

MECHANOCHEMICAL ACTIVATION OF PORTLAND CEMENT AND ITS INFLUENCE ON THE THERMOMECHANICAL CHARACTERISTICS OF CEMENT-WATER COMPOSITIONS AND SOLUTIONS BASED ON THEM

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Abstract. Issues discussed in the article related to determining the influence of mechanical activation in a rotary high-speed mixer of cement-water compositions and solutions based on them. Relevant for this study is the activation of cement in combination with the consumption of ground quartz sand ($S = 250 \text{ m}^2/\text{kg}$), the amount of which was adjusted in the range from 0 to 40 % of the cement mass. The use of this technology, along with reducing cement consumption, ensures acceleration of the processes of cement hydration and intensification of exothermic heating of the hardening composition. Mechanical activation is also reflected in the acceleration of the loss of mobility of cement-water compositions filled with ground sand. The presented experimental data made it possible to evaluate the influence of the activation times (90 and 180 sec) of the binder on the diameter of the spread of the aqueous cement-containing composition. It has been established that the main contribution (up to 90 % of the total value) to the decrease in the water-binder ratio (provided that equal-viscosity compositions are obtained) is achieved when the cement-containing composition is activated for 90 seconds. Subsequent activation of the binder (up to 180 sec) has a slight effect on the growth of the diameter of the composition spread and does not exceed 5-10 %.

The exothermia of the hardening cement-water composition determined by the thermos method indicates a significant influence of mechanical activation both on the kinetics and on the achievement of the maximum temperature of its heating. The introduction of ground sand does not change the overall picture of the effect of mechanical activation on exothermic heating, changing only the decrease in intensity and the decrease in maximum heating of the cement-water composition.

The influence of mechanical-chemical activation of Portland cement with the addition of quartz sand on the strength of a 1:1 mortar at 3 and 7 days of age was revealed. Experimental studies indicate a positive effect of binder activation on the compressive strength of the mortar. The increase in strength of samples using mechanically activated cement reached 15-25 % compared to the control.

Key words: mechanical activation, rotary high-speed mixer, activation, exothermic heating, water-binder ratio, ground quartz sand.

Introduction. Along with the traditional use of surfactants in the composition of a mortar or concrete mixture, a promising method for improving the physical and mechanical characteristics of hardened composites is the mechanochemical activation of Portland cement. Ensuring a high degree of cement activation is effectively achieved through the use of special activators, which dramatically increase the potential capabilities of the binder. It is the use of such activators that makes it possible to obtain cement composites of increased strength and durability.

Analysis of the latest research and publications. Improving the properties of cement stone and concrete based on it is an extremely important and urgent task. Among the various ways to

solve the problem [1-7], mechanical-chemical methods of activating the binder [8-12] deserve attention.

The existing various methods of activating the hydration processes of cement compositions have one technological goal, namely, to control the processes of structure formation and physical and mechanical properties of materials [13-17]. In the practice of preparing mortar and concrete mixtures, turbulent high-speed mixers of various designs are widely used [18-20].

Their use helps solve a set of issues related to both improving the homogeneity of the freshly prepared mixture and increasing the strength of cement stone and concrete based on it [21, 22].

The use of high-speed hydrodynamic mixing to activate cement in combination with an optimal amount of ground quartz sand in terms of consumption ensures acceleration of cement hardening processes and intensification of exothermic heating, which makes it possible to abandon both thermal treatment and the use of fast-hardening cements.

Purpose of the study. The above stated determined the purpose of this work, which is to determine the effect of mechanical activation on the thermomechanical properties of cement-water compositions and solutions based on them.

Research methods. Activation of Portland cement and a mixture of Portland cement with ground sand (mixed binder) was carried out by intensive processing of the aqueous cement and cement-sand composition in a rotary high-speed mixer. The use of a rotary mixer ensures physical and chemical activation of both Portland cement grains and ground quartz sand.

In a turbulent flow, both physical and chemical dispersion of binder particles and ground sand grains are ensured, as well as stripping of new growth products from the surface of a part of the cement. Thus, the activation of Portland cement and a mixture of binder with ground sand will affect both the acceleration of the exotherm of the hardening cement-water composition and the increase in the strength of the mortar in the early stages of hardening. To activate the cement, a specially designed high-speed turbulent type mixer with a working body speed of 1800 rpm was used. The work also determined the effect of mechanical activation on viscosity, which was assessed based on the results of the spreading of the cement-water composition on the Suttard device.

To record the exothermic heating of cement-containing compositions, a thermos was used, which is a glass flask with double walls, between which a vacuum was created. The fluctuation in room temperature during the determination of exothermic heating did not exceed ± 1.5 °C. To record the temperature, a mercury thermometer was used, located in the center of the sample using a copper tube half filled with transformer oil. The temperature was recorded every 30 minutes until the next heating value did not change or was lower than the previous one.

To determine the effect of mechanical activation and the amount of ground sand in the binder on compressive strength, cement-sand samples measuring $4 \times 4 \times 16$ cm were prepared.

The mixture was obtained by mixing one part of the binder with one part of non-milk quartz sand with $Mkr = 2.2$. The amount of mixing water was determined by the mobility of the mortar mixture (the spread of the mixture cone was 105...110 mm) after 30 shaking on the table.

Research results. In the studies, Portland cement PC II/A-Sh-500 was used as a binder (manufacturer – LLC "Cement", Khutorskaya str., 70, Odessa, Ukraine). Portland cement meets the requirements of DSTU B V.2.7-46:2010 "Cements for general construction purposes. Technical conditions." The production of cement-sand binder was carried out by joint grinding of Portland cement and quartz sand in amounts of 20 and 40%. Quartz sand from the Aleksandrovsy quarry in the Odessa region in $Mkr = 2.2$ was used as a filler for the mortar.

To determine the effective viscosity and exothermic heating, the compositions of cement-containing compositions given in Table 1 were used. The experimental conditions provided for the production of equal-viscosity cement-containing compositions with a cone spread in the range of 120 ± 5 mm.

Analysis of the experimental data given in Table 1 indicates that the activation of an aqueous cement-containing composition within 180 sec. allows you to obtain a given spread on the Suttard device at low values of the water-binder ratio. The main contribution to the decrease in the water-

binder ratio is provided by the activation of the cement-containing composition for 90 seconds. Thus, for the composition (cement + water) the activation period increases from 0 to 90 seconds leads to a decrease in the water-cement ratio from 0.387 to 0.351, i.e. by more than 10 %. A further increase in the activation period (from 90 to 180 seconds) causes a decrease in the water-binder ratio by no more than 1.5 % (from 0.351 to 0.346).

Table 1 – Compositions of cement-containing components

№	Portland cement, %	Ground sand, %	B/B	Activation of an aqueous solution of mixed binder, sec.
1	100	0	0.387	0
2	100	0	0.351	90
3	100	0	0.346	180
4	80	20	0.348	0
5	80	20	0.320	90
6	80	20	0.313	180
7	60	40	0.325	0
8	60	40	0.298	90
9	60	40	0.284	180

It should also be noted the influence of mechanical activation on the water-binder ratio for cement-water compositions with the addition of ground quartz sand in amounts of 20 and 40 %. Compatible grinding of Portland cement with the addition of 20 and 40 % quartz sand causes a decrease in the water-binder ratio to 0.348 and 0.324 (while ensuring a given spread of the mixture cone), respectively – there is no activation of the composition (cement + ground sand + water). Mechanical-chemical activation of a cement-water composition in a high-speed mixer with the addition of 20% ground sand (by weight of cement) for 180 seconds helps reduce the water-binder ratio from 0.348 (no activation) to 0.313, that is, by almost 12 %, and with the addition of 40 % ground sand by 14 % (from 0.324 to 0.284).

As for the influence of the period of mechanical activation of aqueous cement-containing compositions on the diameter of the spread of the mixture cone and exothermic heating, it should be noted that for all the compositions under consideration there is a tendency towards faster thickening of mixtures, the activation period of which increases, Table 2.

Table 2 – Effect of activation period and content of ground sand in the binder on the kinetics of reducing the diameter of the cone spread

Hardening time of the CWC, hour	Cone spread of cement-containing compositions (CWC), mm								
	№ composition of cement-containing compositions								
	1	2	3	4	5	6	7	8	9
0	120	120	120	120	120	120	120	120	120
0.5	112	108	106	112	109	108	117	113	110
1.0	107	96	94	108	103	100	113	110	97
1.5	106	87	85	106	99	97	109	103	89
2.0	105	80	74	104	96	94	106	96	83
2.5	98	71	61	100	92	89	102	91	73
3.0	89	60	-	94	85	82	97	85	62
3.5	77	-	-	87	76	73	90	77	-
4.0	63	-	-	78	63	60	84	-	-

The experimental results of exothermic heating of cement-water compositions are given in Table 3.

The experimental results obtained indicate the presence of an induction period for heating the cement-water composition both on Portland cement that is not subject to mechanical activation (this period is approximately 5 hours from the moment of mixing cement with water) and on Portland cement that is subject to mechanical activation.

Table 3 – Effect of mechanical activation period on exothermic heating of cement-water compositions

Composition number	Content of ground quartz sand in the binder, %	Activation period, sec.	Temperature of exothermic heating of compositions, °C, in one hour											
			1	2	3	4	5	6	7	8	9	10	11	12
1	0	0	19.0	19.0	20.5	21.3	22.3	25.0	30.0	37.5	40.5	47.0	47.7	46.5
2	0	90	20.0	21.0	23.5	26.0	28.5	33.0	38.4	45.7	50.0	48.2	45.5	-
3	0	180	20.0	22.1	24.8	27.2	31.0	37.0	40.0	49.2	52.4	49.0	46.8	-
4	20	0	18.0	18.0	18.0	20.4	21.0	21.5	24.6	26.6	31.0	33.0	34.5	34.0
5	20	90	19.0	19.0	20.5	22.5	24.5	25.6	30.5	33.2	35.2	37.0	37.0	36.5
6	20	180	19.0	19.3	21.9	24.2	26.2	27.5	32.8	37.5	37.5	38.0	38.0	37.5
7	40	0	18.0	19.0	19.5	19.6	20.9	22.1	24.5	27.0	28.5	30.0	31.2	30.0
8	40	90	19.0	19.0	19.5	21.2	22.5	25.8	27.6	30.7	32.3	33.5	34.5	34.0
9	40	180	19.0	20.3	22.3	23.7	25.7	28.4	31.3	32.8	34.0	35.5	35.5	35.2

A graphical display of the kinetics of exothermic heating of a hardening activated cement-water composition (NN compositions – 1, 2, 3) is shown in Fig. 1.

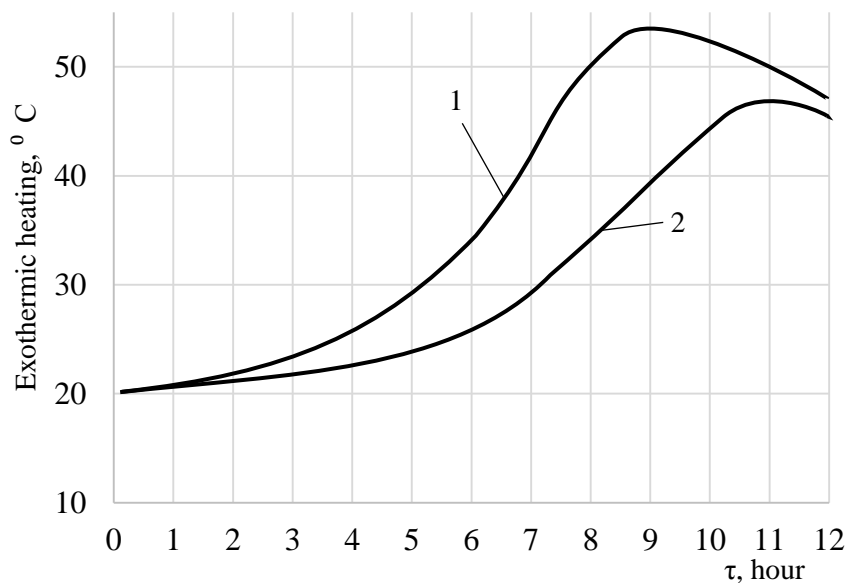


Fig.1. The effect of mechanical-chemical activation on exothermic heating of a cement-water composition:
 1 – cement-water composition activated for 180 seconds; 2 – control

In this case, the induction period was no more than 2 hours. At the end of the induction period, a relatively sharp increase in the temperature of the hardening cement-water composition is observed, reaching a maximum value (52.4 °C) 9 hours after mixing the cement with water.

For the cement-water composition, which is not subject to mechanical activation, the maximum heating did not exceed 47.7 °C, and the peak heating occurred no earlier than 11 hours from the moment of preparation of the cement-water composition. A similar effect of mechanical activation on the kinetics of exothermic heating is observed for cement-water compositions with the addition of 20 and 40% ground quartz sand.

The final stage of the study was to determine the effect of mechanical-chemical activation and consumption of ground quartz sand on the compressive strength at the age of 3 and 7 days of beam samples made from 1:1 mortar.

Compressive strength of samples at the age of 3 and 7 days, depending on:

1) manufacturing technology: a) the use of mechanical activation of the binder; b) control – the binder was not subjected to mechanical activation;

2) the content of ground quartz sand in the binder (0; 20; 40%) indicates that mechanical activation is a useful technological effect on the strength characteristics of the mortar, Table 4.

Table 4 – Effect of mechanical activation period on exothermic heating of cement-water compositions

Hardening period of cement-sand mortar, days	Compositions of cement-containing components								
	1	2	3	4	5	6	7	8	9
	Compressive strength of mortar, MPa								
3	32.3	35.7	36.7	20.7	24.5	25.5	17.6	20.9	22.1
7	40.5	48.3	50.5	25.7	30.0	31.2	23.7	26.7	28.1

An increase in the strength of the solution due to mechanical activation of the binder provides a real opportunity to reduce the consumption of Portland cement, while ensuring the necessary properties of the final product.

Conclusions:

1. The use of mechanical-chemical activation of aqueous cement-containing compositions leads to a decrease in their viscosity, which makes it possible to reduce the water ratio by an average of 10...14 %.

2. Mechanical-chemical activation of aqueous cement-containing compositions causes an increase in both the rate of exotherm and an increase in the maximum heating temperature.

3. The use of mechanical-chemical activation promotes an increase in the compressive strength of cement-sand mortars at 3 and 7 days of age (at all studied consumption of ground quartz sand) by an average of 15...25 % (compared to the control).

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**МЕХАНОХІМІЧНА АКТИВАЦІЯ ПОРТЛАНДЦЕМЕНТУ І ЇЇ ВПЛИВ
НА ТЕРМО-МЕХАНІЧНІ ХАРАКТЕРИСТИКИ ЦЕМЕНТНО-ВОДНИХ КОМПОЗИЦІЙ
ТА РОЗЧИНІВ НА ЇХ ОСНОВІ**

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Анотація. Розглянуті у статті питання пов'язані з визначенням впливу механоактивації у роторному швидкісному змішувачі цементно-водних композицій та розчинів на їх основі. Актуальним для даного дослідження є активація цементу в поєднанні з витратою меленого кварцового піску ($S = 250 \text{ м}^2/\text{кг}$), кількість якого корегувалася в діапазоні від 0 до 40% маси цементу. Застосування даної технології забезпечує, поряд із зниженням витрати цементу, прискорення процесів гідратації цементу та інтенсифікації екзотермічного розігріву тверднучої композиції. Віддзеркалюється механоактивація також на прискоренні термінів втрати рухливості, наповнених меленим піском, цементно-водних композицій. Наведені експериментальні дані дозволили оцінити вплив термінів активації (90 та 180 сек) в'язучого на діаметр розпливу водної цементно-вміщуючої композиції. Встановлено, що основний вклад (до 90% загального значення) в зниження водо-в'язучого відношення (при умові одержання рівнов'язких композицій) досягається при активації цементно-вміщуючої композиції протягом 90 сек. Подальша активація в'язучого (до 180 сек) незначно впливає на зростання діаметру розпливу композиції і не перевищує 5-10 %.

Визначена термосним методом екзотермія тверднучої цементно-водної композиції свідчить про значний вплив механоактивації як на кінетику, так і на досягнення максимальної температури її розігріву. Введення меленого піску не змінює загальної картини впливу механоактивації на екзотермічний розігрів, змінюючи лише зменшення інтенсивності та зниження максимального розігріву цементно-водної композиції.

Виявлено вплив механо-хімічної активації портландцементу з добавкою кварцового піску на міцність будівельного розчину складу 1:1 у 3-х та 7-и добовому віці. Експериментальні дослідження свідчать про позитивний вплив активації в'язучого на міцність при стиску розчину. Зростання міцності зразків на механоактивованому цементі досягало 15-25 % в порівнянні з контролем.

Ключові слова: механоактивація, роторний швидкісний змішувач, активація, екзотермічний розігрів, водо-в'язуче відношення, мелений кварцовий пісок.

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