UDC 666.9.022

MECHANICAL ACTIVATION OF PORTLAND CEMENT WITH THE ADDITION OF GROUND LIMESTONE AND ITS EFFECT ON THE EXOTHERMIC AND STRENGTH OF CEMENT STONE

МЕХАНОАКТИВАЦІЯ ПОРТЛАНДЦЕМЕНТУ З ДОБАВКОЮ МЕЛЕНОГО ВАПНЯКУ І ЇЇ ВПЛИВ НА ЕКЗОТЕРМІЮ І МІЦНІСТЬ ЦЕМЕНТНОГО КАМЕНЮ

Стрельцов К.О., к.т.н., доцент, ORCID: 0000-0002-5463-7395;
Даниленко А.В., к.т.н., доцент, ORCID: 0000-0002-0204-6972 (Одеська державна академія будівництва та архітектури)

Streltsov K. A. PhD, Assistant Professor, ORCID: 0000-0002-5463-7395;
Danylenko A. V. PhD, Assistant Professor, ORCID: 0000-0002-0204-6972 (Odesa State Academy of Civil Engineering and Architecture)

У статті представлено результати експериментальних досліджень, спрямованих на встановлення закономірностей впливу механохімічної активації портландцементу з добавкою меленого вапняку (у кількості до 40 %) на термомеханічні характеристики цементного каменю на стадіях тверднення та після його затвердіння.
Встановлено, що актуальним напрямом удосконалення властивостей змішаного в'яжучого (портландцемент + мелений вапняк) є його активація в присутності суперпластифікуючої добавки типу «Релаксол-Супер ПК» у кількості до 1 % від маси в'яжучого. Використання високошвидкісного активатора (n = 1800 об/хв) забезпечує інтенсифікацію процесів гідратації цементу, стабілізацію необхідної рухливості цементно-вапнякової композиції при зниженій витраті води замішування (порівняно з немеханічно активованою системою), а також підвищує інтенсивність екзотермічного розігріву.
Експериментальні дані дали змогу кількісно оцінити вплив тривалості механохімічної активації та вмісту суперпластифікатора на водовміст цементно-вапнякової композиції. Виявлено домінуючий вплив суперпластифікуючої добавки та активації суміші протягом 180 секунд на зменшення водо-твердого відношення системи, що зумовлює поліпшення її фізико-механічних властивостей.
Встановлено, що введення меленого вапняку до складу цементно-водної композиції спричиняє збільшення водо-твердого відношення при збереженні заданої рухливості. Зокрема, заміна 20 % портландцементу меленим вапняком призводить до зростання В/Т з 0,38 до 0,41 (приблизно на 8 %), а при збільшенні вмісту вапняку до 40 % цей показник

підвищується до 0,42 (приблизно на 11 %).
Ідентифіковано, що механохімічна активація цементно-вапнякової композиції зумовлює інтенсифікацію тепловиділення, зокрема підвищення швидкості та максимальної температури екзотермічного розігріву. Для композицій на основі неактивованого портландцементу індукційний період триває 3–3,5 години від моменту замішування, тоді як для механічно активованого цементу цей період скорочується до 2 годин.
Визначено, що механохімічна активація цементно-вапнякових систем сприяє зростанню міцності цементного каменю у тридобовому віці на 30–35 %, а при використанні суперпластифікатора підвищення міцності сягає близько 70 %. Отримані результати підтверджують ефективність комбінованої дії механічної активації та хімічної модифікації у формуванні структури цементного каменю з підвищеними експлуатаційними характеристиками.

The article presents the results of experimental studies aimed at establishing the regularities of the influence of mechanochemical activation of Portland cement with the addition of ground limestone (up to 40 %) on the thermo-mechanical properties of cement stone during hardening and after setting.
It has been determined that an effective approach to improving the properties of blended binders (Portland cement + ground limestone) is their activation in the presence of a superplasticizing admixture of the "Relaxol-Super PC" type in an amount of up to 1 % by weight of the binder. The use of a high-speed activator (n = 1800 rpm) ensures the intensification of cement hydration processes, stabilization of the required workability of the cement-limestone mixture at a lower water demand (compared to non-activated compositions), and enhances the exothermic heat release during hardening.
The experimental data made it possible to quantitatively assess the influence of the mechanochemical activation duration and the amount of superplasticizer on the water content of the cement-limestone system. A dominant effect of the superplasticizer and activation for 180 seconds on the reduction of the water-to-solid ratio was identified, resulting in improved physical and mechanical properties of the composite.
It was established that the introduction of ground limestone into the cement–water system leads to an increase in the water-to-solid ratio while maintaining the required workability. In particular, replacing 20 % of Portland cement with ground limestone increases the W/S ratio from 0,38 to 0,41 (approximately by 8 %), while a 40% limestone replacement raises this ratio to 0,42 (by about 11 %).
Mechanochemical activation of the cement–limestone composition was found to intensify heat release processes, increasing both the rate of temperature rise and the maximum temperature of the exothermic reaction. For non-activated Portland cement compositions, the induction period of heat release lasts about

3–3,5 hours from the moment of mixing, whereas for mechanochemically activated cement it does not exceed 2 hours.
It was determined that mechanochemical activation of cement–limestone systems increases the compressive strength of cement stone at the age of 3 days by 30…35 %, and in the presence of a superplasticizer — by up to 70 %. The obtained results confirm the efficiency of the combined effect of mechanical activation and chemical modification in forming a cement stone structure with enhanced performance characteristics.

Ключові слова: механоактивація, суперпластифікатор, мелений вапняк, екзотермія, водо-тверде відношення.
mechanical activation, superplasticizer, ground limestone, exotherm, water-hardness ratio.

Problem statement. The article considers issues related to the influence of mechanochemical activation of Portland cement with the addition of ground limestone on the thermo-mechanical characteristics of hardening cement stone. Such cements are obtained both by joint grinding of cement with the addition of limestone and by thorough mixing of Portland cement with ground limestone. It is known that both mechanical activation and the presence of superplasticizing additives have an enhancing effect on the rate of Portland cement hydration. Therefore, in our opinion, issues related to the consideration of the joint influence of mechanochemical activation of Portland cement, the addition of ground limestone and the superplasticizing additive on the exotherm and strength of cement stone are relevant.

Analysis of recent research and publications. One of the effective ways to reduce the cost of Portland cement is to introduce finely ground mineral additives into its composition [1-4]. The use of limestone as a mineral additive to Portland cements is gaining momentum, the number of which is continuously growing and, at present, the volume of such cements exceeds the volume of Portland cements of the PC I type. Along with the economic effect and economic efficiency, the use of limestone ensures the production of cements with improved technological properties[5]. The positive effect of introducing mineral additives into Portland cement is significantly enhanced by mechanochemical activation of the binder in turbulent flows[6-8]. The use of mechanochemical activation contributes to solving a set of issues related to both improving the homogeneity of the freshly prepared mixture and increasing the strength of the cement stone [9-12]. The use of high-speed hydrodynamic mixing for cement activation in combination with optimal amounts of mineral fillers and effective superplasticizer additives provides, along with plasticization of the mixture, a sharp acceleration of cement hydration, which allows for the elimination of both the use of rapid-setting cements and heat treatment.

Research objective. The purpose of the proposed work is to determine the combined effect of mechanical activation, the concentration of ground limestone and superplasticizing additive in the binder to water-hardness ratio (with a stable spread of the cement-limestone composition on the Suttord device in the range of 120±5 mm), exothermic heating and compressive strength of cement stone at a 3-day age.

Research methods. The activation of the tested mixture was carried out in a high-speed mixer for 90 and 180 seconds. For control, mixtures identical in mobility that were not subject to mechanical activation were used. The determination of exothermic heating was carried out by fixing the temperature of the tested composition in a thermos, which is a glass flask with double walls, between which a vacuum was created. The temperature of the hardening mixture was fixed every hour until the next heating indicator did not change, or was lower than the previous one. To determine the influence of varied factors (mechanical activation, the amount of ground limestone and the consumption of superplasticizing additive) on the compressive strength, beam samples measuring 4×4×16 cm were made from cement-limestone compositions of a given mobility.

Research results. In experimental studies, Portland cement PC II/A-Sh-500 was used as a binder, which meets the requirements of DSTU B V.2.7-46:2010 "Cements for general construction purposes. Technical conditions". Ground limestone (S=350 m^2/kg) was used as a mineral additive to cement in an amount of 20 and 40 % of the binder mass. To increase the mobility of the mixture, the superplasticizer Relaxol-Super PC was used in an amount of 0,5 and 1 % of the binder mass.

The results are given in Table. 1 experimental data reflect the influence of formulation and technological factors, namely the content of ground limestone in the binder (20±20 %), the concentration of the superplasticizing additive (0,5±0,5 %) and mechanochemical activation for 180 seconds on the water-hardness ratio (W/T) of the cement-containing composition with a spread of the mixture cone in the range of 120±5 mm. Analysis of experimental data indicates that the introduction of ground limestone into Portland cement leads to an increase in the water-hardness ratio of the cement-containing compositions. Thus, ensuring the necessary mobility (d=120 mm of the spread of the cone) of the mixture (after its mechanochemical activation for 180 seconds) using only Portland cement is achieved at a water-cement (further water-hardness) ratio of 0,38. Replacing 20 % of Portland cement with ground limestone leads to an increase in W/T from 0,38 to 0,41, i.e. by almost 8 %. An increase in the content of ground limestone to 40 % causes an increase in the water-hardness ratio to 0,42, i.e. by almost 11 % compared to the binder without the addition of ground limestone. A similar effect of the content of ground limestone on the increase in the water-hardness ratio is also observed for cement-containing compositions activated for 180 seconds with the addition of a superplasticizer. An increase in water content with an increase in the amount of ground limestone is also observed for non-mechanically activated cement-containing compositions. In this case, an increase in the content of ground limestone in the binder causes an increase in the water-hardness ratio from 0,42 (no ground limestone) to 0,45 (40 % ground limestone).

Table 1

Influence of formulation and technological factors on the water-hardness ratio of cement-containing compositions

№ warehouse	Portland cement, %	Ground limestone, %	Relaxol - Super PC, %	V/T	№ warehouse	Portland cement, %	Ground limestone, %	Relaxol - Super PC, %	V/T
1	2	3	4	5	6	7	8	9	10
CONTROL					MECHANOACTIVATION – 180 sec				
1	100	0	0	0,42	10	100	0	0	0,38
2	100	0	0,5	0,36	11	100	0	0,5	0,32
3	100	0	1,0	0,34	12	100	0	1,0	0,31
4	80	20	0	0,44	13	80	20	0	0,41
5	80	20	0,5	0,39	14	80	20	0,5	0,35
6	80	20	1,0	0,35	15	80	20	1,0	0,33
7	60	40	0	0,45	16	60	40	0	0,42
8	60	40	0,5	0,39	17	60	40	0,5	0,36
9	60	40	1,0	0,36	18	60	40	1,0	0,33

As for the influence of mechanochemical activation on the mobility of the mixture, it should be noted that high-speed mixing of the cement-containing composition for 180 seconds allows to obtain the required spread on the Suttord device at reduced values of the water-hardness ratio. Thus, high-speed mixing of the cement-containing composition (composition No. 10, Table 1) ensures the spread of the mixture (120±5 mm) at W/T = 0,38. A similar spread (120±5 mm) for the cement-containing composition of the given composition, but which was not subject to mechanical activation (Ncomposition-1, Table 1) is ensured at an increased (by 10,5 %) mixing water consumption.

Of the above factors of influence (content of ground limestone, mechanochemical activation, amount of superplasticizer) the greatest influence on the water content of the cement-limestone composition is exerted by the superplasticizer Relaxol-Super PC. An increase in its amount from 0 to 1,0 % causes a decrease in water content by an average of 23…27 %.

The influence of the listed factors on the kinetics of the hydration processes is confirmed by data on exothermic heating of activated cement-water compositions with the addition of ground limestone in the amount of 20 %, Table 2.

Table 2

Exothermic heating of cement-containing compositions

№	Ground limestone content in the binder, %	Concentration of Relaxol-Super PC, %	Binder activation time, sec	Initial temperature of the composition, ºC	Exothermic heating, ºC, in, 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	16
1	0	0	0	25	25,0	25,0	25,2	26,0	30,0	37,5	50,1	60,3	61,6	60,0	59,7
2	0	0	180	25	25,0	26,9	30,0	40,2	51,8	62,0	68,1	67,8	67,4	66,3	64,9
3	0	1	0	25	25,0	25,8	27,0	31,2	37,0	42,1	54,0	71,2	76,9	76,1	74,0
4	0	1	180	25	25,1	25,9	28,7	34,1	42,0	52,6	71,9	84,1	83,7	82,3	79,9

5	20	0	0	25	25,0	25,0	25,2	25,2	29,0	32,5	37,4	42,5	48,8	52,5	50,4
6	20	0	180	25	25,0	26,0	28,6	36,1	42,0	49,8	55,1	59,0	58,6	58,0	57,4
7	20	1	0	25	25,0	25,1	26,0	29,5	34,5	40,4	46,2	50,6	59,0	65,2	64,8
8	20	1	180	25	25,0	25,2	27,0	29,8	40,0	50,0	62,1	70,0	75,1	74,8	74,1

A graphical representation of the influence of mechanochemical activation on the exothermic heating of cement-mixing compositions is shown in Fig. 1.

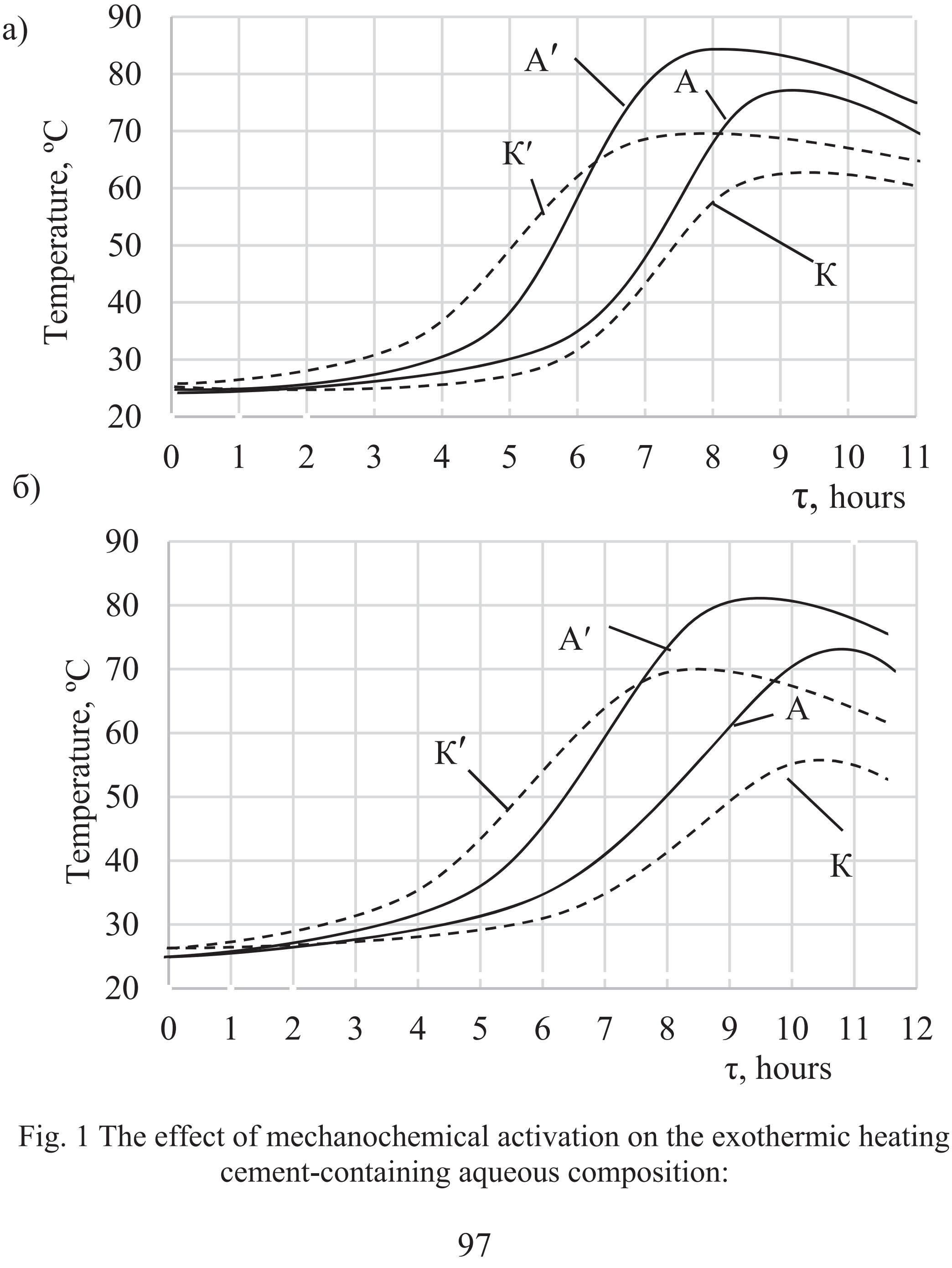

Fig. 1 The effect of mechanochemical activation on the exothermic heating of the cement-containing aqueous composition:

a) – cement-water composition without the addition of ground limestone;
b) – cement-water composition with the addition of 20 % ground limestone;
K – control (no mechanical activation, Relaxol-Super PC = 0 %);
A – mechanically activated cement-containing composition, Relaxol-Super PC = 0 %);
K' – control (no mechanical activation, Relaxol-Super PC = 1 %);
A' – mechanically activated cement-containing composition, Relaxol-Super PC = 1 %);

The experimental data obtained indicate the presence of an induction period of exothermic heating of the cement-water composition both on Portland cement that was not subject to mechanical activation (this period was approximately 3…3,5 hours from the moment of mixing the binder with water) and on Portland cement that was subject to mechanical activation. In this case, the induction period was no more than 2 hours. After the induction period, a relatively sharp increase in the temperature of the hardening cement-water composition is observed, reaching a maximum heating of 82,5 °C 8 hours after mixing the cement with water. The introduction of 20 % ground limestone into Portland cement affects both the reduced intensity and the reduction of the maximum heating temperature of the composition (75 °C).

The final stage of the study was to determine the influence of mechanochemical activation of the binder, the consumption of ground limestone in it and the concentration of superplasticizer on the compressive strength of cement stone beam specimens. The compositions of the cement-containing compositions and the technology of their manufacture were taken according to those given in Table 1. Analysis of the experimental data given in Table 3 indicates that mechanical activation is a powerful technological influence on the strength characteristics of cement stone.

The positive effect of mechanical activation is observed for all studied compositions of cement-containing aqueous compositions. The role of mechanical activation is especially significant for compositions with a superplasticizing additive. Thus, the introduction of 1% Relaxol - Super PC into the composition of cement-containing compositions contributes to an increase in the strength of cement stone at a 3-day age from 32.1 to 43.0 MPa, i.e. by almost 35%. The combined effect of mechanical activation and a superplasticizing additive ensures an increase in the strength of cement stone from 25.5 MPa (control) to 43.0 MPa, i.e. by almost 70%.

This technological method allows introducing 20% of ground limestone into the composition of Portland cement, while ensuring the same compressive strength of cement stone at a 3-day age as in the case of using non-mechanically activated Portland cement, but without the addition of ground limestone. It should be noted that a similar positive effect of mechanochemical activation is also observed for cement stone on a mixed binder with an addition of 40% ground limestone to Portland cement.

Table 3

Influence of recipe and technological factors on the strength of cement stone (MPa)

№	Mixture activation, sec	Composition of the binder mixture		
		Portland cement – 100 %	Portland cement – 80 %, ground limestone – 20 %	Portland cement – 60 %, ground limestone – 40 %
Superplasticizer content – 0 %				
1	0	25,5	14,9	11,4
2	90	32,6	17,7	12,8
3	180	34,6	19,4	14,2
Superplasticizer content – 0,5 %				
4	0	28,7	16,3	12,7
5	90	38,7	22,1	15,8
6	180	40,1	23,9	18,3
Superplasticizer content – 1 %				
7	0	32,1	18,5	13,1
8	90	40,1	22,9	16,7
9	180	43,0	25,3	18,9

Conclusions:

1. Mechanochemical activation of aqueous cement-containing compositions with the addition of ground limestone causes an increase in both the intensity of exotherm and an increase in the value of its maximum heating.

2. The use of the superplasticizer Relaxol-Super PC in combination with mechanochemical activation provides a decrease in the water content of the cement-limestone composition by an average of 23...27%, which is positively reflected in the increase in the strength of the cement stone.

1. Troian V.V. Dobavky dlia betoniv i budivelnykh rozchyniv. Kyiv. Aspekt-Polihraf. 2010.228s.

2. Runova R.F., Nosovskyi Yu.L. Tekhnolohiia modyfikovanykh budivelnykh rozchyniv. K: KNUBA, 2007.256s.

3. Tokarchuk V.V., Sokoltsov V.Iu, Sviderkyi V.A. Osoblyvosti tverdnenn kompozytsiinykh tsementiv z sylikatnymy dobavkamy riznoho pokhodzhennia. Skhidno-Yevropeiskyi zhurnal peredovykh tekhnolohii. 2015. №3/11(75).S.9-14.

4. Vplyv aktyvnykh mineralnykh dodatkiv na vlastyvosti kompozytsiinykh tsementiv /Kh.S. Sobol, T.S. Markiv, M.A. Sanytskyi, H.V. Kohuch //Visnyk Natsionalnoho universytetu «Lvivska politekhnika». – «Khimiia ta khimichna tekhnolohiia». – 2003.№755. S.274-278.

5. Sanytskyi M.A., Kropyvnytska T.P., Heviuk U.M. Shvydkotverdnuchi klinker – efektyvni tsementy ta betony: Monohrafiia – Lviv: Vyd-vo TOV «Prostir –M», 2021.206s.

6. Pirohov D.O., Barabash I.V. Vplyv rezhymu aktyvatsii na vlastyvosti tsementu, tsementnoho tista ta kameniu na yoho osnovi./Zbirnyk tez mizhnarodnoi n/t konferentsii « Strukturoutvorennia ta ruinuvannia kompozytsiinykh budivelnykh materialiv ta konstruktsii». Odesa: ODABA, 2023.S.109-110.

7. Sanytskyi M.A, Modyfikovani kompozytsiini tsementy /M.A.Sanytskyi, Kh.S.Sobol, T.Ie.Markiv //Lviv: Vyd-vo Lviv.politekhniky. – 2010 – 132 s.

8. Vplyv aktyvnykh mineralnykh dodatkiv na vlastyvosti kompozytsiinykh tsementiv /Kh.S. Sobol, T.S. Markiv, M.A. Sanytskyi, H.V. Kohuch //Visnyk Natsionalnoho universytetu «Lvivska politekhnika». – «Khimiia ta khimichna tekhnolohiia». – 2003.№755. S.274-278.

9. Dvorkin L.I. Zhytkovskyi V.V., Marchuk V.V. ta in.. Efektyvni tekhnolohii betoniv ta rozchyniv iz zastosuvanniam tekhnohennoi syrovyny /L.I Dvorkin, V.V. Zhytkovskyi, V.V. Marchuk, Yu.Stasiuk, M.M. Skrypnyk /monohrafiia. Rivne: NUVHP.2017.424s.

10. Sanytskyi M.A, Modyfikovani kompozytsiini tsementy /M.A.Sanytskyi, Kh.S.Sobol, T.Ie.Markiv //Lviv: Vyd-vo Lviv.politekhniky. – 2010 – 132 s.

11. Bashynskyi O.I.,Peleshko M.Z.,Berezhanskyi T.H.Vibroaktyvovani portlandtsementy ta yikh mitsnist za riznykh temperaturnykh rezhymakh/ Zbirnyk naukovykh prats LDU BZhD. Pozhezhna bezpeka. №21. 2012. S.28-32. {

12. Pushkarova K.K., Zaichenko M.M., Pluhin A.A. ta in. Enerhozberihaiuchi mineralni viazhuchi rechovyny ta kompozytsiini budivelni materialy na yikh osnovi: monohrafiia. Kyiv: Zadruha.2014.272s.