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COMPARISON OF THE EFFECT OF SUPERPLASTICIZING ADMIXTURES ON THE PROCESSES OF CEMENT HYDRATION DURING MECHANOCHEMICAL ACTIVATION

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Наводяться результати дослідження та порівняльний аналіз впливу механохімічної активації цементної суспензії з добавками різних хімічних основ на процеси і характер гідратації цементу, гранулометричний і фазовий склад гідратів новоутворень. Наведено результати кінетики тепловиділення, pH рідкої фази цементного тесту після механохімічної активації з досліджуваними добавками. Вивчено технологічні властивості бетонної суміші і фізико-механічні властивості важкого бетону, отриманого механохімічною активацією цементної суспензії

Ключові слова: модифікація, добавки, механохімічна активація, цементна суспензія, важкий бетон

Приводятся результаты исследования и сравнительный анализ влияния механохимической активации цементной суспензии с добавками различной химической основы на процессы и характер гидратации цемента, гранулометрический и фазовый состав гидратных новообразований. Приведены результаты кинетики тепловыделения, pH жидкой фазы цементного теста после механохимической активации с исследуемыми добавками. Изучены технологические свойства бетонной смеси и физико-механические свойства тяжелого бетона, полученного механохимической активацией цементной суспензии

Ключевые слова: модификация, добавки, механохимическая активация, цементная суспензия, тяжелый бетон

1. Introduction

A number of methods in the technology of production of cements and concretes on their base have been actively developed over the last decade, aimed at decreasing material and energy consumption during production. Among them are the search and implementation of alternative types of binders, replacement of the part of cement by the waste of industries [1–4], maximal utilization of inner potential of cement with the aid of the activation [5–7].

It is known that the physic-mechanical properties of cement concretes depend on the set of the indicators: granulometric and mineralogical compositions and also the formed structure of cement stone.

An increase in dispersity must contribute to the formation of more finely dispersed, therefore more durable structure, which is explained by the joint influence of two factors: by an increase in the strength of individual structural elements of crystalline hydrate ligament and by an increase in the number of contacts [8].

In this case, for obtaining cement concretes with increased strength it is important to observe technological methods, which would make it possible to minimally decrease the activity of cement after fine grinding. Cement activation in the process of the preparation of concrete mixture is one of such solutions.

The development of cement concretes with the aid of the joint mechanoactivation and modification of cement in the energy-intense equipment is a scientifically substantiated solution for increasing physicomechanical properties of cement concretes. This solution is specified by intensive physical chemical action on a binder with the purposeful formation of the required properties of cement concretes [9].

The relevance of the work in this direction consists in the study of the influence of super-plasticizing admixtures of different chemical base on the peculiarities of the processes of hydration and structure formation of cement stone, obtained by mechanochemical activation.

2. Analysis of scientific literature and problem statement

Studies of the effect of the medium of cement dispergation on the grinding process proved increased efficiency during the dispergation in liquid medium as compared to the dry one [10, 11]. Moreover, an increase in the efficiency of the grinding is noted during additional introduction of different admixtures into water, which perform the role of the intensifiers of grinding [12, 13].

Dispergation and activation of cement in a liquid medium is facilitated by the phenomena of adsorption and chemical dispergation. Grinding cement in a liquid medium makes it possible to obtain increased specific surface area without considerable reduction in the productivity of equipment [14].

As is known, the main method of intensification of cement grinding in a liquid medium, as well as in a dry one, is introduction of surfactants (SAS). The particles of SAS, moving towards the grains of cement, are adsorbed and migrate over their surface. In this case, the smallest molecules of SAS, penetrating the cracks of a grain of cement, move to their mouths and in so doing they ensure wedging out effect that favorably influences the process of dispergation of cement in the equipment for fine grinding.

In this case, the selection of equipment for cement grinding must be predetermined by high efficiency of dispergation. Rotary-pulsating device (RPD) has recently manifested itself as such equipment.

Earlier, the [13] determined optimum parameters of the activation of cement suspension in RPD (duration of activation, the share of cement for the activation by the calculated mass). The selection of optimum parameters was specified by obtaining the best physicomechanical properties of cement compositions while power consumption during the work of RPD was considered. The optimum duration of activation in RPD was 2 min., in this case 50 % of an estimated amount of cement was exposed to activation [13, 17].

Analysis of literary sources [15, 16] displayed that the efficiency of cement grinding with SAS depends on its most important factors: their nature, concentration, humidity, the working mode of the grinding equipment.

In connection with this, of scientific interest is the study of the influence of different admixtures of SAS on the intensification of dispergation of a binder in RPD. The application of different admixtures of SAS in the process of mechanochemical activation (MCA) of cement suspension will be reflected in the special features of the hydration of cement, technological properties of concrete mixture and the kinetics of concrete hardening. The received data will make it possible to base the selection of the area of application of concretes, obtained with the application of MCA, cement suspension and SAS admixtures.

The comparison of the effect of SAS admixtures of two chemical bases is the most actual:

– naphthalene formaldehyde, the most widely used in the world;

– polycarboxylate, that inspired the greatest interest among researchers and specialists in recent time [18–20].

The studies were carried out on the influence of MCA of cement suspension, modified by the SAS admixtures of different chemical bases in RPD on the processes of hydration of cement, granulometric and phase composition of hydrated new formations of cement stone during hardening.

3. The purpose and objectives of the study

The purpose of the work is the comparison of the influence of two different SAS admixtures in the process of mechanochemical activation of cement suspension on the peculiarities of forming the microstructure of cement stone and the physicomechanical properties of heavy-weight concrete.

To study the given peculiarities, the following tasks are to be solved:

– to examine the influence of mechanochemical activation of cement suspension on the processes of cement hydration (kinetics of heat release, alkalinity of the liquid phase of cement slurry);

– to examine the influence of mechanochemical activation of cement suspension on the technological properties of concrete mixture and the kinetics of hardening of heavy-weight concrete;

– to examine the influence of mechanochemical activation of cement suspension on the phase composition of hydrated new formations of cement stone during different periods of hardening by the methods of X-ray phase analysis.

4. 1. Materials and equipment used in the study

For the preparation of concrete mixture we used a binder, fine and coarse fillers, water, super-plasticizing admixtures.

As a binder, we used portland cement CEM II/A-Sh 32,5N of the Ulyanovsk plant in line with the requirements of GOST 31108-2003. The main minerals included in the composition of portland cement are C_3S – 54 %, C_2S – 20 %, C_3A – 11 %, C_4AF – 12 % and the admixtures: casting-box – 9,2 %, SO_3 – 2,8 %.

As fine filler, we used sand from the Kamsko-Ustinskiy deposit with the module of coarseness 2,7 in line with the requirements of GOST 8736-2014.

As coarse filler, we used granite rubble of the Uralskiy field with the size of fractions 5–20 mm in line with the requirements of GOST 8267-93.

Two super-plasticizing admixtures were used as SAS:

– admixture Relamix T-2, produced in line with EN 934-2:2009 (on the base of naphthalene formaldehyde);

– admixture Remicrete SP60, produced in line with EN 934-2:2009 (on the base of polycarboxylate ether).

The admixtures under consideration were used in the amount of 1 % by the mass of cement [13].

For the experiment we detfined heavy-weight concrete with production composition class (C:S:G=490:555:1315) with the strength V25.

The water-cement ratio (W/C) of the examined concrete compositions was selected for reaching identical mobility of the concrete mixture of the mark P2 (O.K.=7–9 cm).

Mechanochemical activation of cement suspension was conducted in the rotary-pulsating device, produced in accordance with TU 5132-001-70447062, with the frequency of rotation of the operating unit at 5000 r/min.

The study of the kinetics of heat release of cement slurry was carried out by a thermos method using measuring complex "Thermochrone DS1921".

pH of the liquid phase of cement slurry was determined with the use of a pH-meter appliance testo 206-pH1.

Specific surface area was determined by the method of air permeability with the application of the PSH-9 appliance.

Dispersed composition was determined on the laser analyzer of the coarseness of the particles "Horiba La-950V2".

X-ray phase analysis (XPA) was carried out on the diffractometer D2 Phaser (Brucker, Germany) for the measurements of powder preparations in the geometry of Bragg-Brentano using monochromatized CuKα-emission (λ=1,54178 Å), in the mode of step scanning.

The modes of measurements and registration: the voltage of X-ray tube is 30 kV, current 30 mA. The step of scanning is 0.02°. The speed is 1 deg./min. The range of the angles of scanning in the geometry of Bragg-Brentano is 3–60°.

4. 2. Methods of the study of influence of mechanochemical activation of cement suspension with the examined admixtures on the processes of cement hydration

For obtaining dry cement powder and further determining of its dispersed composition, obtained after activation in the aqueous medium in RPD, we carried out dehydration of cement suspension with the aid of the Buechner funnel, connected with a water-jet pump. Immediately after separation of the liquid phase, the sample on the filter was filled with pure alcohol, and then it underwent conservation in acetone, in this case the quantity of acetone taken was not less than five-fold volume of the selected sample. Then the material was dried in a drying chamber at the temperature of 105 °C.

Cement slurry of normal thickness was prepared as follows: about 50 % of the estimated amount of cement was mixed in advance with the estimated amount of water containing a SAS admixture in optimum quantity; then the obtained suspension was loaded into a RPD bunker to undergo activation during 2 minutes; after the activation, the suspension was unloaded from the RPD and was mixed with the remaining part of the cement.

Concrete mixture was prepared using the following method. About 50 % of the estimated amount of cement was mixed in advance with mixing water and a SAS admixture. Then the obtained suspension was loaded into a RPD bunker to undergo activation during 2 minutes. After the activation, the suspension was unloaded from the RPD and was mixed for 5 minutes with the remaining part of the cement, coarse and fine filler in a concrete-mixer [21].

The specimens were made out of concrete mixtures – cubes with the dimensions of 10×10×10 cm. After 1, 3 and 28 days of normal hardening, the specimens were subjected to mechanical tests. The strength of the specimens was determined in accordance with GOST 18105-2010.

5. Results of the research into the influence of mechanochemical activation of cement suspension with the studied admixtures on the processes of cement hydration

During the first stage of the study we determined the influence of MCA of cement suspension with the examined admixtures on the kinetics of heat release of cement slurry of normal thickness.

A composition without an admixture and without cement activation is accepted as a reference composition. The results of the study are given in Fig. 1.

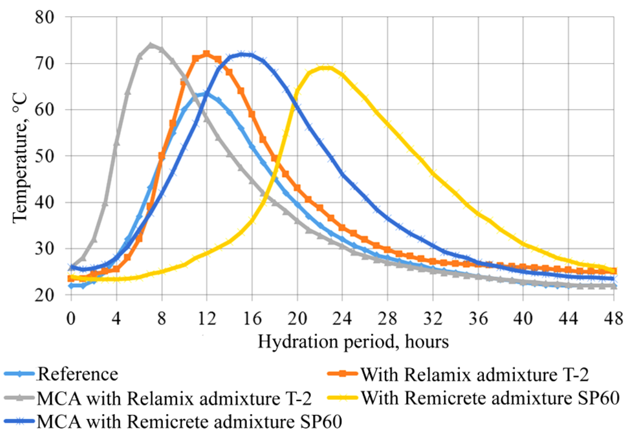

Fig. 1. Kinetics of the heat release of cement slurry

The application of MCA of cement suspension with Remicrete SP60 admixture makes it possible to increase the maximum temperature of hydration by 4 °C and to shift the temperature maximum by 7 hours towards the beginning of the process of hydration in comparison with the composition with Remicrete SP60 admixture without the activation.

The MCA of cement suspension with Relamix T-2 admixture ensures the highest value of the temperature of cement hydration – 74 °C, which exceeds the temperature maximum of the composition with Relamix T-2 admixture without the activation by 3 °C. In this case the induction period is shortened by 2–3 hours, which is connected to mechanical and chemical dispergation of cement, ensuring increase in the quantity of colloidal fraction. The acceleration of crystallization period of structure formation is observed, too – the temperature maximum is shifted by 5 hours towards the beginning of the process of hydration.

The studies were carried out regarding the kinetics of change in pH of the liquid phase of cement slurry in the initial stage of cement hydration (first 90 min.) with or without the application of MCA of cement suspension. The pH indicator of the mixing water amounted to 7,24, the temperature t=21,9 °C.

We see from the data of Fig. 2 that the pH of the liquid phase of cement slurry substantially increases both after the mechanoactivation without admixtures and after MCA with admixtures.

The studies were carried out regarding technological properties of concrete mixtures in accordance with [22], obtained by MCA of cement suspension. The following indicators of concrete mixtures were determined and compared: air-content, temperature, density, water separation, concrete mix retentive mobility.

Fig. 3 presents results of the influence of MCA of cement suspension on the concrete mix retentive mobility.

which is 10–21 times less in comparison with the reference composition.

Table 1 presents technological properties of concrete mixtures of the examined compositions.

We see from the data of Table 1 that the MCA of cement suspension with Relamix T-2 admixture (composition No. 4) leads to the increase in the density of concrete mixture by 4 %, to the reduction in the volume of entrained air by 39 %, to a substantial increase in the strength limit of heavy-weight concrete at the age of 24 hrs by 231 %, at the mature age – by 55 %.

MCA of cement suspension with Remicrete SP60 admixture (composition No. 6) leads to the increase in the density of concrete mixture by 3,5 %, to the reduction in the volume of entrained air by 33 %, to the increase in the strength limit of heavy-weight concrete at the age of 24 hrs by 176 %, at the mature age – by 62 %.

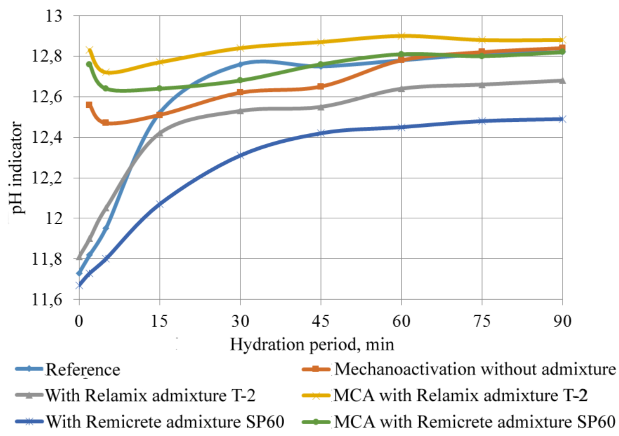

Fig. 2. Kinetics of pH of the liquid phase of cement slurry

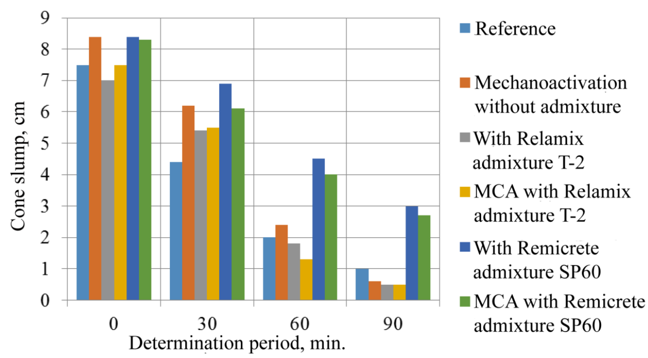

Fig. 3. Change in the mobility of concrete mixture in the course of time

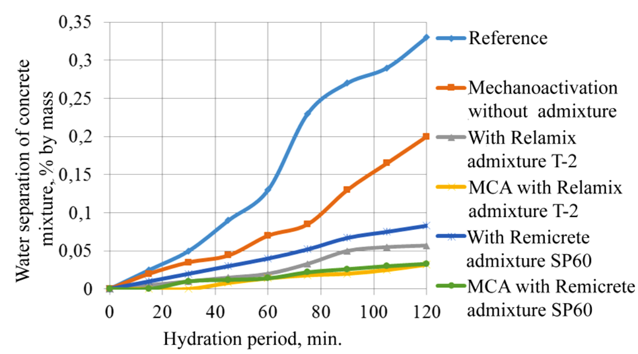

Fig. 4. Water separation of the concrete mixture

Table 1

Properties of concrete mixture and the strength limit of heavy-weight concrete at compression

No. of composition**	W/C	Density of concrete mixture, kg/m^3	Air content of concrete mixture, %	Temperature of concrete mixture °C	Strength limit at compression, MPa		
					1 day	3 days	28 days
1	0,42	2389	1,05	21,6	7,1* 100 %	19,57* 100 %	40,53* 100 %
2	0,42	2424	0,94	22,7	13,76 194 %	29,01 148 %	46,15 114 %
3	0,31	2472	0,88	22,3	12,81 180 %	32,42 166 %	51,7 128 %
4	0,31	2485	0,64	23,1	23,53 331 %	46,38 237 %	62,81 155 %
5	0,30	2476	0,69	22,0	12,32 174 %	31,89 163 %	57,55 142 %
6	0,30	2472	0,70	23,5	19,62 276 %	45,01 230 %	65,72 162 %

*Note: * – the average value of indicator is given above the line; under the line is the relative value of indicator in % by the reference; ** – 1 – reference; 2 – mechanoactivation without admixture; 3 – with Relamix T-2 admixture; 4 – MCA with Relamix T-2 admixture; 5 – with Remicrete SP60 admixture; 6 – MCA with Remicrete SP60 admixture*

The measurements were conducted immediately and in 30, 60 and 90 min after the preparation of the concrete mixture. We see from the data of Fig. 4 that reduction in the mobility of concrete mixture is observed for all compositions in the course of time. The mobility of concrete mixtures of the reference composition, composition with mechanoactivation, composition with Relamix T-2 admixture and the composition with MCA and Relamix admixture T-2 in 90 min after the preparation of concrete mixtures is reduced by 85–92 % while that of the composition with Remicrete SP60 admixture and the composition with MCA and Remicrete SP60 admixture – by 60–70 %.

Fig. 4 displays the kinetics of water separation of concrete mixture in the course of time. We see from the data of Fig. 4 that the largest amount of separated water is noticeable in the reference composition and it is 0,33 % of the mass of the concrete mixture.

Mechanoactivation of cement suspension without an admixture makes it possible to decrease the water separation of concrete mixture by 1,5–1,9 times. The introduction of SAS admixtures to the composition of concrete mixture makes it possible to decrease water separation by 5–7 times. The lowest amount of separated water from the concrete mixtures is observed in the compositions obtained by MCA of cement suspension,

The dispersed composition of the specimens of cement powder of the following compositions is determined: 1 – initial portland cement (CEM II/A-Sh 32,5N); 2 – reference (after mixing of cement with water during 2 minutes); 3 – composition subjected to mechanoactivation; 4 – with Relamix T-2 admixture; 5 – composition subjected to MCA with Relamix T-2 admixture; 6 – with Remicrete SP60 admixture; 7 – composition subjected to MCA with Remicrete SP60 admixture. The results of the studies are given in Table 2.

We see from the data in Table 2 that the specific surface area of cement powder, subjected to mechanoactivation without an admixture (composition No. 3), increases by 10 % in comparison with the reference composition (composition No. 2). With the MCA of cement suspension with Relamix T-2 admixture (composition No. 5), the specific surface area of cement powder increases by 29 % in comparison with the composition with Relamix T-2 admixture (composition No. 4). With the MCA of cement suspension with Remicrete SP60 admixture (composition No. 7), the specific surface area of cement powder increases by 26 % as compared to the composition with Remicrete SP60 admixture without the activation (composition No. 6).

The average particle size of the initial portland cement (composition No. 1) is larger than the particles of the cement powder subjected to mechanoactivation without an admixture (composition No. 3) by 1,26 times; larger than the particles subjected to MCA in the presence of Relamix T-2 admixture by 2,8 times and larger than the particles subjected to MCA in the presence of Remicrete SP60 admixture by 3,3 times.

of normal-humid hardening. Fig. 6 depicts the curves of XPA of the examined compositions at the mature age of normal-humid hardening.

Table 3 displays quantitative-mineral composition of the studied compositions.

Table 3

Quantitative-mineral composition of the studied specimens

No. of specimen*		1		2		3	
Age of specimen, day		1	28	1	28	1	28
Mineral composition	SiO_2	2.41	2.78	3.73	2.57	4.91	2.61
	$Ca_6Al_2(SO_4)_3(OH)_{12}{\cdot}26H_2O$	9.07	8.90	9.41	10.77	10.12	8.91
	Ca_2SiO_4 α-Ca_2SiO_4	13.00	11.33	10.34	11.74	16.85	11.56
	$Ca_2(Al, Fe^{+3})_2O_5$	13.83	15.75	14.38	15.77	13.78	19.91
	$Ca(OH)_2$	8.64	11.69	3.30	23.74	9.52	17.88
	Ca_3SiO_5	53.05	34.45	55.66	25.69	44.82	27.04
	$CaCO_3$	–	15.10	–	9.72	–	12.09
	$Ca_2SO_4{\cdot}2H_2O$	–	–	3.18	–	–	–
Total, %		100	100	100	100	100	100

*Note: * – numeration of specimens corresponds to the numeration in Fig. 5, 6*

Table 2

Specific surface area and granulometric composition of the examined compositions

№	Average size, microns	Specific surface area, m^2/kg	Content of fractions, %				
			<20 microns	20÷40 microns	40÷60 microns	60÷80 microns	>80 microns
1	48,47	298,33	40,27	18,43	13,95	7,21	20,14
2	45,87	324,66	40,79	18,31	14,06	7,6	19,24
3	38,35	356,35	54,01	21,12	10,41	8,74	5,72
4	42,25	331,62	42,28	19,28	12,86	7,76	17,82
5	17,10	427,84	73,68	24,45	1,87	–	–
6	38,22	358,75	48,26	24,13	17,54	5,64	4,43
7	14,68	452,35	85,42	13,92	0,66	–	–

The influence of Remicrete SP60 admixture on the phase composition of the products of cement hydration was studied, obtained both during usual introduction and at mechanochemical activation of the binder. Fig. 7 depicts the curves of XPA of the studied compositions at the age of 24 hrs of normal-humid hardening. Fig. 8 displays the curves of XPA of the studied compositions at the mature age of normal-humid hardening.

Table 4 displays quantitative-mineral composition of the studied compositions.

With the MCA of cement suspension, the output of fractions less than 20 microns increases by 1,83–2,12 times in comparison with the initial portland cement. When determining the dispersed composition of cement powder, obtained by MCA, the particles larger than 60 microns were not discovered.

We studied the influence of Relamix T-2 admixture on the phase composition of the products of cement hydration, obtained both during the usual introduction and with the mechanochemical activation of the binder. The specimens of cement stone, prepared from the slurry of normal thickness, of the following compositions, were tested: 1 – reference; 2 – with Relamix T-2 admixture; 3 – the composition subjected to MCA with Relamix T-2 admixture.

Fig. 5 depicts the curves of XPA of the studied compositions at the age of 24 hours

Table 4

Quantitative-mineral composition of the studied specimens

No. of specimen*		1		2		3	
Age of specimen, day		1	28	1	28	1	28
Mineral composition	SiO_2	2.8	1.1	1.4	0.9	1.0	1.6
	$Ca_6Al_2(SO_4)_3(OH)_{12}{\cdot}26H_2O$	13.7	10.6	12.5	11.1	13.2	7.8
	Ca_2SiO_4 α-Ca_2SiO_4	31.3	16.6	24.7	17.9	23.4	16.1
	$CaAl_2Si_2O_8(H_2O)_4$	10.7	11.2	7.6	13.1	8.3	12.4
	$Al_{4.59}Si_{1.41}O_{9.7}$	4.2	5.9	4.7	2.5	2.1	2.9
	$Ca(OH)_2$	12.8	24.1	17.1	26.2	22.7	17.9
	Ca_3SiO_5	22.1	17.5	29.1	14.9	26.6	24.8
	$CaCO_3$	–	3.0	–	3.7	–	9.8
	$Ca_{2.25}(Si_3O_{7.5}(OH){\cdot}1.5)(H_2O)$	1.2	0.5	1.6	1.4	1.5	1.9
	$Ca_2SiO_3(OH)_2$	–	4.1	–	3.2	–	2.5
	$CaSO_4$	1.3	2.3	1.4	2.7	1.3	0.4
	$Ca_2SO_4{\cdot}2H_2O$	–	3.1	–	2.3	–	1.9
Total, %		100	100	100	100	100	100

*Note: * – numeration of specimens corresponds to the numeration in Fig. 7, 8*

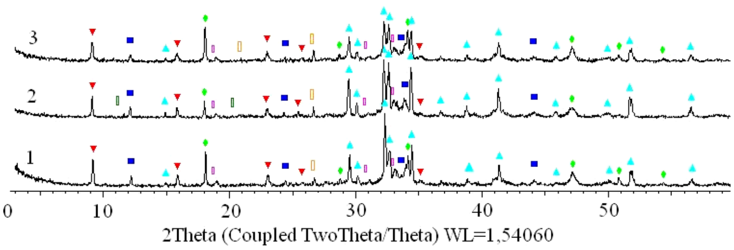

Fig. 5. Curves of XPA of the studied specimens at the age of 24 hours of normal-humid hardening: 1 — reference; 2 — with Relamix T-2 admixture; 3 — composition subjected to MCA with Relamix T-2 admixture. Symbols: ▯ — SiO_2; ▼ — $Ca_6Al_2(SO_4)_3(OH)_{12}*26H_2O$; ▯ — Ca_2SiO_4 α-Ca_2SiO_4; ▲ — Ca_3SiO_5; ♦ — $Ca(OH)_2$; ■ — $Ca_2(Al, Fe^{+3})_2O_5$; ▯ — $Ca_2SO_4*2H_2O$

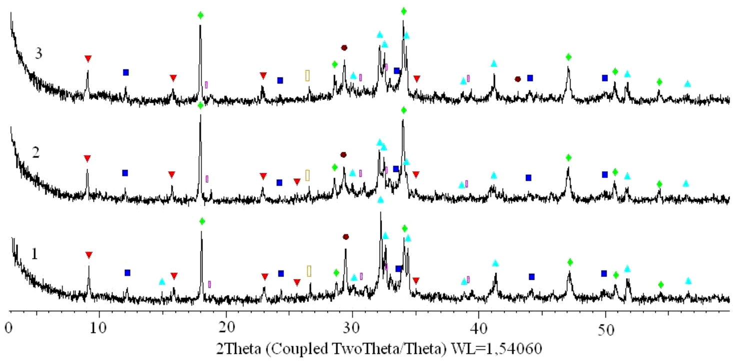

Fig. 6. Curves of XPA of the examined specimens at the mature age of normal-humid hardening: 1 — reference; 2 — with Relamix T-2 admixture; 3 — composition subjected to MCA with Relamix T-2 admixture. Symbols: ▯ — SiO_2; ▼ — $Ca_6Al_2(SO_4)_3(OH)_{12}*26H_2O$; ▯ — Ca_2SiO_4 α-Ca_2SiO_4; ▲ — Ca_3SiO_5; ♦ — $Ca(OH)_2$; ■ — $Ca_2(Al, Fe^{+3})_2O_5$; ● — $CaCO_3$

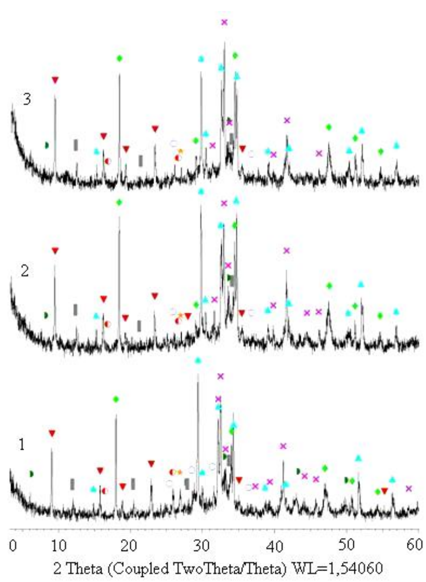

Fig. 7. Curves of XPA of the studied specimens at the age of 24 hrs of normal-humid hardening: 1 —reference; 2 — with Remicrete SP60 admixture; 3 — composition subjected to MCA with Remicrete SP60 admixture. Symbols: ★ — SiO_2; ▼ — $Ca_6Al_2(SO_4)_3(OH)_{12}*26H_2O$; ✕ — Ca_2SiO_4 α-Ca_2SiO_4; ▲ — Ca_3SiO_5; ♦ — $Ca(OH)_2$; ▌ — $CaAl_2Si_2O_8(H_2O)_4$; ◐ — $Al_{4.59}Si_{1.41}O_{9.7}$; ○ — $CaSO_4$; ◗ — $Ca_{2.25}(Si_3O_{7.5}(OH)_{1.5})(H_2O)$

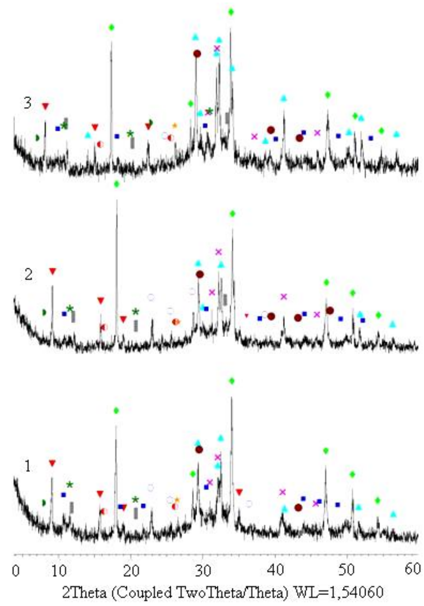

Fig. 8. Curves of XPA of the examined specimens at the mature age of normal-humid hardening: 1 — reference; 2 — with Remicrete SP60 admixture; 3 — composition subjected to MCA with Remicrete SP60 admixture. Symbols: ★ — SiO_2; ▼ — $Ca_6Al_2(SO_4)_3(OH)_{12}*26H_2O$; ✕ — Ca_2SiO_4 α-Ca_2SiO_4; ▲ — Ca_3SiO_5; ♦ — $Ca(OH)_2$; ▌ — $CaAl_2Si_2O_8(H_2O)_4$; ◐ — $Al_{4.59}Si_{1.41}O_{9.7}$; ○ — $CaSO_4$; ◗ — $Ca_{2.25}(Si_3O_{7.5}(OH)_{1.5})(H_2O)$; ✱ — $CaSO_4*2H_2O$; ■ — $Ca_2SiO_3(OH)_2$

We see from the data of Tables 3, 4 that the MCA of cement suspension, along with the intensifiers of dispergation of Relamix T-2 and Remicrete SP60, leads to a deeper hydration of alite and belite, to the increase in the content of calcium hydrosilicates and ettringite in comparison to the compositions with the studied admixtures without MCA.

6. Discussion of the results of studying the influence of MCA of cement suspension with the examined admixtures on the processes of cement hydration

According to the data of Fig. 1, it is evident that cement hydration deceleration is observed in the compositions No. 2 and No. 4, which is caused by the adsorption of molecules of super-plasticizers on the particles of cement with formation of a SAS film that impedes instantaneous reaction of cement with water. Considerable deceleration of hydration is noticeable in the composition No. 4, obtained with Remicrete SP60 admixture. In this case, the time of reaching the temperature maximum increases by 10 hours.

Due to the MCA of cement suspension with the studied SAS admixtures, the hydration of cement is accelerated.

An increase in the alkalinity of the medium of liquid phase even at the moment of activation is predetermined by a considerable increase in the quantity of colloidal fraction of cement, which creates favorable conditions for forming ettringite in earlier periods. This in turn contributes to the relaxation of internal tensions of the hardening system.

During the first ten minutes, the tendency of a pH decrease (Fig. 2) is connected to a decrease in the temperature of cement slurry after activation.

Reduction in the water separation of concrete mixture with the MCA of cement suspension is connected to the opening of active centers of cement clinker, to the increase in its specific surface area that leads to increased consumption of water for cement hydration.

Considerable acceleration of the strength build-up of heavy-weight concrete at MCA is connected to the dispergation of the particles of cement in an aqueous medium along with a super-plasticizer, which leads to active growth of crystalline new formations and strengthening of the structure of cement stone.

Based on the performed X-ray phase analysis of the specimens, modified by Relamix T-2 admixture, one sees that during the first twenty-four hours of hardening, the largest amount of ettringite is revealed in the composition No. 3 (obtained by MCA of the binder), which indicates high build-up rate of the strength of cement stone. Also during the first day of hardening, the X-ray graphs reveal the smallest amount of alite and the largest volume of portlandite, which is connected to the high dissolution rate of Ca_3SiO_5 in the composition, obtained by MCA of the binder.

The composition of new formations in the studied specimens changes by the 28th day of hardening. Thus, the amount of ettringite substantially decreases in the composition No. 3 that is important when designing the concretes with high durability because the increased content of ettringite leads to the increase in internal tensions in cement stone [23]. The smallest amount of initial phases of portland cement (alite and belite) is observed in the composition No. 3, which is confirmed by higher physicomechanical characteristics of concrete at compression.

With the introduction of Remicrete SP60 admixture, the largest amount of ettringite is observed in the reference composition, which indicates deceleration of cement hydration in the compositions containing Remicrete SP60. The smallest amount of alite in the first twenty-four hours of hardening is observed in the composition No. 3, which indicates an increase in the velocity of alite hydration with the MCA of cement suspension. The largest amount of portlandite is contained in the composition No. 3 during the first day of hardening and the least amount also in the composition No. 3 by the 28th day of hardening, which indicates a recrystallization of portlandite into calcium hydrosilicates.

7. Conclusions

1. MCA of cement suspension with the studied admixtures leads to consuderable intensification of cement hydration, especially with Relamix T-2 admixture. With the MCA of cement suspension with Relamix T-2 admixture, the induction period of hydration is shortened by 2–3 hours, the crystallization period of structure formation is accelerated, reaching a temperature maximum 5 hours faster than in the composition with Relamix T-2 admixture without MCA. The MCA of cement suspension with Remicrete SP60 admixture makes it possible to reduce the induction period of cement hydration by 3–5 hours, to reach the temperature maximum during heat release faster by 6–7 hours than with the composition with Remicrete SP60 admixture. MCA of cement suspension increases the pH indicator of the liquid phase of cement slurry from 11,7–11,8 to 12,7–12,8 when processing the suspension in a rotary-pulsating device for 2 minutes.

2. MCA of cement suspension with the studied admixtures leads to the decrease of the amount of separated water from the concrete mixture by 10–21 times in comparison to the composition without an admixture and without the activation. The MCA of cement suspension with Relamix T-2 admixture leads to the increase in the density of concrete mixture by 4 %, to the reduction in the volume of entrained air by 39 %, to a substantial increase in the strength limit of heavy-weight concrete at the age of 24 hrs by 231 % in comparison to the reference composition. The MCA of cement suspension with Remicrete SP60 admixture leads to the increase in the density of concrete mixture by 3,5 %, to the reduction in the volume of entrained air by 33 %, to the increase in the strength limit of heavy-weight concrete at the age of 24 hrs by 176 % in comparison with the reference composition.

3. With the MCA of the binder, modified by Relamix T-2 admixture, a 12 % increase in the amount of ettringite occurs, of portlandite by 10 % in the first twenty-four hours of hardening, which indicates an increase in the speed of hydration of cement clinker. Within the same periods of hardening, during the introduction of admixture based on the ether of polycarboxylate Remicrete SP60, the decrease is observed of the initial phases of cement clinker – of alite by 34 %, in this case the content of portlandite increases by 77 %, which by the 28th day of hardening is recrystallized into calcium hydrosilicate.

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