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INFLUENCE OF MECHANICAL ACTIVATION ON THE PROPERTIES OF CEMENT-WATER COMPOSITIONS WITH THE ADDITION OF GROUND LIMESTONE

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Abstract. The paper considers the issue related to determining the effect of mechanical activation of a mineral binder on the properties of both hardening and hardened cement-water compositions. The mechanical activation of cement in combination with the consumption of ground limestone, the amount of which was adjusted in the range from 0 to 40 % of the cement mass, is relevant for this study. The effect of mechanical chemical activation of Portland cement only and Portland cement with the addition of 20 and 40 % ground limestone on changing the water-solid ratio of equiviscous compositions was studied. It was shown that mechanical and chemical activation of a cement-water composition has a positive effect on reducing the W/S ratio of equiviscous compositions from 0.42 (no activation) to 0.38 (activation period 180 sec). The obtained experimental results indicate the presence of an induction period of heating of the cement paste both on Portland cement not subject to mechanical activation (this period is approximately 6 hours from the moment of interaction of cement with water) and on Portland cement subject to mechanical activation. In this case, the induction period was no more than 2 hours. Joint mechanical activation of an aqueous mixture of Portland cement and ground limestone ensures acceleration of the hydration processes of the binder, which is confirmed by the intensification of the exothermic heating of the filled cement-mixing compositions. The positive role of mechanical activation is also reflected in the acceleration of the thickening rate of the compositions, which was recorded by the kinetics of the decrease in the diameter of their spread over time. The positive role of mechanical activation in reducing the effective viscosity of cement-containing compositions is confirmed, which ensures a decrease in their water-solid ratio by an average of – 8 ... 10 %. A positive effect of mechanochemical activation of Portland cement with the addition of ground limestone on the strength of cement stone at the age of 3 days has been revealed. Experimental studies indicate that only due to mechanical activation the strength of samples made of cement stone with the addition of ground limestone can be increased by almost 25...30 %.

Keywords: mechanical activation, Portland cement, ground limestone, exothermic heating, cement stone.

Introduction. In the technology of production of mixed cements, Portland cement with the use of ground limestone is widely used. Such cement is obtained both by compatible grinding of Portland cement clinker, limestone and the addition of dihydrate gypsum and by careful mixing of Portland cement with ground limestone.

A promising method for improving the physical and mechanical characteristics of hardened composites based on such mixed cements is their mechanochemical activation in a high-speed mixer. The issues considered in the article are related to determining the effect of the addition of ground limestone on the properties of cement-water compositions, namely water-hardening ratio, exothermic heating and compressive strength of cement stone.

Analysis of the latest research and publications. One of the important problems in the technology of production of mixed cements is the creation of optimal combinations of Portland cement with mineral additives, including ground limestone, the presence of which increases the potential capabilities of the binder [1-3]. In this regard, the replaceable part of Portland cement with mineral additives, in addition to economic efficiency, helps to obtain a binder with improved properties [4, 5].

The effect of introducing mineral additives into Portland cement significantly enhances the mechanical and chemical activation of mixed cement in turbulent flows [6-10]. In works [11-13] it is shown that the use of activators helps to solve a set of issues related to both the improvement of a homogeneous freshly prepared mixture and the increase in the strength of cement stone and concrete based on it [14-16]. The use of high-speed mixers for cement activation in combination with the use of mineral additives, in our opinion, will ensure acceleration of cement hardening processes and intensification of exothermic heating, which will make it possible to abandon both heat-moisture treatment and the use of energy-intensive fast-growing cements.

Purpose of the study. The aim of the proposed work is to determine the effect of activation of a mixed binder in a rotary high-speed mixer (n = 1800 rpm) on the water-solid ratio (with a constant flow of the composition in the range of 120±5 mm), its exothermic heating and the compressive strength of the cement.

Research methods. Activation of Portland cement and a mixture of Portland cement with ground lime (mixed binder) was carried out by intensive processing of water cement and cement-lime compositions in a rotary high-speed mixer. The use of a rotary mixer provides physical and chemical activation of both Portland cement grains and ground limestone grains. In the turbulent flow, the chemical dispersion of limestone particles is ensured, as well as the peeling off of neoplasms from the surface of cement particles. The activation time of Portland cement and the mixture of binder with ground limestone was 90 and 180 seconds. An inactivated mixture of identical composition, which was subject to mechanical activation, was used as a control.

To determine the exotherm of cement compositions, the thermal method was used, which is characterized by the relative simplicity of conducting the experiment. The thermal method involves effective thermal insulation of the hardening sample at a constant ambient temperature. The temperature of the sample, which is equal to the ambient temperature at the beginning of the experiment, will change over time as a result of two processes, namely:

a) exothermic reaction resulting from the chemical interaction of cement with water;

b) heat exchange between the sample and the environment.

Ensuring the same temperature throughout the volume of the sample is achieved by creating a high thermal resistance, for which a thermos is used, which is a glass flask with double walls between which a vacuum is created. Fluctuations in room temperature in the process of determining exothermic heating do not exceed ±1.5 % ºC. The prepared cement dough is placed in a container with a volume of 150 ml. Fixation of the temperature of the sample was carried out at the expense of a mercury thermometer, which was placed in the center of the sample with the help of a copper tube half filled with transformer oil. Fixation of the temperature of the hardening cement dough was carried out every hour until the moment when the next heating indicator did not change or was lower than the previous one.

The influence of mechanical activation and the amount of ground limestone in the binder on strength was determined by mechanical compression tests of beam samples measuring 4×4×16 cm.

The compositions of the mixtures for the preparation of the samples were taken as given in Table 1.

Research results. The studies were conducted using Portland cement M500 (manufacturer "Yugcement", branch of PJSC "Dikerhoff Cement Ukraine"), which meets the requirements of DSTU B V.2.7-46:2010 "Cements for general construction purposes. Specifications and mixtures of Portland cement with ground lime are 20% and 40 %. To determine the effect of activation of the cement-water composition with the addition of ground limestone on the change in the water-solid ratio, the compositions of the mixed binder were used, which are given in Table 1.

Table 1 – Mixed binder compositions

Composition number	Portland cement, %	Ground limestone, %	Activation of mixed binder, s	Spreading of the mixture cone, mm	W/S
1	100	0	0	120	0.42
2	100	0	90	118	0.39
3	100	0	180	120	0.38
4	80	20	0	121	0.44
5	80	20	90	122	0.42
6	80	20	180	120	0.41
7	60	40	0	11	0.45
8	60	40	90	120	0.43
9	60	40	180	120	0.42

The experimental data presented in Table 1 indicate that the mechanochemical activation of the cement-water composition has a positive effect on the decrease in the water-solid ratio of equiviscous compositions from 0.42 (no activation) to 0.38 (activation period of 180 sec). It should be noted that the main contribution to the decrease in the water-solid ratio is provided by the activation of the cement-water composition for 90 sec (the W/S ratio decreases from 0.42 to 0.39, i.e. by almost 8 %). Subsequent activation causes an insignificant decrease in the water-solid ratio and does not exceed 2...3 %.

A similar effect of mechanical activation on the change in the water-solid ratio (provided that the specified cone spread of the mixture is obtained) is also observed for cement-water compositions with the addition of ground limestone in the amount of 20 and 40 %. Thus, mechanical activation for 180 sec of a cement-water composition with the addition of 20 % ground limestone causes a decrease in the W/T ratio from 0.44 (no mechanical activation) to 0.41, and with the addition of 40% ground limestone from 0.45 (mechanical) to 0.42, i.e. by more than 7 %. It should also be noted that an increase in the content of ground limestone in the binder causes an increase in the water-solid ratio, which, in our opinion, requires the use of plasticizing additives.

As for the kinetics of changes in the diameter of the spread of water-cement-containing compositions depending on the duration of mechanical activation and the content of ground limestone, the following should be noted:

1) mechanical activation causes a more intense thickening of the mixture, which is appeared in a sharp decrease in the diameter of its spread over time;

2) an increase in the content of ground limestone in the binder largely neutralizes the effect of mechanical activation on the increase in the mobility of cement-water compositions, Table 2.

Table 2 – Kinetics of the decrease in the diameter of the mixture cone spread depending on the activation period and the limestone content in the binder

Curing period, h	№ composition								
	1	2	3	4	5	6	7	8	9
0	120	120	120	120	120	120	120	120	120
0.5	109	105	95	112	115	104	115	109	111
1	104	91	76	105	109	93	109	102	105
1.5	95	75	63	95	98	71	98	92	96
2	83	61		81	81	63	87	83	80
2.5	70			75	68		83	76	66
3	61			69	63		77	68	64
3.5				62			70	62	
4							65		
4.5							61		

* № composition corresponds to the data shown in the Table. 1

The high-speed mixing of cement-containing aqueous compositions with the addition of ground limestone also affects the kinetics of their exothermic heating. The experimental results of exothermic heating are given in Table 3.

Table 3 – Exothermic heating of cement-containing aqueous compositions with the addition of ground limestone

№ composition	Content of ground limestone in binder, %	Binder activation time, s	Initial temperature of the composition (cement + ground limestone + water), %	Temperature of exothermic heating of compositions, ºC, after, hour										
				1	2	3	4	5	6	7	8	9	10	11
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
1	0	0	25	25.2	25.3	25.4	27.5	30.0	38.1	50	61	61	61	60
2	0	90	25	25.0	25.1	27.1	36.0	39.5	59.1	65.3	65.3	65.0	64.5	64.4
3	0	180	25	25.0	27.0	30.0	40.0	62.0	68.2	68.2	68.0	67.6	67.4	67.0
4	20	0	25	25.0	26.5	27.0	27.0	31.0	37.0	48.0	52.1	52.0	49.7	49.5
5	20	90	25	25.0	26.7	27.7	30.0	38.0	47.1	55.8	55.6	55.4	55.0	55.0
6	20	180	25	25.0	27.0	27.5	35.2	54.3	59.0	59.0	58.8	58.6	58.3	58.0
7	40	0	25	25.0	26.1	27.2	28.0	30.0	37.5	42.0	43.4	43.4	43.2	42.1
8	40	90	25	25.5	27.0	29.2	30.0	35.5	40.2	47.3	47.3	47.1	47.0	46.8
9	40	180	25	25.0	27.2	28.0	31.2	46.5	51.3	51.3	57.1	57.0	50.8	50.6

A graphical representation of the kinetics of exothermic heating of the hardening activated cement-water composition (composition Nos. 1, 3 and 6, 8) is shown in Fig. 1.

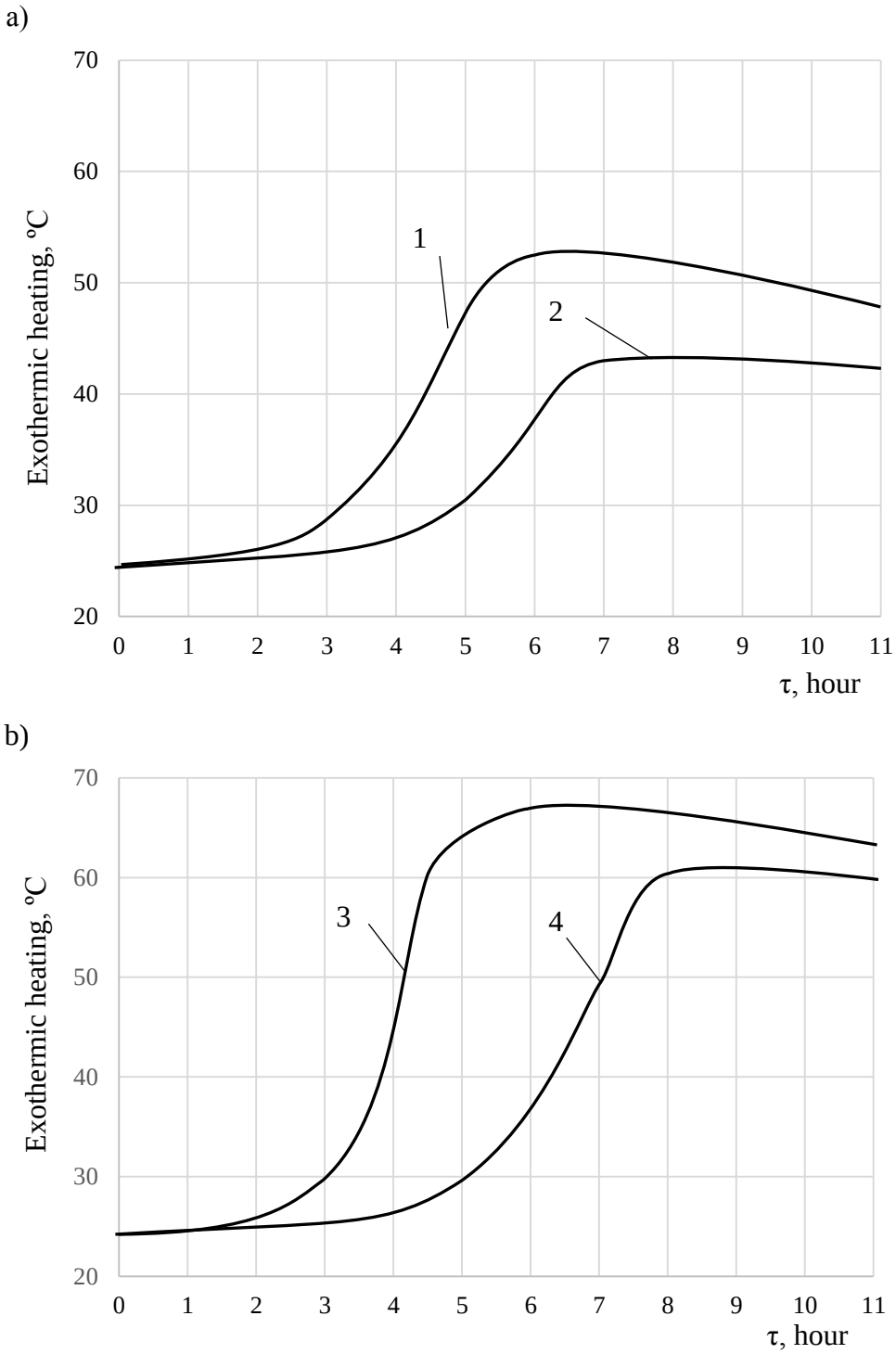

Fig. 1. Effect of mechanical chemical activation on exothermic heating of cement-water composition: a – cement-water composition without addition of ground limestone (warehouses 1, 3); b – cement-water composition with addition of 40% ground limestone (warehouses 6, 8); 1 – cement-water composition activated for 180 sec; 2 – control (no mechanical activation); 3 – cement-water composition activated for 180 sec with addition of 40% ground limestone; 4 – control (no mechanical activation of the given composition)

The results of sample tests given in Table 4 indicate a significant influence on the strength of cement stone of both the mechanical activation of the binder and the amount of ground limestone in the binder.

Table 4 – Compressive strength of cement stone (MPa) depending on the duration of mechanical activation and the content of ground limestone in the binder

Mixture activation time, sec	Composition of the binder		
	Portland cement – 100 %	PC – 80 %; ground limestone – 20 %	PC 60 – %; ground limestone – 40 %
1	2	3	4
0	19.1	15.4	12.1
90	24.2	18.9	16.4
180	25.7	19.7	17.9

Conclusions:

1. Mechanochemical activation of cement-containing compositions with the addition of ground limestone ensures a decrease in their viscosity, which allows to reduce the water-binding ratio by 8...10% and, at the same time, to increase the compressive strength of cement stone at the age of 3 days (compared to control) on average by 25...35%.

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ВПЛИВ МЕХАНОАКТИВАЦІЇ НА ВЛАСТИВОСТІ ЦЕМЕНТНО-ВОДНИХ КОМПОЗИЦІЙ З ДОБАВКОЮ МЕЛЕНОГО ВАПНЯКУ

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Анотація. В роботі розглядаються питання, пов'язанні з визначенням впливу механоактивації мінерального в'яжучого на властивості як тверднучих, так і затверділих цементно-водних композицій. Актуальним для даного дослідження є механоактивація цементу в поєднанні з витратою меленого вапняку, кількість якого корегувалася в діапазоні від 0 до 40 % маси цементу.

Досліджувався вплив механохімічної активації тільки портландцементу та портландцементу з добавкою 20 і 40 % меленого вапняку на зміну водотвердого відношення рівнов'язких композицій. Показано, що механохімічна активація цементно-водної композиції позитивно відображається на зменшенні В/Т відношення рівнов'язких композицій з 0,42 (активація відсутня) до 0,38 (термін активації 180 сек). Одержані експериментальні результати свідчать про наявність індукційного періоду розігріву цементного тіста як на портландцементі, що не підлягав механоактивації (цей період складає приблизно 6 год з моменту взаємодії цементу з водою) так і на портландцементі, який підлягав механоактивації. В цьому разі індукційний період складав не більше 2-х годин. Сумісна механоактивація водної суміші портландцементу та меленого вапняку забезпечує прискорення процесів гідратації в'яжучого, що підтверджується інтенсифікацією екзотермічного розігріву наповнених цементо-вмішуючих композицій.

Позитивна роль механоактивації відображається також на прискоренні темпів загустівання композицій, що фіксувалося кінетикою зменшення діаметру їх розпливу в часі. Підтверджена позитивна роль механоактивації в зменшенні ефективної в'язкості цементно-вміщуючих композицій, що забезпечує зниження їх водотвердого відношення в середньому на – 8…10 %.

Виявлено позитивний вплив механохімічної активації портландцементу з добавкою меленого вапняку на міцність цементного каменю в 3-х добовому віці. Експериментальні дослідження свідчать про те, що тільки за рахунок механоактивації міцність зразків із цементного каменю з добавкою меленого вапняку може бути підвищена майже на 25…30 %.

Ключові слова: механоактивація, портландцемент, мелений вапняк, екзотермічний розігрів, цементний камінь.

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