reasons, such as the territorial and quantitative limitations of kaolinite clays, the high cost of the resulting enriched raw materials, etc. In this regard, expanding the raw material base of aluminosilicate rocks to obtain effective mineral additives for cement systems is promising direction. Calcined polymineral clays are among the most promising aluminosilicate sedimentary rocks, in view of the fact that their effectiveness can be ensured due to structural features, in particular, the presence of several clay minerals capable of synergetic interaction in composition [17, 18, 19, 20].

In addition to aluminosilicate modifiers, carbonate mineral additives are characterized by increased efficiency in the cement systems. The action of carbonate rocks (limestones, dolomite limestones, dolomites) is based on the ability of the rock-forming mineral (calcite) to act as the crystallization center of new phases [21, 22, 23]. The papers [24, 25] show that the efficiency of carbonate rocks is increased in the presence of aluminosilicate components, which, in addition to tricalcium aluminate contained in cement, can be such aluminum-containing mineral additives, for example, as slags, fly ashes, thermally activated clays, etc. In this connection, the combined use of calcined clays and carbonate rocks in the compositions of modified cement composites is relevant trend.

The purpose of this study was to establish the influence regularities of the prescription and technological parameters (material and granulometric compositions, temperature calcination) to obtain mineral additives based on calcined clays and carbonate rocks on their activity in cement systems.

To achieve this objective, the following tasks were solved:

1) the grinding ability of the initial clays and carbonate rocks was studied with the establishment of the specific surface area and granulometric composition of the obtained mineral powders;

2) the physical-chemical processes occurring during the heat treatment of polymineral clays and carbonate rocks were researched;

3) the influence of composition and calcination temperature of clay-carbonate mixtures on the cement binder activity was studied;

4) the interrelations and regularities were revealed in the system "modifier composition – calcination temperature of clays and carbonate rocks – mixed binder activity", which allow optimizing the prescription and technological parameters for obtaining mineral additives to achieve the required level of strength characteristics of cement composites.

METHODS AND MATERIALS

Materials

The main component of binder in the cement system recipes was Portland cement 500-D0-N (PC) produced by Mordovcement PJSC. The raw materials for obtaining mineral additives (MA) were represented by sedimentary rocks from several deposits of the Republic of Mordovia:

1) clayey rocks such as polymineral clays from the Nikitsky (CN) and Staroshaigovsky (CS) deposits;

2) carbonate rocks such as dolomite from the Yelnikovsky deposit (DY) and chalk of the Atemarsky deposit (CA).

The research of the physical-chemical efficiency of mineral additives based on calcined clays and carbonate rocks was carried out on fine-grained concrete compositions containing standard monofractional sand according to the Russian State Standard GOST 6139 as fine aggregate.

Methods

The evaluation of the grinding ability of the initial mineral raw materials was carried out based on the study results of the grinding time effect on the specific surface area value of the obtained powders of clays and carbonate rocks.

The raw materials were previously dried to a constant weight and mechanically crushed until the pass of particles through screen with hole size of 2.5 mm. The grinding of prepared sedimentary rocks weighing 500 g was carried out in a ball drum mill at a rotation speed of 73 rpm. The milled rocks were sifted through screen with hole size of 0.16 mm while fixing the final product yield by weight. The analysis of the powders obtained as result of grinding and sieving and the determination of their specific surface area were carried out using the PSX-12 dispersion analysis device.

The specific surface area using the PSX-12 dispersion analysis device was determined by the Kozeny-Carman method based on the air permeability and porosity establishment of the powder compacted layer. The gas permeability of the powder layer was measured according to the filtering time of given air volume through the device at fixed vacuum in its working volume.

The study of the granulometric composition of sedimentary rock powders was carried out by laser diffraction method using the Shimadzu Sald-3101 particle size analyzer, which makes it possible to analyze finely dispersed materials in the particle size range from 50 nm to 3 mm.

The research of physical-chemical processes occurring during the heat treatment of polymineral clays and carbonate rocks was carried out using the synchronous thermal analysis method (STA), when combining thermogravimetric and differential thermal analysis methods. TGA/DSC1 thermogravimetric analyzer was used for the study in addition to data on changes in the weight of the sample (thermogravimetry (TGA)), it automatically provides information about the thermal processes thanks to the signal of differential scanning calorimetry (DSC). During the thermal analysis, the temperature rise rate was 10°C/min. The corresponding experimental TG, DTG and DTA curves were obtained as the research results.

Optimization of calcination temperature of clay-carbonate mixtures was carried out based on the research results on the effect of their additives on the cement binder activity with the determination of the modifier activity index. The activity index of obtained mineral additives was determined under the Russian State Standard GOST R 56178-2014 method by comparing the results of compression strength tests after steaming cement-sand samples-beams of 40×40×160 mm, made using of modified binders consisting of 90% Portland cement and 10% mineral additive (by weight of the binder (PC+MA)), and control samples of unmodified composition with a ratio of cement binder and standard monofractional sand equal to $^1/_3$. The water-binder ratio was taken the same for all compositions, it equated to the value established for the most water-demanding composition when the flow spread diameter of fine-grained concrete mixture from the Hagermann cone was reached of 106–108 mm. The procedure for manufacturing and testing of samples-beams adopted following the requirements of the Russian State Standard GOST 310.4, the mode of heat and humidity treatment is selected following the Russian State Standard GOST R 56178-2014 equal to (3+3+6+2) hours at isothermal holding temperature of 80°C.

Based on the results of determining the compressive strength of steamed samples (the activity of cement binders), the activity index of applied mineral additives (C_{MA}) was calculated using the formula

$$C_{MA} = \frac{R_2}{R_1}, \qquad (1)$$

where R_1 and R_2 are compressive strength of samples of unmodified (control) and modified (main) compositions, respectively, MPa.

RESULTS AND DISCUSSION

Analysis of the grinding ability of clays and carbonate rocks

The study results of the grinding time effect on the specific surface area value of the obtained powders of clays and carbonate rocks are presented in Table 1.

According to the results of grinding clays and carbonate rocks in the ball mill, the following values of the specific surface area (S_{ss}) of powders were achieved: 4,950–7,800 cm²/g for the Nikitsky clay (grinding time of 0.5–1.0 hours); 3,100–5,200 cm²/g for the Staroshaigovsky clay (grinding time of 0.5–2.0 hours); 11,100–13,500 cm²/g for the Atemarsky chalk (grinding time of 0.25–3.0 hours); 3,150–4,550 cm²/g for the Yelnikovsky dolomite (grinding time of 0.25–5.0 hours). Thus, among the studied rocks chalk of the Atemarsky deposit has the highest grinding ability, for which powder specific surface area of 13,000 cm²/g was achieved during hourly grinding, which is 199%, 67% and 271% higher than the similar indicator of the Yelnikovsky dolomite, Nikitsky clay and Staroshaigovsky clay (4,350 cm²/g; 7,800 cm²/g and 3,500 cm²/g, respectively).

Taking into account the experimental data (Table 1) on achieving the optimal balance in the system "grinding time (energy consumption) – particle size – powder yield by weight", in further studies the grinding time of the Nikitsky clay, Staroshaigovsky clay, Atemarsky chalk and Yelnikovsky dolomite was taken at 1 hour, 2 hours, 1 hour and 3 hours with the corresponding values of the specific surface area of the obtained powders equal to 7,800 cm²/g, 5,200 cm²/g, 13,000 cm²/g and 4,450 cm²/g.

The granulometric composition of powders of carbonate rocks and polymineral clays is analyzed taking into account the accepted grinding time. The integral curves of the volumetric particle size distribution for sedimentary rock powders are shown in Figure 1. The key indicators of the granulometric composition of the studied materials, determined by the laser diffraction method, are generalized in Table 2.

According to the study results (Fig. 1 and Table 2) the particle size ranges equal to 0,2–15,3 μm, 0.3–45.9 μm, 0.3–8.8 μm and 0.2–17.0 μm for powders of the Nikitsky clay, Staroshaigovsky clay, Atemarsky chalk and Yelnikovsky dolomite, respectively. At the same time, the average volumetric diameter (d 50%) of the powder particles increases in sequence CA → DY → CN → CS (1.3 μm, 2.9 μm, 3.8 μm and 5.7 μm, respectively).

Physical-chemical processes occurring during the heat treatment of polymineral clays and carbonate rocks

According to the data shown in Figures 2 and 3, it is possible to distinguish the main stages of the mineral

Table 1
Specific surface area of powders of polymineral clays and carbonate rocks depending on the grinding time of material

No.	Grinding time	Specific surface area, cm²/g
Clay from the Nikitsky deposit		
1	30 minutes	4,950
2	1 hour	7,800
Clay from the Staroshaigovsky deposit		
3	30 minutes	3,100
4	1 hour	3,500
5	2 hours	5,200
Chalk of the Atemarsky deposit		
6	15 minutes	11,100
7	30 minutes	12,200
8	1 hour	13,000
9	3 hours	13,500
Dolomite from the Yelnikovsky deposit		
10	15 minutes	3,150
11	30 minutes	3,850
12	1 hour	4,350
13	3 hours	4,450
14	5 hours	4,550

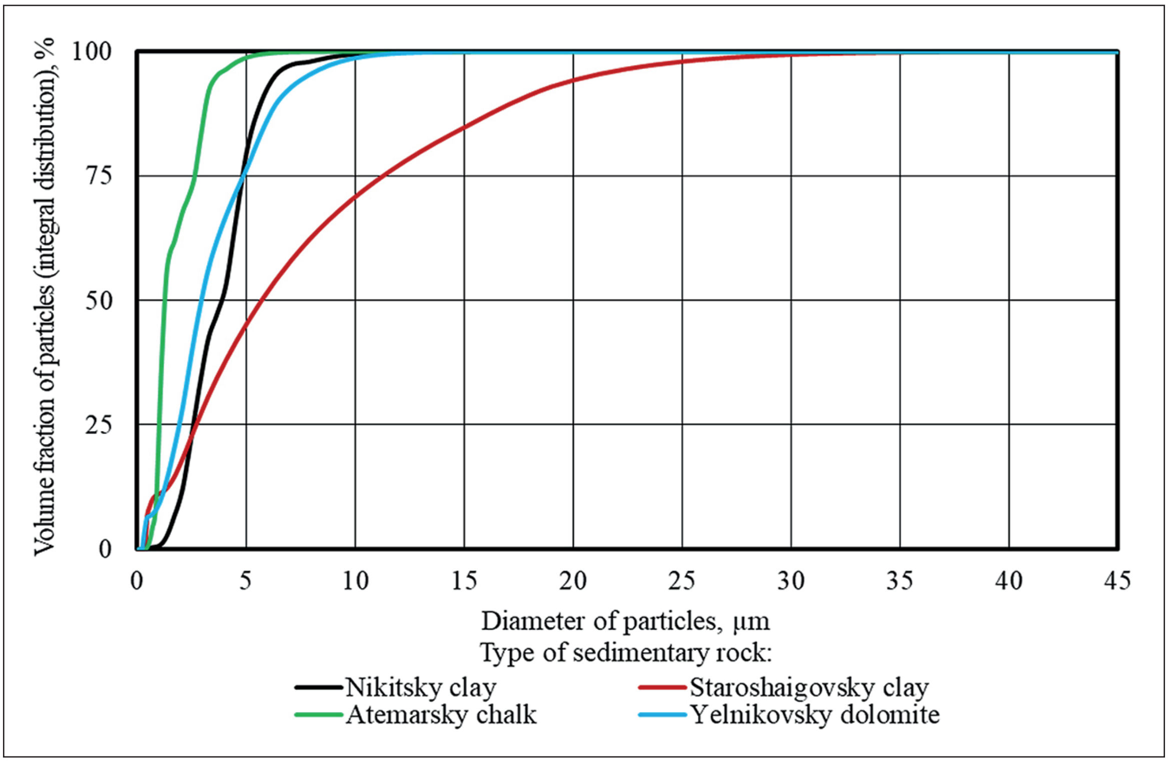

Fig. 1. **Integral curves of the volumetric distribution of powder particles of the studied sedimentary rocks**

Table 2

Key indicators of the granulometric composition of the studied sedimentary rock powders according to the laser diffraction method

Type of sedimentary rock	Particle size range, µm	Particle size, µm		
		d 90%	d 50%	d 10%
Nikitsky clay (grinding time of 1 hour)	0.2–15.3	5.8	3.8	1.9
Staroshaigovsky clay (grinding time of 2 hours)	0.3–45.9	17.4	5.7	0.7
Atemarsky chalk (grinding time of 1 hour)	0.3–8.8	3.2	1.3	0.9
Yelnikovsky dolomite (grinding time of 3 hours)	0.2–17.0	6.5	2.9	1.1

dehydration processes of the Nikitsky clay and Staroshaigovsky clay during gradual and continuous heating.

A number of endothermic effects are observed on the DTA curves for the researched clay rocks. Endoeffects in the temperature range from 40°C to 300°C (temperature maximums at 85°C, 125°C and 265°C (Nikitsky clay); 90°C, 140°C and 265°C (Staroshaigovsky clay)) are caused by the loss of chemically unbound water (free, adsorbed, zeolite) by clay rocks [18, 19]. The increased content of free iron hydroxides characteristic of the Nikitsky clay gives noticeable additional endothermic effect in the range of 350–450°C with temperature peak at 405°C (DTA curve), as well as mass loss in the region of 300–400°C (TG and DTG curves) (Fig. 2).

The following endothermic effects in the temperature range of 450–600°C and 600–750°C are associated with successive processes of separation of constitutional water from the main clay minerals of the kaolinite and illite groups. Temperature maximums of kaolinite and illite dehydroxylation endoeffects for the Nikitsky and Staroshaigovsky clays are 495°C and 680°C, 485°C and 650°C, respectively (Figs. 2 and 3). In this case, according to the TG and DTG curves of dehydration, a more significant mass loss in the temperature range of 400–550°C for the Nikitsky clay indicates the increased total content of minerals of the illite and kaolinite groups in its phase composition compared to the Staroshaigovsky clay.

It is worth noting that in addition to the presence of successive endothermic effects of separation of constitutional water from minerals of the kaolinite and illite groups, in the temperature range of 550–600°C it is possible to endoeffect overlay associated with the polymorphic transformation of quartz from α to β modification.

In the temperature range of 900–950°C on the DTA curve for the Nikitsky clay (Fig. 2), a blurred exoeffect is observed with peak in the region of 905–915°C, which can characterize the formation of sillimanite or mullite from dehydrated kaolinite.

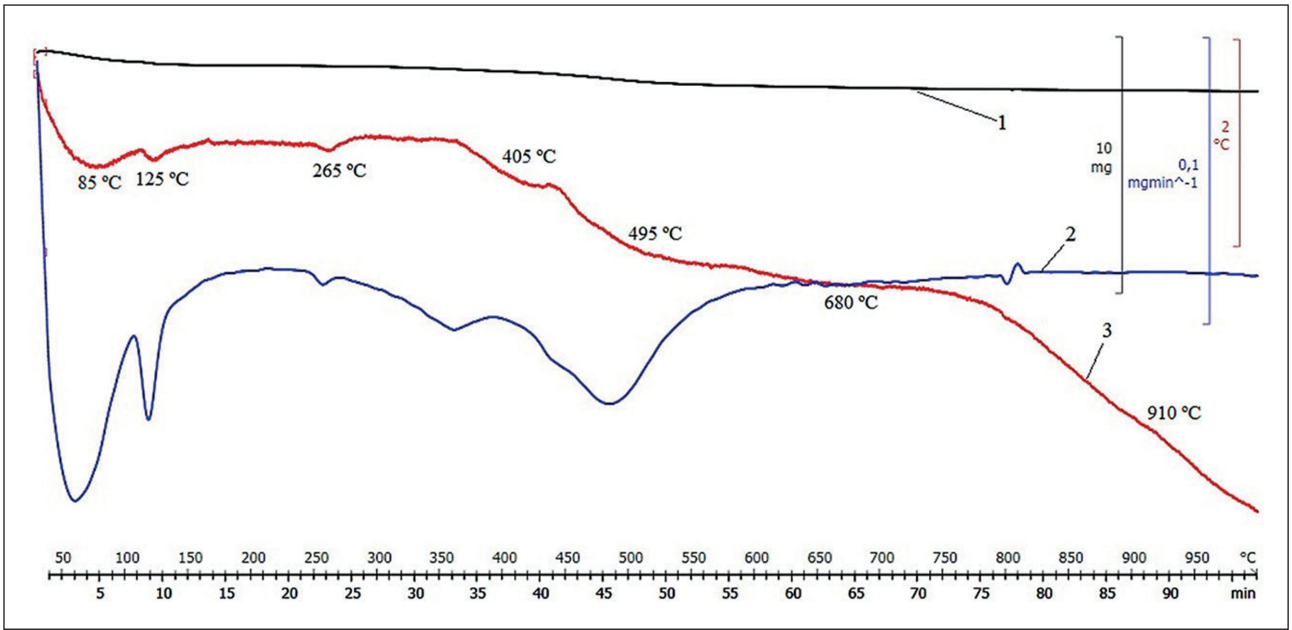

Fig. 2. **TG (1), DTG (2) and DTA (3) curves for the Nikitsky clay powder**

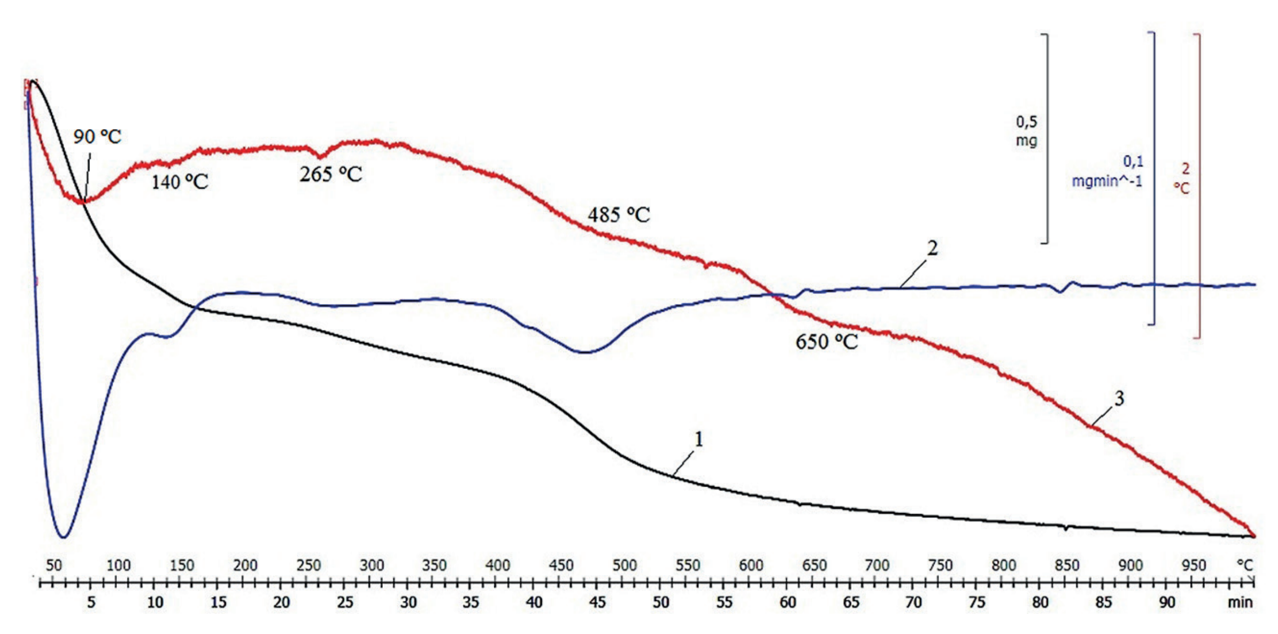

Fig. 3. **TG (1), DTG (2) and DTA (3) curves for the Staroshaigovsky clay powder**

From the literature data [18], it is known that from the beginning of the dehydration process to its completion, the crystal structure of clay minerals undergoes gradual changes until the total destruction of the crystal lattice (amorphization). Changes in the state and shape of the crystal lattice, the break of individual bonds lead to an increase in the pozzolanic (chemical) activity of minerals. At the same time, the initial thermal destruction products of clay minerals with metastable crystal lattice are characterized by increased activity.

Thus, summarizing the obtained results of thermal analysis, we can conclude that the optimal calcination temperature of the Nikitsky and Staroshaigovsky clays is in the area of 500–800°C. This temperature range corresponds to the initial restructuring processes in the crystal structure of minerals of the kaolinite and illite groups, associated with their dehydroxylation, which contributes to the transition of these phases to the active form.

The study results of the physical-chemical processes occurring during the calcination of carbonate rocks

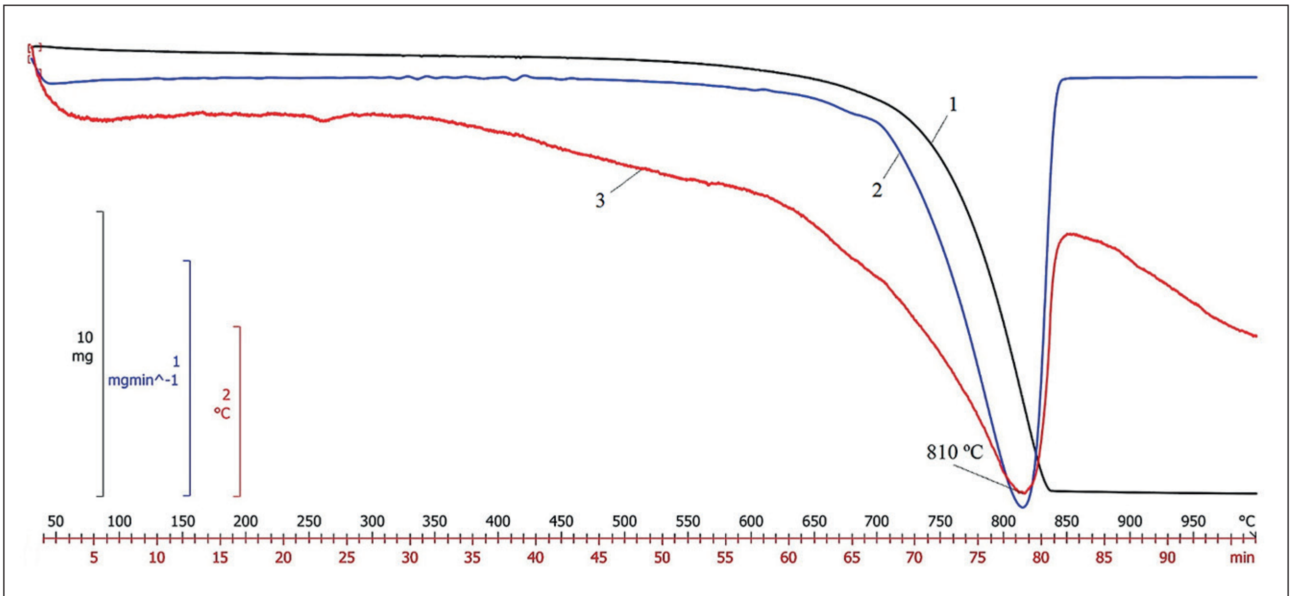

Fig. 4. **TG (1), DTG (2) and DTA (3) curves for the Atemarsky chalk powder**

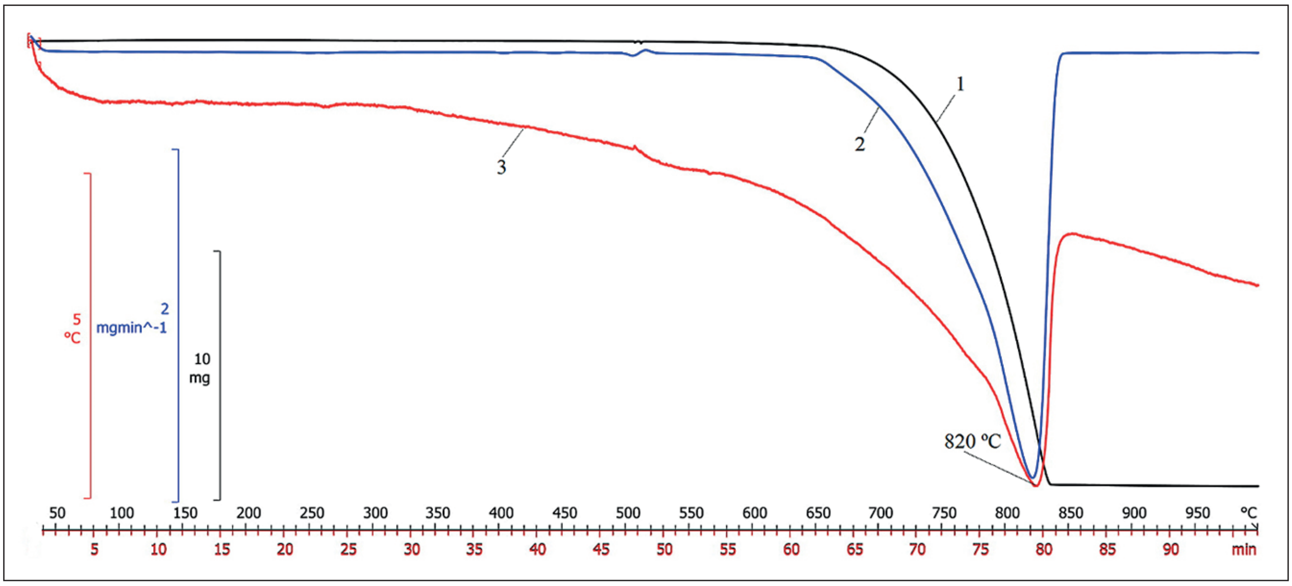

Fig. 5. **TG (1), DTG (2) and DTA (3) curves for the Yelnikovsky dolomite powder**

(Atemarsky chalk and Yelnikovsky dolomite) are shown in Figures 4 and 5.

According to Figure 4, deep endothermic effect with the temperature maximum at 810°C is observed on the DTA heating curve for chalk of the Atemarsky deposit. At the same time significant weight loss in the temperature range of 700–850°C, characterizing the dissociation of calcite ($CaCO_3$) to CaO and CO_2, is established on the TG dehydration curve.

The DTA, TG and DTG curves of the Yelnikovsky dolomite (Fig. 5) have a close similarity to the corresponding thermograms of the Atemarsky chalk. In particular, the endoeffect corresponding to the calcite decomposition is represented by temperature peak at 820°C, and the main weight loss occurs in the temperature range of 650–850°C. At the same time, the existence of inflection at 770–800°C is established on the DTA curve in area of the main endoeffect. This segment of the DTA curve can characterize the decomposition of dolomite ($CaMg(CO_3)$) to calcite ($CaCO_3$) and magnesite ($MgCO_3$) with their subsequent dissociation.

Optimization of calcination temperature of clay-carbonate mixtures according to the effect of their additives on the cement binder activity

At the first stage, the influence of additives of thermally activated clays of the Nikitsky and Staroshaigovsky deposits on the mixed cement binder activity was studied when the calcination temperature of sedimentary rocks varied at the levels of 200°C, 400°C, 600°C, 700°C, 800°C, 900°C. At the same time, the calcination time at the specified temperature levels (the isothermal holding time) was fixed at 2 hours. In addition to unmodified composition, the control composition was cement system with additive of metakaolin MKZhL-2 (MKN) (10% of the binder weight (PC+MA)) with specific surface area of 16,500 cm²/g produced by Plast-Rifey LLC. The study results are shown in Figure 6.

It was found that the calcination of the Nikitsky and Staroshaigovsky clays allows increasing the compressive strength of fine-grained concrete from 32.9 MPa and 31.1 MPa (for compositions with additives of non-calcined clays) to 33.6–36.4 MPa and 31.2–32.7 MPa, respectively (Fig. 6). At the same time, the activity of cement binder with additives of the thermally activated Nikitsky clay is higher than in compositions with the Staroshaigovsky clay at any calcination temperature in the studied range, which is explained by higher content of reactive clay minerals (kaolinite and illite) in the phase composition of the first clay compared to the second one.

Heat treatment of the Staroshaigovsky clay does not allow to get mixed cement binder with activity higher than the same indicator for Portland cement (the activity index of calcined clay C_{MA} = 0.90–0.94 < 1). At the same time, a number of compositions with thermally activated Nikitsky clay have compressive strength exceeding that of the unmodified composition. In particular, replacing 10% of Portland cement with additive of the Nikitsky clay calcined at 600–700°C allows achieving the mixed binder activity of 35.5–36.4 MPa, which is higher than the activity of Portland cement and mixed binder based on Portland cement and metakaolin (Fig. 6).

Thus, according to the study results, the optimal temperature interval of calcination of the polymineral clays is 600–700°C, which is consistent with the data of thermal analysis for the temperature range of dehydroxylation of the main reactive minerals, such as

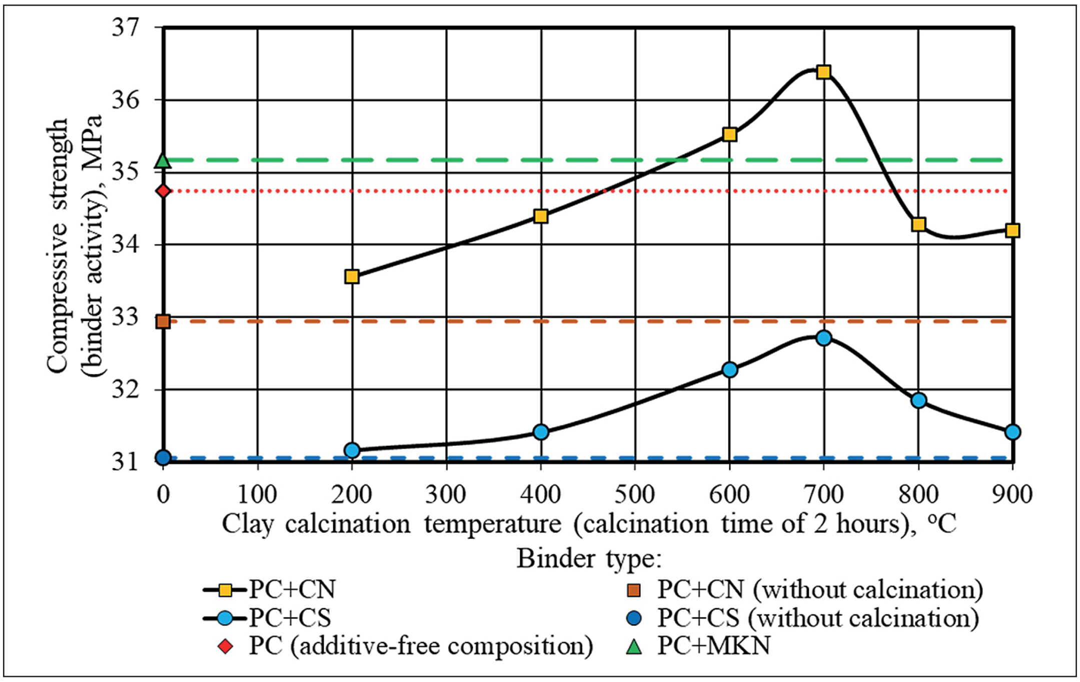

Fig. 6. **Influence of clay calcination temperature on the activity of mixed cement binders (calcination time of 2 hours)**

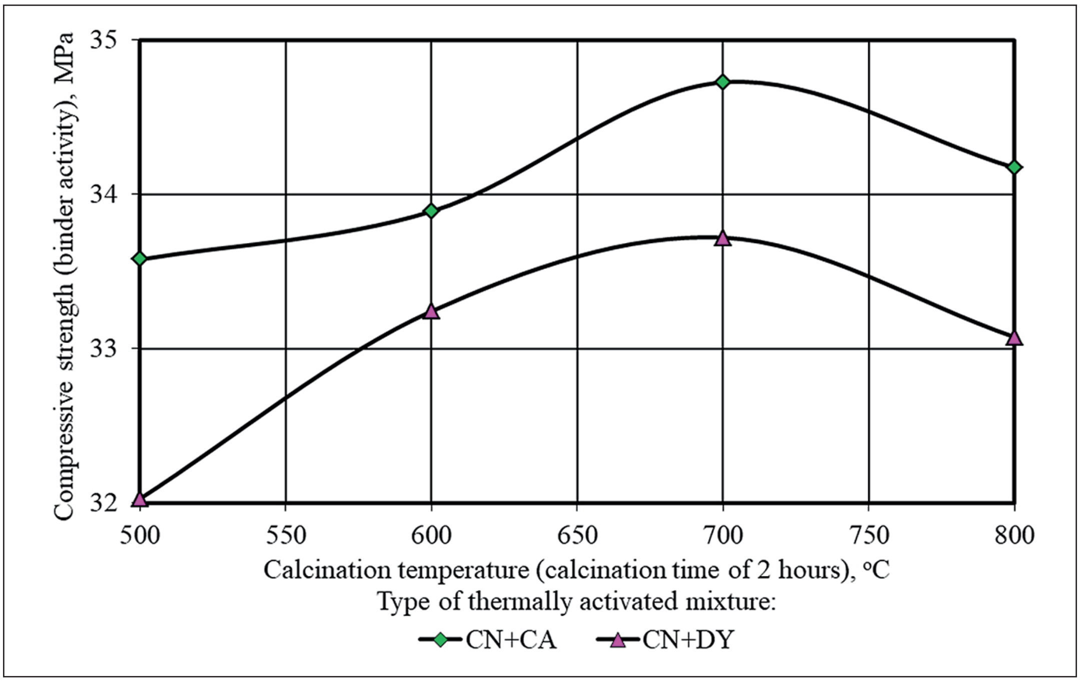

Fig. 7. **Influence of calcination temperature of mixtures of the Nikitsky clay and carbonate rocks on the cement binder activity (calcination time of 2 hours)**

kaolinite and illite (Figs. 2 and 3). Thermal activation of clays in the specified range contributes to the obtaining of mineral additives with the highest values of activity index. In particular, modifiers based on the Nikitsky clay calcined at 600–700°C are active mineral additives with the activity index of C_{MA} = 1.02–1.05 > 1, which is higher than the similar index of metakaolin MKZhL-2 (C_{MA} = 1.01).

At the second stage, the influence of additives of calcined mixtures of Nikitsky clay (as the most effective clay in cement systems according to the previous study results) and carbonate rocks (Atemarsky chalk and Yelnikovsky dolomite) at the ratio of components equal to $^1/_1$ on the cement binder activity was researched when the calcination temperature of sedimentary rocks varied at the levels of 500°C, 600°C, 700°C and 800°C. At the same time, the calcination time at the specified temperature levels (the isothermal holding time) was fixed at 2 hours. The study results are shown in Figure 7.

It was found that the strength characteristics of cement composites with additives of thermally activated mixtures of the Nikitsky clay and Atemarsky chalk are 2.1–5.0% higher than those of compositions using calcined mixtures of the Nikitsky clay and Yelnikovsky dolomite at the same calcination temperature.

In compositions with additives of the calcined mixtures of clay and chalk as well as clay and dolomite, the highest values of the mineral modifier activity index, respectively, equal to 1.00 and 0.97 rel. units, were achieved with the thermal activation temperature of 700°C. At the same time, at this calcination temperature the maximum activity of the mixed binder recorded in the composition with additive of the calcined mixture "Nikitsky clay + Atemarsky chalk" (34.7 MPa), which is equal to the same indicator of Portland cement in the additive-free composition (34.7 MPa, Fig. 6) and 4.7% lower than parameter of binder with individual additive of the Nikitsky clay (36.4 MPa, Fig. 6).

CONCLUSIONS

The following results were obtained from experimental studies:

1) the evalution of the grinding ability of the initial clays and carbonate rocks was carried out according to the specific surface area and granulometric composition of the obtained mineral powders;

2) the physical-chemical processes occurring during the heat treatment of polymineral clays and carbonate rocks were disclosed using the synchronous thermal analysis method;

3) the influence of composition and calcination temperature of clay-carbonate mixtures was established on the cement binder activity (the Russian State Standard GOST 310.4) with determination of the activity index of mineral modifier;

4) the interrelations and regularities were revealed in the system "modifier composition – calcination temperature of clays and carbonate rocks – mixed binder activity", which allow optimizing the prescription and technological parameters for obtaining mineral additives to achieve the required level of strength characteristics of cement composites.

According to the study results of dehydration processes of clay minerals using the synchronous thermal analysis method, it was established that the optimal calcination temperature for clays of the Nikitsky and Staroshaigovsky deposits located in the area of 500–800°C. This temperature range corresponds to the initial restructuring processes in the crystal structure of minerals of the kaolinite and illite groups, associated with their dehydroxylation, which contributes to the transition of these phases to the active form.

The study results of influence of additives of calcined clay-carbonate mixtures on the cement binder activity confirmed the thermal analysis data. It was found that calcination of clays and clay-carbonate mixtures at 700°C contributes to obtaining of the most effective mineral modifiers. Using this calcination temperature, replacing 10% of Portland cement with additive of the thermally activated Nikitsky clay allows achieving the binder activity exceeding the same indicator of mixed binder based on Portland cement and high-quality metakaolin.

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