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CONSTRUCTION MORTAR BASED ON MECHANOACTIVATED PORTLAND CEMENT WITH THE ADDITION OF GROUND LIMESTONE

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Abstract. In the practice of production of building solutions, cements with the use of mineral additives and, in particular, ground limestone are widely used. Technologically, such mixed cements can be obtained both by compatible grinding of Portland cement clinker, dihydrate gypsum and limestone additive, and by thorough mixing of Portland cement with ground limestone. A promising method for improving the mechanical characteristics of building solutions is intensive mechanic-chemical activation of mixed cements in high-speed turbulent mixers. The issues considered in the article related to determining the influence of recipe and technological factors on the strength of building mortar at the age of 3, 7 and 28 days were investigated. The compressive strength of samples made from a mixture solution on both a mechanically activated binder and a binder of similar composition, but which was not subject to mechanical activation, was studied. The experimental studies were carried out using the D-optimal mathematical plan with variation of the following factors: X_1 – the ratio of the mass of the mixed binder to the mass of unground quartz sand in the construction mortar (from 1:3 to 1:1); X_2 – ground limestone content in the mixed binder (20 ± 20 %); X_3 – consumption of the superplasticizing additive Relaxol-Super PC (0.5 ± 0.5 % of the binder weight). The obtained mathematical models indicate that the maximum effect (of the listed factors) on the strength of the mortar is exerted by the content of the mechanically activated binder in it. An increase in its consumption in the composition of the mortar mix causes an increase in the strength of the mortar at the age of 3 days from 24 to 40.5 MPa, i.e. by almost 70 %. At the age of 28 days, the effect of the consumption of the activated mixed binder on the strength of the mortar is somewhat reduced and does not exceed 60 %. The next factors influencing the strength of the mortar are the consumption of superplasticizer and the percentage of ground limestone. The combined effect of mechanochemical activation in the presence of 1 % Relaxol-Super PC allows the introduction of up to 40 % ground limestone into Portland cement, while providing the same compressive strength of the mortar as when using non-mechanically activated Portland cement, but without the addition of ground limestone.

Keywords: mortar, mechanochemical activation, lime mixture, binder, portland cement, ground limestone.

Introduction. In the practice of manufacturing concrete and reinforced concrete products, cements using ground limestone are widely used. Such cements are obtained both by joint grinding of Portland cement clinker, gypsum dihydrate and limestone mineral additive, and by thorough mixing of Portland cement with ground limestone. A promising method for improving the mechanical characteristics of a building solution is the mechanochemical activation of Portland cement in combination with the use of superplasticizing additives and mineral fillers. Ensuring a high degree of cement activation is achieved through the use of high-speed forced-action activators that provide the binder with additional chemical activity, thereby increasing the quality indicators of the final product. Mechanochemical methods of activating Portland cement fit quite easily into existing technological schemes for obtaining mortar mixtures, which allows, in our opinion, to more fully reveal the potential of both the binder and the building solutions based on it.

Analysis of the latest research and publications. Considering the realities of the production of Portland cements with mineral additives in Europe, as well as Ukraine's desire to take its place in the European cement market, issues related to the study of their influence, and in particular, limestone, on the properties of mortars and concretes are becoming very important [1-5]. The use of mineral additives in the technology of Portland cement production makes it possible to save both fuel energy and electrical energy [6]. In addition, the introduction of a finely dispersed carbonate additive ($S \geq 650$ m^2/kg) into the composition of Portland cement leads to an increase in the specific surface area of the binder, which contributes to the compaction of hardened cement stone [7]. It is known [8] that as a result of the chemical interaction between ground limestone and aluminate phases of Portland cement clinker, calcium hydrocarboaluminates $3CaO \cdot Al_2O_3 \cdot CaCO_3 \cdot 12H_2O$ are formed, which contribute to increasing the strength of cement stone [9]. Thus, it can be stated that $CaCO_3$ has a positive effect on both the structure of cement stone and the mechanical characteristics of mortars and concretes.

The issues considered in the article are related to determining the influence of ground limestone on the strength of the mortar. In this regard, the need to create optimal combinations of Portland cement with this finely dispersed mineral additive (mixed binder) becomes obvious. The presence of ground limestone helps to increase the potential of the mixed binder both from an economic point of view and from an environmental point of view [10-12]. The fact of increasing the efficiency of introducing finely ground mineral additives into cement during its mechanical activation using high-speed activators is undeniable [13, 14]. The use of high-speed activators helps to solve a set of issues related to both improving the homogeneity of the freshly prepared mortar mixture and increasing the mechanical characteristics of the hardened composite[15].

Purpose of the research. The aim of this work is to experimentally confirm the production of a building mortar with improved mechanical characteristics through the use of mechanical activation of Portland cement in the presence of ground limestone (mixed binder) and a superplasticizing additive (SP).

Research methods. Mechanochemical activation of the aqueous composition of Portland cement, as well as a mixture of binder with ground limestone and superplasticizer, was carried out in a high-speed mill (n = 1800 rpm) for 180 sec. A mixture of similar composition was used for control, but it was not subject to mechanochemical activation. For the joint determination of the influence of the studied factors on the compressive strength of the mortar, a three-factor experiment was carried out, where the following independent factors were taken: consumption of mixed binder in the mortar, consumption of ground limestone in the mixed binder and consumption of SP Super PK).

Research results. Portland cement PC II/A-SH-500, which meets the requirements of DSTU B V.2.7-46:2010 "General-purpose cements. Specifications", was used as a binder in the experimental studies. The mineralogical composition of Portland cement clinker includes, "mass %": C_3S – 7.5 ... 7.7; C_2S –13 ... 15; C_3A – 7.5 ... 7.7; C_4AF – 10.6 ... 11.6. The content of alkali oxides (in terms of Na_2O) is 0.18 ... 0.24 %. Limestone from the Odessa quarry "Yuzhny" was used as a carbonate additive. Before use, the limestone was ground to a specific surface of 625 m^2/kg. Along with Portland cement, a homogeneous mixture of Portland cement with the addition of ground limestone in the amount of 20 and 40 % was used in the studies.

To determine the effect of mechanical 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 given in Table 1 were used.

The experimental data given 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). A similar effect of mechanical activation on the change in the water-solid ratio is also observed for cement-water compositions with the addition of ground limestone in the amount of 20 and 40 %. A special feature of the effect of adding ground limestone is that increasing its content in the binder to 40 % causes an increase in the W/S ratio for both mechanically activated and non-mechanically activated binders by an average of 7...10 %.

Table 1 – Mixed binder compositions

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

As for the kinetics of the change in the spread diameter of aqueous cement-containing compositions depending on the duration of mechanical activation and the content of ground limestone, it should be noted that mechanical activation causes a more intense thickening of the mixture, which is manifested in a sharp decrease in the spread diameter over time, Table 2.

Table 2 – Kinetics of reduction of 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
0	120	120	120	120	120	120
0.5	109	95	112	104	115	111
1	104	76	105	93	109	105
1.5	95	63	95	71	98	96
2	83		81	63	87	80
2.5	70		75		83	66
3	61		69		77	64
3.5			62		70	
4					65	
4.5					61	

The compressive strength of 4×4×16 cm beam samples made of mortar mix both on mechanically activated binder and on binder of similar composition, but which was not subject to mechanochemical activation, was investigated.

Experimental studies were conducted using the D-optimal plan. The following factors were varied in the experiment:

X_1 – ratio of the mass of mixed binder to the mass of unground quartz sand in the mortar composition – (1:3; 1:2; 1:1);

X_2 – consumption of ground limestone in mixed binder – (20±20 %);

X_3 – consumption of Relaxol-Super PC – (0.5±0.5 %).

The consumption of mixing water for each line of the mathematical plan was taken based on obtaining the spread diameter on the shaking table in the range of 140±5 mm. The specified spread diameter of the mixture was taken to be the same for the two comparative technologies. The experimental plan and compositions of the studied building solutions are presented in Table 3.

Table 3 – Experimental plan and compositions of building solutions

№	Levels of independent factors			C:S	Content of dry components of the mortar mixture per batch			
					Composition of mixed binder		Quartz sand, g	Superplasticizer, g
	X_1	X_2	X_3		Portland cement, g	Ground limeston, g		
1	-	-	-	1:3	500	-	1500	0.0
2	-	+	-	1:3	300	200	1500	0.0
3	0	0	-	1:2	534	133	1333	0.0
4	+	-	-	1:1	1000	-	1000	0.0
5	+	+	-	1:1	600	400	1000	0.0
6	-	0	0	1:3	400	100	1500	2.5
7	0	-	0	1:2	667	-	1333	3.4
8	0	0	0	1:2	534	133	1333	3.4
9	0	+	0	1:2	400	267	1333	3,4
10	+	0	0	1:1	800	200	1000	5.0
11	-	-	+	1:3	500	-	1500	5.0
12	-	+	+	1:3	300	200	1500	5.0
13	0	0	+	1:2	534	133	1333	6.7
14	+	-	+	1:1	1000	-	1000	10.0
15	+	+	+	1:1	600	400	1000	10.0

As a result of statistical processing of experimental data, polynomial models (1-4) were obtained for the dependence of the compressive strength of mortar at 3 and 28 days of age on the studied factors:

$$R_{com}^{m.3} = 23{,}6 + 6{,}6X_1 + 2{,}5X_1^2 - 0{,}9X_1X_2 + 0{,}7X_1X_3 - 3{,}0X_2 - 0{,}9X_2^2 + 0{,}6X_2X_3 + 3{,}6X_3 - 0{,}2X_3^2 \quad (1)$$

$$R_{com}^{m.28} = 39{,}0 + 10{,}7X_1 + 4{,}4X_1^2 - 1{,}3X_1X_2 + 0{,}8X_1X_3 - 4{,}9X_2 - 1{,}7X_2^2 - 0{,}7X_2X_3 + 5{,}7X_3 \quad (2)$$

$$R_{com}^{c.3} = 13{,}3 + 3{,}6X_1 + 1{,}3X_1^2 - 0{,}5X_1X_2 + 0{,}2X_1X_3 - 1{,}7X_2 - 0{,}4X_2^2 + 1{,}8X_3 \quad (3)$$

$$R_{com}^{c.28} = 29{,}8 + 8{,}2X_1 + 3{,}3X_1^2 - 0{,}9X_1X_2 + 0{,}6X_1X_3 - 3{,}9X_2 - 1{,}2X_2^2 - 0{,}5X_2X_3 + 4{,}5X_3 \quad (4)$$

where: $R_{com}^{m.3}$, $R_{com}^{m.28}$ – strength of mortar on mechanically activated mixed Portland cement at 3 and 28 days of age, MPa;

$R_{com}^{c.3}$, $R_{com}^{c.28}$ – strength of mortar on mixed Portland cement, which was not subject to mechanical activation (control) at 3 and 28 days of age, MPa.

The consideration of the coefficients for independent factors in mathematical models (1-4) shows that for a building mortar both on a mechanically activated binder and on a binder that has not been subjected to mechanical activation, the maximum effect on the strength of the composite is exerted by both the content of the mixed in (X_1) in it and the consumption of SP. This is confirmed by the single-factor graphical dependencies shown in Fig. 1.

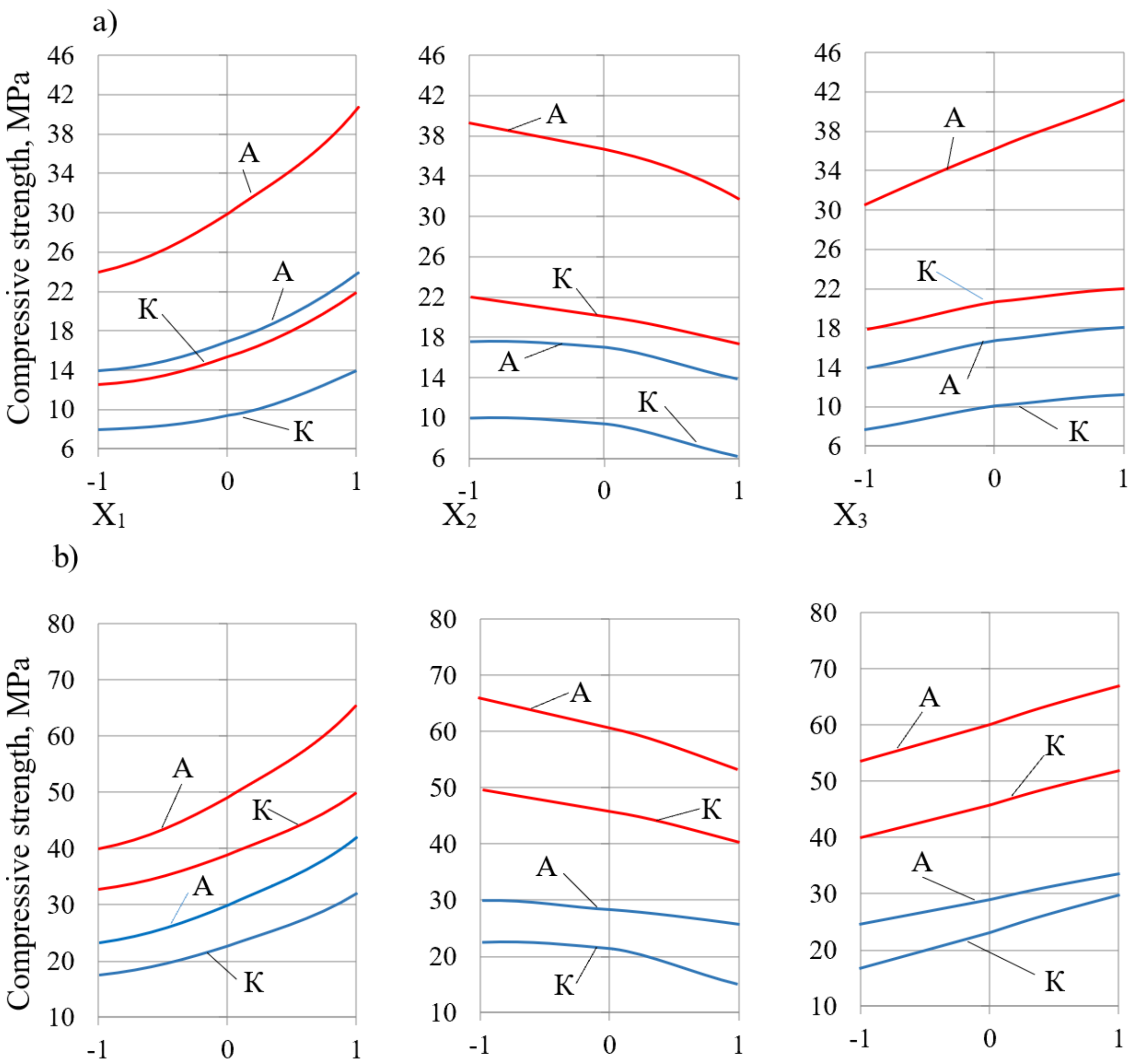

Fig. 1. The influence of formulation factors on the strength of the mortar under compression in the maximum (red line) and minimum (blue line) zones:
a – strength of mortar at 3 days of age; b – strength of mortar at 28 days of age; K – control (strength of samples on binder that was not subject to mechanical activation); A – strength of samples on mechanically activated binder

Analyzing the experimental data, it should be noted that an increase in the content of mechanically activated mixed binder in the composition of the mortar mixture (the ratio of the mass of binder to the mass of quartz sand) leads to an increase in the strength of the mortar at a 3-day age from 24 MPa to 40.5 MPa, i.e. by almost 70%. At the age of 28 days, the effect of the content of activated mixed binder on the strength of the mortar is slightly reduced and is 62.5%. With respect to the effect of the superplasticizing additive on the strength of the mortar on the mechanically activated binder, it should be noted that an increase in the consumption of SP from 0 to 1% leads to an increase in the strength of the cement-mixed samples at the age of 3 days from 31 MPa to 41.2 MPa, i.e. by almost 35 %, and at the age of 28 days from 52 MPa to 67 MPa. As for the effect of ground limestone content on the compressive strength of the mortar in the maximum zone, it should be noted that at the age of 3 days, an increase in limestone consumption in the mixed binder from 0 to 40% causes a decrease in the compressive strength of the mortar from 40.5 to 32 MPa, i.e. by almost 23 %. For a mortar on a mechanically activated binder at the age of 28 days, the introduction of 40 % ground limestone into the binder leads to a decrease in the strength of the samples (compared to the use of Portland cement without the addition of ground limestone) by 23 % to 35 MPa. As for the effect of mechanical activation on the strength of the mortar, it should be noted that the maximum effect from high-speed processing of the cement-mixing composition with the addition of ground limestone is observed at the age of 3 days – in this case, the increase in the strength of the mortar is at least 60 %. At 28 days of age, the effect of mechanical activation decreases and the increase in the strength of samples on activated binder (compared to the control) is no more than 30...32 %.

Conclusions:

1. The combined effect of mechanical activation of the mixed binder and the use of the superplasticizer Relaxol-Super PC in an amount of 1 % ensures the production of a building mortar with a compressive strength of 65 MPa at 28 days of age, which is 30...32 % higher than the strength of a mortar of similar composition of a mixed binder that is not subject to mechanical activation.

2. Mechanochemical activation of a cement-containing aqueous composition with the addition of 40 % limestone ensures the production of a mortar with the same compressive strength at 28 days of age as in the case of using non-mechanically activated Portland cement, but in the complete absence of limestone addition to it.

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БУДІВЕЛЬНИЙ РОЗЧИН НА МЕХАНОАКТИВОВАНОМУ ПОРТЛАНДЦЕМЕНТІ З ДОБАВКОЮ МЕЛЕНОГО ВАПНЯКУ

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Анотація. В практиці виробництва будівельних розчинних сумішей та розчинів на їх основі широке розповсюдження одержали цементи з використанням мінеральних добавок і зокрема, меленого вапняку. Технологічно такі змішані цементи можливо отримувати як сумісним помелом портландцементного клінкеру, двоводного гіпсу та добавки вапняку так і ретельним змішуванням портландцементу з меленим вапняком. Перспективним методом покращення механічних характеристик будівельних розчинів є інтенсивна механохімічна активація змішаних цементів в швидкісних змішувачах турбулентного типу. Розглянуті у статті питання пов'язані з визначенням впливу рецептурно-технологічних факторів на міцність будівельного розчину в 3-х, 7-ми та 28-и добовому віці. Досліджувалась міцність при стиску зразків, які були виготовлені із розчину суміші як на механоактивованому в'яжучому так і на в'яжучому аналогічного складу, але яке механоактивації не підлягало. Експериментальні дослідження проводилися з використанням Д-оптимального математичного плану з варіюванням наступних факторів: X_1 – цементно-піщане відношення (від 1:3 до 1:1); X_2 – вміст меленого вапняку у змішаному в'яжучому (20 ± 20 %); X_3 – витрата суперпластифікуючої добавки Релаксол-Супер ПК (0,5 ± 0,5 % від маси в'яжучого). Одержані математичні моделі свідчать про те, що максимальний вплив (із перерахованих факторів) на міцність будівельного розчину надає вміст механоактивованого в'яжучого в ньому. Зростання його витрати в складі розчинової суміші викликає підвищення міцності будівельного розчину в 3-х добовому віці з 24 до 40,5 МПа, тобто майже на 70 %. В 28-и добовому віці вплив витрати активаваного змішаного в'яжучого на міцність будівельного розчину дещо зменшується і не перевищує 60 %. Наступними по впливу факторами на міцність будівельного розчину є витрата суперпластифікатору та процентний вміст меленого вапняку. Сумісний вплив механохімічної активації в присутності 1 % Релаксол-Супер ПК дозволяє вводити в портландцемент до 40 % меленого вапняку, забезпечуючи при цьому таку ж міцність при стиску будівельного розчину, як у разі використання немеханоактивованого портландцементу, але без добавки меленого вапняку.

Ключові слова: будівельний розчин, механохімічна активація, вапняна суміш, в'яжуче, портландцемент, мелений вапняк.

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