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Structure and properties of cement systems with additives of calcined clay and carbonate rocks

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Abstract. Currently, one of the primary areas of technical progress in the field of construction is creating modern high performance concretes based on modified cement binders using various chemical and mineral additives that allow effective control of the structure formation and properties of material. The stock of the conventional additives for cement systems is failing to meet the increasing demand, which is related to territorial limitations and high cost of the most popular and efficient mineral modifiers (silica fume, metakaolin, fly ash, granulated slag, etc.). In this respect, thermally activated polymineral clays used as individual mineral additives and in complexes with carbonate rocks are promising for many regions of the Russian Federation, including the Republic of Mordovia. The paper presents results of studying the patterns in which mineral additives obtained on the basis of local raw materials of the Republic of Mordovia (calcined polymineral clay, dolomite and thermally activated mixture of clay and limestone) influence the technological characteristics of plasticized cement paste, phase composition and physical-mechanical properties of cement stone. Optimal dosages of mineral additives of calcined clay and thermally activated mixture of clay and limestone were identified: they did not exceed 19 and 12 % by binder weight, respectively. These dosages improved strength characteristics of cement systems in comparison with the control composition without the additives. X-ray powder diffraction established that using the developed mineral additives based on calcined polymineral clay and carbonate rocks increased hydration rate of Portland cement and allowed a targeted guidance of the cement stone phase composition: optimizing the ettringite concentration, reducing the number of the weakest and corrosion-exposed Portlandite crystals, increasing the density and strength of the bulk of calcium hydrosilicates by shifting the balance towards an increased content of highly dispersive low basic phases of C–S–H(I) type instead of high basic C–S–H(II) compounds. All of these factors determined the chemical efficiency of these mineral modifiers in cement systems.

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1. Introduction

The late 20th century and early 21st century were marked by revolutionary changes in concrete technology [1–6], which was and is one of the main building materials. The most important achievements in the field of cement concretes were those that broadened the understanding of processes taking place at the micro-level and promoting improved primary characteristics of the material – strength, deformability, corrosion resistance, etc. [7, 8]. Among them were scientific justification of cement hydration processes and development of scientific bases for modifying cement systems with chemical and mineral additives that allowed for efficient control over concrete structure formation at all stages of technology ensuring the high quality of products and structures based on it [9–16].

Out of many types of mineral modifiers for the compositions of high-strength cement systems, highly dispersive pozzolanic additives have increased efficiency. These additives contain amorphous silica or alumina and have high reactive activity: condensed silica fume, high-dispersive fly ash of heat power plants with a minimal content of non-combusted residues, blast-furnace granulated slag, etc. [9, 10, 17–20]. It was confirmed by the results of the authors' studies [21–24].

One of the most efficient pozzolanic additives is metakaolin [25–32] representing a product of thermal treatment of mono-mineral kaolinite clays $Al_2(OH)_4[Si_2O_5]$ or $Al_2O_3{\cdot}2SiO_2{\cdot}2H_2O$ within the range of 650–800 °C. Removal of about 14 wt. % of chemically bonded water results in the destruction of the initial crystalline structure and formation of the amorphous phase (metakaolinite). Calcination at a higher temperature (900–1000 °C) promotes the mullite formation by transformation the crystalline grid of metakaolinite with the detachment of γ-Al_2O_3. At the same time, it should be noted that the high cost of the resulting enriched raw materials, the large specific surface requiring the use of plasticizers, and the growing needs of the paper and medical industries that are also kaolin consumers cause a low degree of its application in the cement industry. Moreover, the kaolin reserves are limited both spatially and quantitatively. According to [33], only 3 % of the global kaolin reserves are found in Russia that occupies about 1/9 of the land area of the whole world.

In this connection, it is important to create an efficient substitute for deficient and expensive imported mineral modifiers with cheaper additives based on common local raw materials. In this respect, thermally activated polymineral clays used as individual mineral additives and in complex with other modifiers are the most promising for many regions of the Russian Federation, including the Republic of Mordovia.

The papers [34–40] were defined the optimal parameters for baking polymineral clays based on the evaluation of their reactivity depending on the chemical and mineralogical composition of raw materials. It has been found that the initial products of dehydration and thermal destruction of clay minerals with a partially restructured (meta-stable) crystalline grid are of increased activity. A transition to an active form of most clay minerals (kaolinite, montmorillonite, illite, bentonite, etc.) was reached within 400–800 °C.

Apart from active mineral additives, an important component of modern concretes is relatively chemically inert additives (fillers) of carbonate rocks such as limestones, dolomitic limestones, and dolomites [41]. However, the lack of reactivity of such additives is doubtful, which was proved by researchers [42] who studied hydration of C_3S in the presence of a superplasticizer and $CaCO_3$ using calorimetry. As a result of the application of highly dispersive limestone the additional centers of crystallization of new formations in cement systems was installed. The papers [43–46] showed that the efficiency of additives of carbonate rocks is increased in the presence of aluminosilicate components that, 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, a relevant trend is the combined use of thermally activated clays and carbonate rocks in the formulations of modified cement composites.

Thus, according to the results of literature review, it has been found that the resources of currently used additives for cement systems do not meet the increasing demand, which is related to territorial limitation and high cost of the most popular and efficient mineral modifiers (silica fume, metakaolin, fly ash, blast-furnace granulated slag). Currently, most studies in the area of aluminosilicate modifiers carried out by foreign and national scientists are dedicated to the efficiency of the calcination product of kaolinite monomineral clays (metakaolin). At the same time, such sedimentary rocks as polymineral low-kaolinite clays, widely distributed in many regions of the Russian Federation, are not considered as components of complex additives for cement systems. Of particular interest at present is the use of thermally activated mixtures of polymineral clays and carbonate rocks (limestones, dolomites) as complex additives in the formulations of cement systems. The highest attention in creating efficient complex modifiers based on calcined clays and carbonate rocks must be paid to studying their physical-chemical and technological compatibility between each other, with Portland cements, superplasticizers, other components of the formulation with identification of synergistic effects. It is also required to have detailed studies of the effects of the chemical and mineral compositions of both clays and carbonate rocks on the structure formation of cement stone and properties of modified cement concretes of various types.

The aim of the current research was to establish the patterns of influence of mineral additives based on calcined polymineral clay and carbonate rocks of the Republic of Mordovia on the structure formation and physical-mechanical properties of plasticized cement systems with the identification of the most effective modifiers. To achieve this aim, the following tasks were solved:

– mineralogical (phase) composition of the initial clay and carbonate rocks was established;

- the effect of dosages of mineral additives based on calcined clay and carbonate rocks on the mobility of plasticized cement paste was studied;
- the influence of mineral additives based on thermally activated clay and carbonate rocks on the phase composition and physical-mechanical properties of cement stone was studied;
- interrelations and regularities in the “composition – structure – property” system were revealed, which allow optimizing the formulations of modified cement compositions to achieve the required levels of technological and physical-mechanical characteristics.

2. Materials and methods

2.1. Materials

The primary component of binder in the formulations of cement systems was Portland cement CEM I 42.5 R (PC) manufactured by Mordovtsement PJSC (Russian State Standard GOST 31108). Melflux 5581 F polycarboxylate superplasticizer was used as modifier using in complexes with the following types of mineral additives:

1. thermally activated clay of the Nikitsky deposit (TCN) (temperature and time of calcination: 700 °C and 2 hours; S_{SS} = 7800 cm^2/g (grinding for 1 hour)) located in the north-western part of Saransk, the Republic of Mordovia, the Russian Federation;
2. dolomite of the Yelnikovsky deposit (DY) (S_{SS} = 4450 cm^2/g (grinding for 3 hours)) located near the village of Budayevo, Yelnikovsky district, the Republic of Mordovia, the Russian Federation;
3. thermally activated mixture of Nikitsky clay and limestone of the Atemarsky deposit (TM(CN+LA)) (clay to limestone ratio = 2/1; temperature and time of calcination: 700 °C and 2 hours) located near the village of Atemarsky, Lyambirsky district, the Republic of Mordovia, the Russian Federation.

This ratio of clay and carbonate rock (2/1) in the thermally activated mixture was adopted as the most optimal taking into account its correspondence to the proportion of the chemical reaction of the interaction of 1 mol of alumina metakaolin with 1 mol of calcium carbonate in the presence of excess of calcium ions in a water solution with the formation of 1 mol of calcium hydromonocarboaluminate as described in [47].

2.2. Methods

The first stage included the study of the mineralogical (phase) composition of Nikitsky clay, Yelnikovsky dolomite, and Atemarsky limestone.

The phase composition analysis of clay and carbonate rocks was done using X-ray powder diffraction (X-ray phase analysis). X-ray structural measurements were conducted using an Empyrean automated diffractometer by PANalytical (Netherlands) with a vertical goniometer in the radiation of a copper anode with a nickel filter ensuring suppression of the background and spectral line K_β together with the monochromator on the secondary beam. Shooting was done in the geometry according to Bragg-Brentano (θ–2θ scanning) using a spectral doublet Cu $K_{\alpha1,2}$ with weighted average wavelength λ = 1.5406 Å. X-ray powder diffraction patterns were obtained using PIXcel^{3D} two-coordinate semiconductor detector operating in the linear detector mode.

Qualitative phase analysis was done in semi-automatic mode using the HighScore Plus software linked with the base of the International Center for Diffraction Data ICDD PDF-2. Matches between the position and intensity of specimen reflexes and the card of a respective standard were searched. In the case of automatic selection of a large number of standard phases by the software from the PDF-2 library, the results were additionally specified in manual mode.

To specify the concentration and primary structural characteristics of the identified phases of the Nikitsky deposit clay, full-profile Rietveld analysis was used (quantitative X-ray phase analysis). The method was to calculate the theoretical model of the diffraction pattern using the structural models of phase components of the analyzed powder and reduce the calculated profile of the model diffraction pattern to the profile of the experimental diffraction pattern when varying profile and structural parameters and evaluating the level of discrepancy by the least square method. In order to find the relative concentration of crystalline phases of Atemarsky limestone and Yelnikovsky dolomite, the method of corundum numbers was used.

The second stage found the effects of dosages of mineral additives (MA) of the thermally activated Nikitsky clay, Yelnikovsky dolomite and Atemarsky limestone on the flowability of plasticized cement paste and physical-mechanical properties of cement stone (average density in normal humidity conditions at the age of 28 days, compressive strength at the age of 1, 7 and 28 days). The study was carried out for cement systems with the Melflux superplasticizer dosage of 1 % by weight of binder (Portland cement (PC) + mineral additive (MA)) and water-binder ratio W/B = W/(PC + MA) = 0.21 with varying content of used mineral modifiers in compositions within 0–20 % of binder weight (PC + MA) with increment of 5 % (Table 1).

Analysis of changes in the flowability of the plasticized cement paste depending on the content of mineral additives was done using a mini-cone (ring of the Vicat apparatus under the Russian State Standard GOST 310.3). The optimal dosage of the mineral modifier was deemed to be the amount that ensures the required consistency of cement paste defined by the mini-cone spread diameter of at least 250–255 mm.

The compression strength of cement stone was measured using Wille Geotechnik® press (13-PD/401 model). The primary parameters were configured and obtained experimental results were recorded using the GEOSYS 8.7.8 software.

Table 1. The researched compositions of cement systems.

Composition number	Portland cement	Type of mineral additives		
		TCN	DY	TM(CN+LA)
	% by weight of binder (Portland cement + mineral additive)			
1	95	5	–	–
2	90	10	–	–
3	85	15	–	–
4	80	20	–	–
5	95	–	5	–
6	90	–	10	–
7	85	–	15	–
8	80	–	20	–
9	95	–	–	5
10	90	–	–	10
11	85	–	–	15
12	80	–	–	20
Control	100	–	–	-

The third stage included the study of the effects of mineral additives based on thermally activated Nikitsky clay, Yelnikovsky dolomite, and Atemarsky limestone on the phase composition of cement stone aged 28 days using the X-ray phase analysis method. As study subjects, in addition to the non-modified composite of control composition, cement systems were selected, which had the dosage of mineral additives TCN, DY and TM (CN+LA) of 20 % of binder weight (PC + MA). The primary controlled parameters were as follows:

1. the level of Portland cement hydration (α) evaluated by the decrease in the intensity of one of the primary reflexes C_3S for d = 1.76–1.77 Å (2θ = 51.6–51.9°) in the hydrated powder samples of cement stone at the studied moment of time relative to the samples of the initial binder (Portland cement + mineral additive) until hydration;

2. the relative amount of Portlandite ($Ca(OH)_2$) evaluated by comparing the intensity of primary reflexes for d = 4.94–4.96 Å (2θ = 17.87–17.94°) and d = 1.93–1.94 Å (2θ = 46.8–47.0°) for powder samples of cement stone of modified and control compositions;

3. the relative content of ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12}\cdot 26H_2O$) evaluated by the ratio of the intensity of one of the primary reflexes for d = 9.80–9.84 Å (2θ = 8.98–9.02°) for powder samples of cement stone of modified and control compositions;

4. the relative content of low basic (C–S–H(I)) and high basic (C–S–H(II)) calcium hydrosilicates evaluated by comparing the intensities of one of the primary reflexes α-CS (d = 3.23–3.25 Å and 2θ = 27.4–27.6°) and β-CS (d = 2.97–2.99 Å and 2θ = 29.9–30.1°) for C–S–H(I) and β-C_2S (d = = 2.79–2.80 Å and 2θ = 31.9–32.1°) for C–S–H(II) in powder samples of cement stone of modified and control compositions calcined at 980–1000 °C.

3. Results and Discussion

3.1. Phase composition of the initial components of mineral additives

The results of qualitative and quantitative X-ray phase analysis to determine the primary crystalline phases and their relative concentrations for clay of the Nikitsky deposit are given in Table 2. It was found that the phase composition of the studied clay rock was represented predominantly by minerals of the kaolinite and illite (hydromicas) groups, as well as by quartz modifications, feldspars, and gypsum at their relative content in the overall mass of crystalline phases (wt. %): 39.8; 23.1; 19.8; 14.2 and 3.1, respectively, i.e. the represented clay was polymineral.

Table 2. Phase composition of Nikitsky deposit clay (before calcination).

Crystalline phase	Kaolinite	Illite group (hydromicas)	Quartz modifications	Feldspars	Gypsum
Phase content, wt. %	39.8	23.1	19.8	14.2	3.1

The mineralogical composition of the Yelnikovsky deposit dolomite was represented by phases of the dolomite $CaMg(CO_3)_2$ and calcite $CaCO_3$ with the relative phase contents of 52 wt. % and 48 wt. % for dolomite and calcite, respectively. The phase composition of the Atermarsky deposit limestone was predominantly represented by calcite $CaCO_3$ with inclusions of quartz SiO_2 with the relative phase contents of 96 wt. % and 4 wt. %, respectively (Table 3).

Table 3. Phase composition of carbonate rocks.

Type of carbonate rocks	Content of crystalline phases, wt. %		
	Calcite	Dolomite	Quartz modifications
Dolomite of the Yelnikovsky deposit	48	52	–
Limestone of the Atemarsky deposit	96	–	4

3.2. Effects of mineral additives dosages on the flowability of plasticized cement paste and physical-mechanical properties of cement stone

The study results confirmed the thickening capability of applied mineral additives increasing in the row of Yelnikovsky dolomite – thermally activated Nikitsky clay – thermally activated mixture of Nikitsky clay and Atemarsky limestone. Dependencies was found (Fig. 1), according to which the production of modified cement paste of required flowability (spread diameter of at least 250–255 mm) was possible for the contents of DY, TCN and TM(CN+LA) of no more than 18, 11 and 9 % of binder weight, respectively. If these dosages of applied modifiers were increased, this resulted in a significant drop in the flowability of cement systems indicated by a bend with an increased angle of inclination to the X-axis of respective curves expressing dependencies between the content of mineral additives and the mini-cone spread diameter of cement paste.

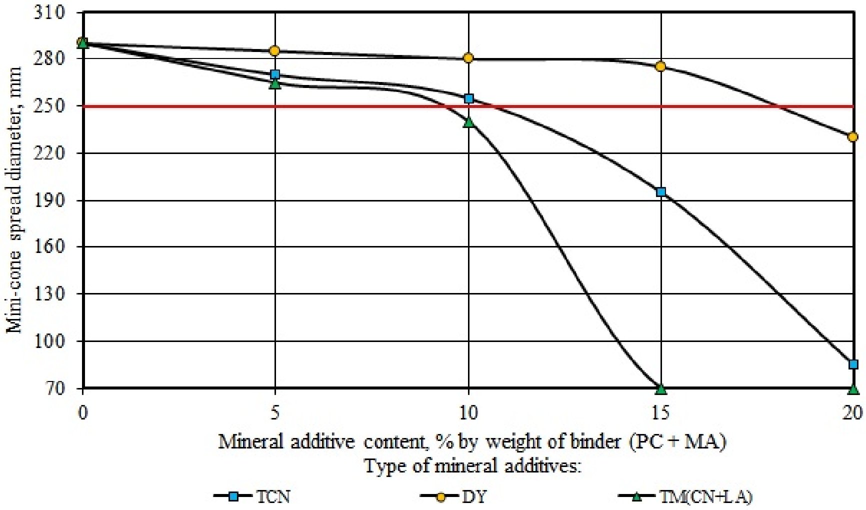

Figure 1. Influence of the type and dosage of mineral additives on the cement paste flowability.

Figs. 2 and 3 represent the study results for the effects of the dosages of mineral additives on the primary physical-mechanical properties of cement stone – average density in normal humidity conditions at the age of 28 days, compression strength at the age of 1, 7 and 28 days.

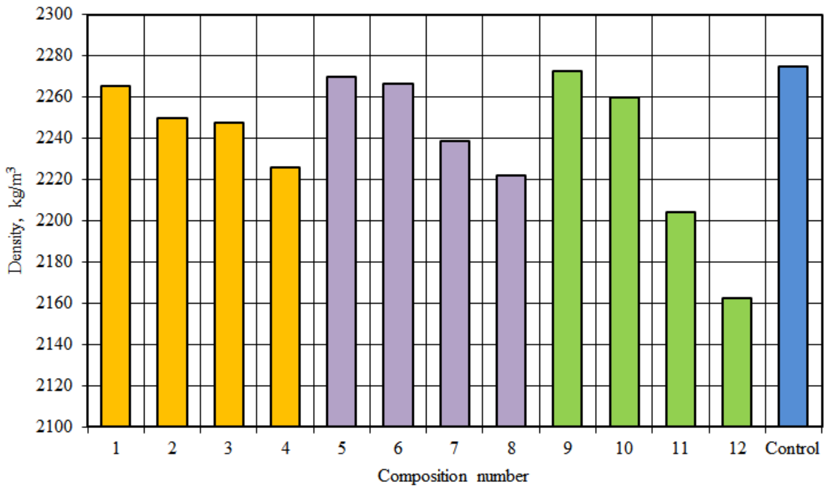

Figure 2. Average density of the researched cement paste compositions (Table 1).

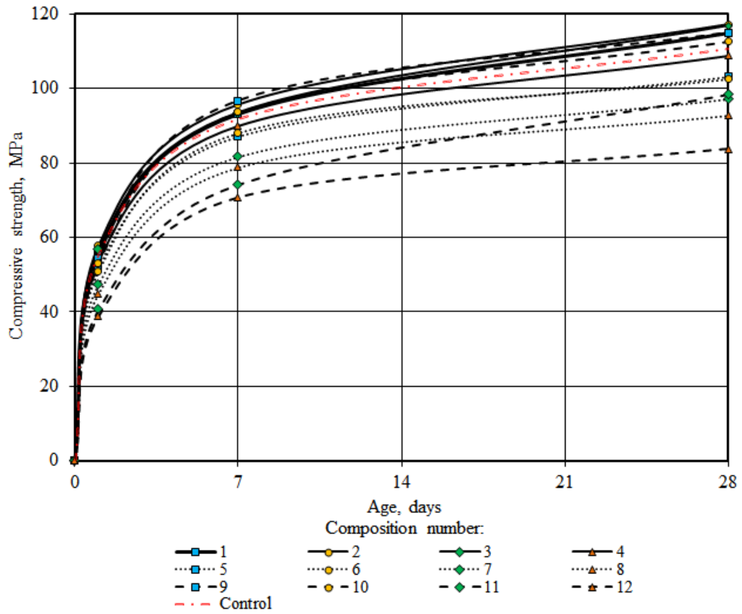

Figure 3. Compressive strength growth kinetics of the researched cement paste compositions.

According to the data (Fig. 2), the average density of cement stone for compositions with 5 % of mineral additives of thermally activated Nikitsky clay, Yelnikovsky dolomite and the thermally activated mixture of Nikitsky clay and Atemarsky limestone was 2265, 2270 and 2272 kg/m^3, respectively (compositions 1, 5, 9). This was close to a similar indicator for the control additive-free composition (2275 kg/m^3). It was found that when the dosages of mineral modifiers were increased, the average density of cement stone was reduced insignificantly. It was reaching the minimal values in compositions 4, 8 and 12 with the content of TCN, DY and TM(CN+LA) of 20 % of binder weight (PC + MA) – 2226, 2222 and 2163 kg/m^3, which is 2.2, 2.3 and 4.9 % less than the control composition. The recorded decrease in the average density of cement stone can be caused by the reduced flowability and compaction efficiency of cement paste when the content of TCN, DY, and TM(CN+LA) additives in the compositions is increased, which have a thickening effect on cement systems.

The results of experimental studies (Fig. 3) showed that the compositions with TCN, DY and TM(CN+LA) mineral additives under study differed in high rates of increasing cement stone compression strength at the age of 1 and 7 days: 41–50 and 75–86 % of the strength at the age of 28 days, respectively.

Data analysis in Fig. 3 showed that when using the additives of calcined polymineral Nikitsky clay and thermally activated mixture of Nikitsky clay and Atemarsky limestone, the highest compression strength of cement stone at the age of 28 days was reached in compositions 2 and 9 (Table 1) with these modifiers having the content of 10 and 5 % of binder weight (PC + MA) – 117.2 and 114.9 MPa, respectively. The analysis results in Fig. 4 showed the optimal content of TCN and TM(CN+LA) mineral additives promoting increased strength of cement systems – max. 19 and 12 % of binder weight, respectively. With the indicated levels of dosages, mineral additives based on calcined Nikitsky clay and thermally active mixture of Nikitsky clay and Atemarsky limestone were active and had increased physical-chemical efficiency. Exceeding these content levels of mineral additives led to decreased compressive strength of cement stone below the level typical of the control composition. The results obtained are confirmed by data of a number of publications [33, 36], which showed that individual additives of calcined polymineral clays to Portland cement, depending on the activation temperature and grinding fineness, contributed to more significant increase in the strength of cement stone than similar additives of high-quality metakaolin.

The study results (Figs. 3 and 4) showed that Yelnikovsky dolomite was an inert mineral additive. The increased content of this filler from 5 to 20 % of binder weight (PC + MA) in the formulation of cement systems resulted in consistent reduction of cement stone compression strength from 103.1 to 92.8 MPa, respectively. The achieved compressive strength level of the researched cement stone compositions under study by 7–16 % was less than that of the control composition (110.6 MPa).

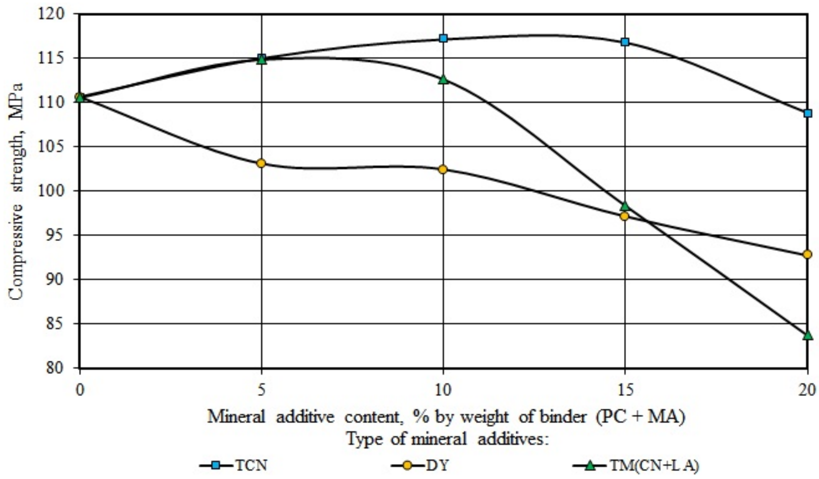

Figure 4. Influence of the type and dosage of mineral additives on the compressive strength of cement paste at the age of 28 days.

3.3. Influence of mineral additives on the cement paste phase composition

Fig. 5 represents the X-ray diffraction patterns of cement stone powders aged 28 days for compositions 4, 8, 12 containing 20 % of mineral additives and for the control additive-free composition (Table 1).

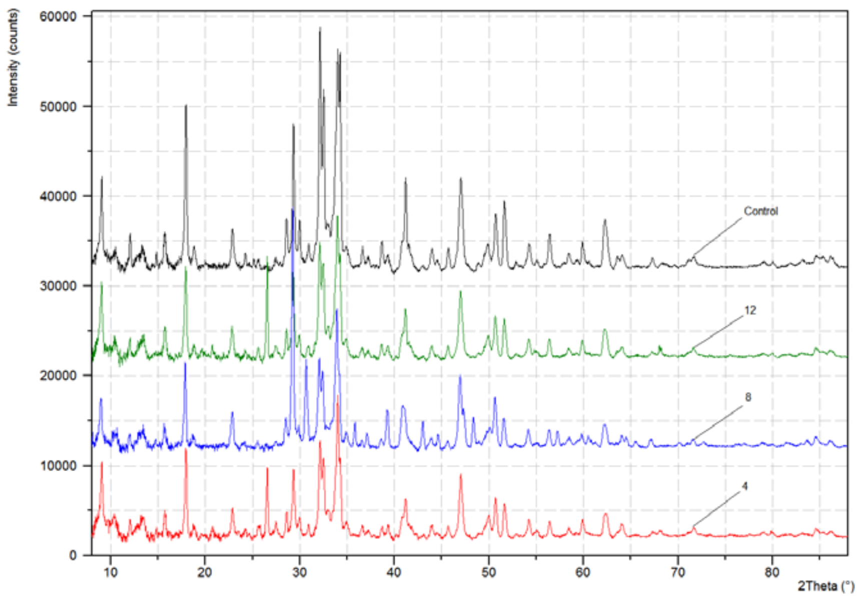

Figure 5. X-ray powder diffractograms of the researched cement paste compositions at the age of 28 days (Nos. 4, 8, 12 and control additive-free composition).

The qualitative analysis of the diffraction patterns (Fig. 5) showed that the crystalline part of the cement stone structure of both control additive-free composition and the compositions modified by mineral additives Nos. 4, 8, 12 was represented by the following minerals:

1. the phases of Portland cement clinker not subject to the hydration reaction: alite (Ca_3SiO_5) with number of inter-plane distances d = […; 3.04; ...; 2.78; 2.75; …; 2.62; …; 2.19; …; 1.77 Å; …]; belite (β-Ca_2SiO_4) with d = […; 2.89; …; 2.79; 2.75; 2.72; …; 2.62; …; 2.19 Å; ...];

2. the hydrate phases: Portlandite ($Ca(OH)_2$) with d = [4.95; 3.12; 2.64; …; 1.93; 1.80; 1.69; …; 1.49 Å; …]; ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12}·26H_2O$) with d = [9.82; …; 5.65; …; 4.72; …; 3.89; …; 3.48; …. 2.78; …; 2.57; …; 2.21 Å; …].

Semi-qualitative X-ray phase analysis of cement stone powders aged 28 days (Table 4) showed that the introduction of mineral additives of thermally activated polymineral Nikitsky clay, Yelnikovsky dolomite and the thermally activated mixture of Nikitsky clay and Atemarsky limestone in cement systems increased hydration levels of Portland cement as compared to the control additive-free composition from 65 to 79, 82 and 77 %, respectively, i.e., by 18–26 %. In this manner, the data showed an intensified processes of Portland cement hydration in the presence of TCN, DY and TM(CN+LA) mineral additives in the cement systems, which was caused by the presence of reactive minerals (kaolinite and illite) in the phase composition of Nikitsky clay, and by the capability of Yelnikovsky dolomite minerals to act as the centers of crystallization of new formations. The established regularities are consistent with the data of other authors, in particular [34].

Table 4. XRD results of the researched cement paste compositions at the age of 28 days.

Composition number	Binder composition (Portland cement + mineral additive)	Hydration degree of Portland cement, %	Relative ettringite content $Ca_6Al_2(SO_4)_3(OH)_{12}·26H_2O$	Relative portlandite content $Ca(OH)_2$	Relative content of low basic calcium hydrosilicates C-S-H(I)	Relative content of high basic calcium hydrosilicates C-S-H(II)
Control	100 % PC	65	100	100	100	100
4	80 % PC + 20 % TCN	79	80	73	255	59
8	80 % PC + 20 % DY	82	62	91	108	130
12	80 % PC + 20 % TM(CN+LA)	77	94	75	238	94

The analysis of experimental data represented in Table 4 showed the content of ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12}·26H_2O$) reduced by 6–38 % in the cement stone samples with additives of calcined polymineral Nikitsky clay, Yelnikovsky dolomite and the thermally activated mixture of Nikitsky clay and Atemarsky limestone relative to the control composition. Decreasing the concentration of the tri-sulfate form of calcium hydrosulfoaluminate could be related to the changes occurring in the composition of the liquid phase (pH, the concentration of Ca^{2+}, Al^{3+}, SO_4^{2-} ions, etc.) when hardening cement stone in the presence of these modifiers. This promoted the shift of the balance to the formation of compounds of another chemical and mineralogical nature (calcium hydrosilicates, AF_m-phases, etc.).

Silicate phases of Portland cement 500-D0-N amounted to 78 % (C_3S = 60.4 % and β-C_2S = 17.5 %), which caused the predominance of calcium silicate hydrate phases (C–S–H) in the hardening cement stone. Calcium hydrosilicates formed in normal conditions were characterized by widely varying compositions and degrees of crystallization, so they were conditionally divided into two groups [48, 49]: those who had high strength, low basic C–S–H(I) with $CaO/SiO_2 \leq 1.5$ and less durable high basic C–S–H(II) with $CaO/SiO_2 > 1.5$.

The results of experimental studies given in Table 4 showed that introducing mineral additives of Nikitsky clay, Yelnikovsky dolomite and the thermally activated mixture of Nikitsky clay and Atemarsky limestone into the formulation of cement systems promoted substantial quantitative change in the ratio between the primary hydrate phases in the cement stone – Portlandite and calcium hydrosilicates of various basicity. In particular, as compared to the control composition, in the powder samples of cement stone with TCN and TM(CN+LA) additives aged 28 days, the content of high basic C–S–H(II) and large low-strength crystals of Portlandite $Ca(OH)_2$ was reduced by 6–41 % and 25–27 %, respectively. At the same time, the content of fine and high strength low basic C–S–H(I) was increased 2.4–2.6 times.

The discovered change of balance between hydrate phases in the cement stone with additives of Nikitsky clay, Yelnikovsky dolomite and the thermally activated mixture of Nikitsky clay and Atemarsky limestone towards a rise in the volume of the most durable and most stable low-basic C–S–H(I) with $CaO/SiO_2 \leq 1.5$ instead of primary crystalline hydrates such as the Portlandite and high-basic C–S–H(II) indicated chemical effect [50] in the action mechanism of these mineral modifiers. This chemical effect was related to the pozzolanic activity of TCN and TM(CN+LA) mineral additives in cement systems and caused by the presence of active silica-containing components in their chemical and mineralogical composition (reactive minerals with amorphized structure).

4. Conclusions

The following results were obtained upon the completed experimental studies:

1. Phase composition was established for the initial components of mineral additives – polymineral clay, dolomite and limestone of the Nikitsky, Yelnikovsky, and Atemarsky deposits, the Republic of Mordovia, the Russian Federation, respectively.

2. Effects were found for dosages of mineral additives based on the thermally activated clay and carbonate rocks on the mobility of plasticized cement paste and physical-mechanical properties of cement stone (average density in normal humidity conditions at the age of 28 days, compression strength at the age of 1, 7 and 28 days).

3. We found that mineral additives based on thermally activated clay and carbonate rocks have influence on the phase composition of cement stone aged 28 days.

4. Interrelations and regularities were revealed in the “composition – structure – property” system, which allow optimizing the formulations of modified cement compositions to achieve the required levels of technological and physical-mechanical characteristics. Optimal dosages of mineral additives of calcined clay and thermally activated mixture of clay and limestone were identified, the sizes of which did not exceed 19 and 12 % by binder weight, respectively, which contributed to an increase in strength characteristics of cement systems relative to the control composition without additives. At the same time, the highest compressive strength values of cement stone aged 28 days were recorded for the modifiers contents equal to 10 and 5 % by binder weight.

By generalizing the results of experimental studies, it could be noted that the use of mineral additives of thermally activated polymineral Nikitsky clay and the thermally activated mixture of Nikitsky clay and Atemarsky limestone allowed increasing the rate (level) of Portland cement hydration and consistently changing the phase composition of cement stone:

- optimizing the ettringite concentration,
- decreasing the number of the weakest and corrosion-exposed Portlandite crystals,
- increasing the density and strength of the primary mass of newly formed calcium hydrosilicates by shifting the balance towards an increased content of highly dispersive low basic C–S–H(I) phases instead of high basic C–S–H(II) compounds.

At the same time, the data given in Table 4 proved relative chemical inertness of the Yelnikovsky dolomite additive: concentrations of Portlandite and low basic C–S–H(I) phases in the cement stone sample of composition No. 8 with carbonate filler are close to those of the control composition without mineral additives.

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