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Article

Production of white cement by low-temperature firing

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https://journals.uran.ua/tarp/article/download/290427/284132/670970.
doi:10.15587/2706-5448.2023.290427.

14. Felgenhauer, M., Hamacher, T. (2015). State-of-the-art of commercial electrolyzers and on-site hydrogen generation for logistic vehicles in South Carolina. *International Journal of Hydrogen Energy, 40 (5)*, 2084–2090. doi: https://doi.org/10.1016/j.ijhydene.2014.12.043
15. Krivtcova, V. I., Levterov, A. A., Grushko, A. I. (2006). Analiz pozharovzryvobezopasnosti sistem khraneniia i podachi vodoroda na osnove reaktcii samorasprostraniaiushchegosia vysokotemperaturnogo sinteza intermetallidov. *Problemi nadzvichainikh situatcii, 3,* 145–151.
16. Vasylkovskyi, O. M., Leshchenko, S. M., Vasylkovska, K. V., Petrenko, D. I. (2016). *Pidruchnyk doslidnyka.* Kirovohrad, 204.

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PRODUCTION OF WHITE CEMENT BY LOW-TEMPERATURE FIRING

The object of research was silicate systems based on $CaO–SiO_2–Al_2O_3$ oxides for the production of white cement under the condition of reducing the maximum firing temperature and energy intensity of the products. A complex of raw materials of different genesis was chosen for the study – chalk, pyloquartz, aluminum hydroxide. The criteria for the selection of raw materials were increased reactivity during firing and minimization of the content of colored oxides. During the research, methods of physico-chemical analysis of silicates and standardized testing of properties were comprehensively applied. Determination of the rational compositions of the raw material mixture was carried out using the created computer program «RomanCem». Based on the analysis of the calculation results, a significant value of the quantitative ratio of aluminum-silica-containing components Ca/Cp was determined. It was established that in the interval of the quantitative ratio Ca/Cp from 0.4 to 0.6, the silica modulus of the binder changes in an inversely proportional dependence within n=3.8–2.5 at a low content of colored iron oxides at the level of C=0.14–0.17 %. The compositions of the raw material mixture based on chalk with the use of an aluminum-silica-containing complex of aluminum hydroxide-powder quartz were determined, which allow, at the maximum firing temperature of 1100–1200 °C, to obtain a mineral binder that exceeds natural or Roman cement in terms of strength (21–27 MPa versus 10–15 MPa) and whiteness (80–85 % versus 55–60 %). Peculiarities of phase transformations in the material during low-temperature firing as a factor of structure and properties are noted. The development and practical use of white cement, obtained by reducing the maximum firing temperature and, accordingly, specific fuel consumption, reveals additional reserves for the production of mineral binders, contributes to the comprehensive solution of issues of resource conservation and production technology of silicate building materials.

Keywords: *white cement, raw material mixture, low-temperature firing, phase composition, silica-containing component, colored oxides.*

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1. Introduction

The production of the most common mineral binder, Portland cement, is characterized by significant energy costs during high-temperature firing (1400–1500 °C) of clinker and its grinding with additives to a highly dispersed state [1–3].

To a large extent, this applies to the technology of white cement production, where special requirements regarding the chemical composition of raw materials with the minimization of the content of colored oxides are added to the high energy intensity specified for Portland cement [4, 5].

Modern resource conservation requirements increase the relevance of the production of hydraulic mineral binders of low-temperature firing (≤1200 °C) such as natural cement [6–8] or Roman cement [9–11], which can become a substitute for more energy-intensive and expensive Portland cement in a number of construction works (Fig. 1).

The production of white hydraulic mineral binder under low-temperature firing conditions requires the development of new compositions of raw material mixtures, the chemical composition of which corresponds to the system of $CaO–SiO_2–Al_2O_3$ oxides [12]. At the same time, a high degree of dispersion and, accordingly, the free energy of the particles of the selected components can become a factor in increasing the reactivity during the firing of the starting mixtures.

Fig. 1. White cement in the architecture of Kyiv

Solving such a task is connected with the search for suitable varieties of aluminum- and silica-containing raw materials, determination of the rational ratio of the components of the mixture, analysis of the features of phase formation and properties of the material, which became *the aim of the presented work.*

2. Materials and Methods

The selection of research objects in this work was carried out in accordance with the main aim – the synthesis of a mineral binding material of low-temperature firing of the Roman cement type with increased strength and whiteness. According to this, the raw materials must have:

– increased reactivity, ensuring the intensification of physical and chemical reactions in the silicate system during firing with a decrease in the maximum temperature;

– the minimum content of colored oxides to increase the degree of whiteness of the final product.

For the production of the raw material mixture, the following was used:

– chalk from the Zdolbuniv deposit of the Rivne region, which is industrially used by PJSC «Volyn-Cement»;

– aluminum hydroxide of PJSC Mykolaiv Alumina Plant;

– pyloquartz of PJSC «Novoselivskyi GZK» of Kharkiv region.

According to the chemical composition, among the studied raw materials, the sample of Zdolbuniv chalk is characterized by a high content of CaO, the sample of aluminum hydroxide is characterized by the largest amount of aluminum oxide, and the sample of pyloquartz is characterized by the highest content of silica (Table 1).

The raw materials were prepared by dosing the components by weight, mixing and homogenizing in a ball mill, firing and grinding the final product according to the modern dry method of cement production.

The samples were fired for 15 hours at a maximum temperature of 1100 °C with a holding time of 1.5 hours. All samples of the mixtures compared were fired simultaneously and together to exclude differences in the degree of heat treatment. The properties of the binding material were determined according to standardized methods.

The methods of physical and chemical analysis of silicate raw materials and testing the properties of binders included:

– determination of the chemical composition according to current standards;

– X-ray phase analysis of powder preparations using DRON-3M and DRON-4-07 diffractometers.

Analysis of the mineralogical composition of the studied raw materials showed:

– the main rock-forming mineral of the Zdolbuniv Chalk is calcite (97.6 wt. %) with admixtures of dolomite (1.2 wt. %), quartz and kaolinite – 0.5 and 0.6 wt. %, respectively;

– aluminum hydroxide is characterized by the presence of hydrargillite (gibbsite), diaspore, boehmite with a minor admixture of ilmenite (Fig. 2);

– the main rock-forming mineral of pyloquartz is crystalline β-quartz.

Table 1

Chemical composition of raw materials

Sample name	Content of oxides, wt. %									
	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	SO_3	Na_2O	K_2O	LOI
chalk	0.77	0.25	0.13	–	55.0	0.25	0.08	–	–	43.49
aluminum hydroxide	–	65.0	–	–	–	–	–	–	–	35.0
pyloquartz	99.66	0.16	0.06	–	–	–	–	–	–	0.12

Note: LOI – Loss on Ignition

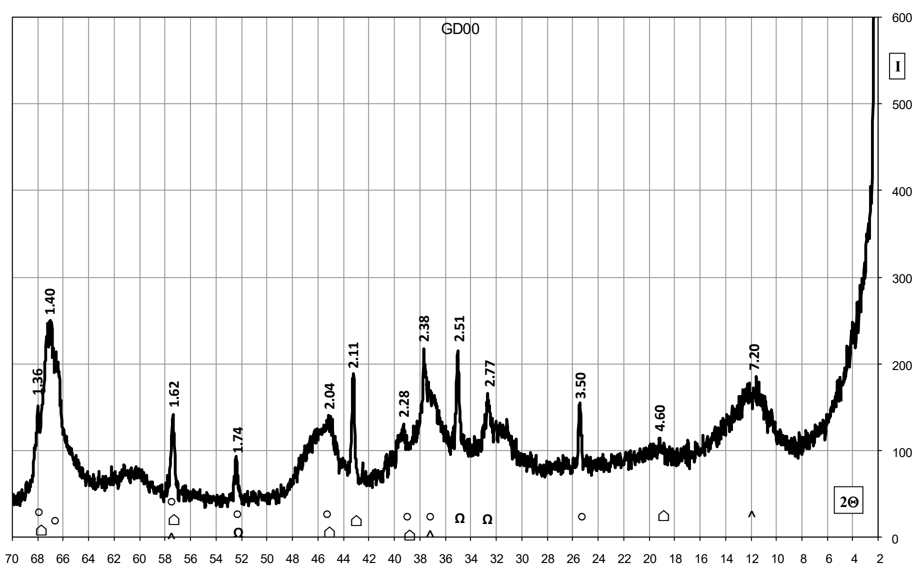

Fig. 2. X-ray diffraction of pattern of aluminum hydroxide GD-00:
○ – hydrargillite (gibbsite), ⌂ – diaspore, Ω – ilmenite, ∧ – boehmite

In the investigated silicate system, the increased reactivity in physicochemical processes during the firing of mixtures in the case of calcium and aluminum oxides is caused by their formation during the destruction of calcite and aluminum hydroxide lattices, and in the case of silicon dioxide, by the fine dispersion of pyloquartz.

3. Results and Discussion

3.1. Analysis of raw mixtures. The composition of the initial 3-component raw mixtures based on the chalk-aluminum hydroxide-powder quartz system was determined according to the known recommendations for low-temperature firing cement technology in the range of values of the hydraulic modulus *HM*=1.1–1.7 using the created program «RomanCem» for computer calculations [13].

The composition of the mineral binding low-temperature firing of the romance cement type is calculated according to the given value of the hydraulic modulus *HM*, which is characterized by the ratio between the most important oxides according to the formula:

$$HM=\frac{CaO}{SiO_2+Al_2O_3+Fe_2O_3}.$$

The principle of solving the problem based on the software is reduced to the following:

1. Data on the chemical composition of probable raw components are entered.
2. The value of the hydraulic module *HM* is set.
3. According to the accepted calculation formula, all combinations of components are determined that provide the specified values of *HM* and correspond to the silica modulus values recommended for cements.

The accuracy of the obtained results depends solely on the error value of the initial data entered into the PC, that is, on the accuracy of determining the chemical composition of raw materials.

The developed «RomanCem» program has been debugged and is used for quantitative determination of the composition of raw mixtures and analysis of the characteristics of mineral binders. At the same time, the operational speed of calculations allows obtaining a significant amount of analytical information.

On the basis of computer calculations, it was established that the possible composition and characteristics of the studied silicate system significantly changes in the specified range of *HM* values, while the significant role of the quantitative ratio of aluminum-silica-containing components is determined.

It was determined that in the interval of the quantitative ratio of the content of aluminum hydroxide and pulverized quartz *Ca/Cp* from 0.4 to 0.6, the silica modulus of the binder changes in an inversely proportional dependence within n=3.8–2.5 (Fig. 3).

From the point of view of the purpose of this study, it is important that in the indicated ranges of *HM* and *Ca/Cp* values, the compositions of raw mixtures are characterized by a low level of the content of colored iron oxides C=0.14–0.17 %.

Regarding the issues of industrial ecology, there is interest in the possibility of reducing the content of the amount of the carbonate component – chalk in the starting mixtures, with a corresponding reduction in CO_2 emissions into the atmosphere (Fig. 4).

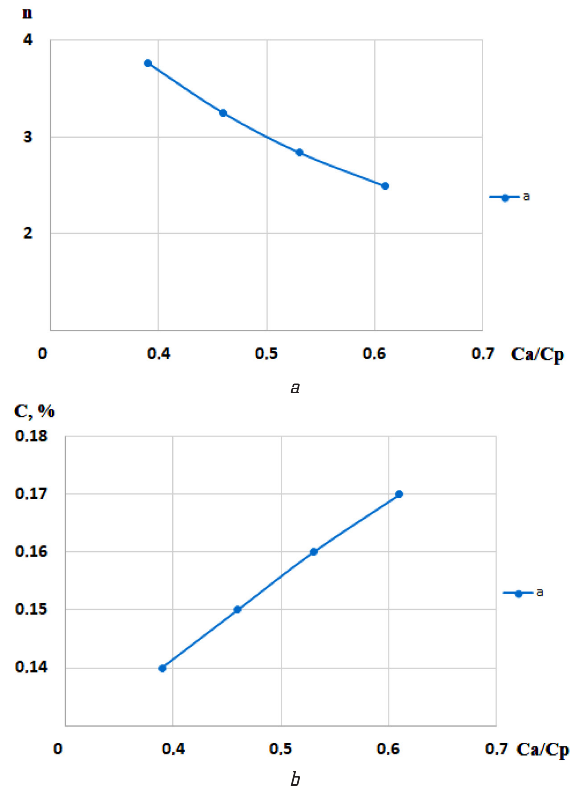

Fig. 3. Dependence of the silica modulus (n) of the binder (a) and of the content (C) of colored oxides (b) from the quantitative ratio of hydrate of aluminium oxide and pyloquartz (*Ca/Cp*) in the chalk-based system

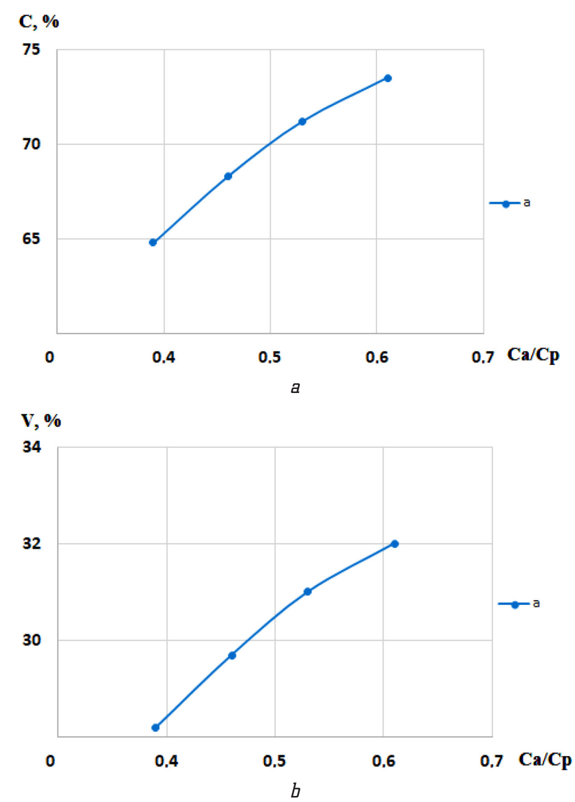

Fig. 4. Dependence of the content (C) of chalk (a) and emissions (V) of CO_2 (b) on the quantitative ratio of aluminum hydroxide and pyloquartz (*Ca/Cp*)

Mineral binders selected on the basis of the analysis of the composition of raw materials and computer calculations for further research are characterized by differences in the

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quantitative ratio of the components of the initial mixture and the numbers of hydraulic and silica modules (Table 2).

It is obvious that the K7 mixture with $Ca/Cp=0.4$ differs from K9 with $Ca/Cp=0.6$ in terms of chemical composition: the content and quantitative ratio of oxides: $SiO_2:Al_2O_3=3.8$ versus 2.5, $CaO:SiO_2=1.4$ versus 2.4, $CaO:Al_2O_3=5.3$ versus 6.0 with a low content of iron oxides – 0.10–0.11 % (Table 3).

Table 2

Compositions of raw mixtures

Mixture code	Content of components, wt. %		
	chalk	aluminum hydroxide	pyloquartz
K7	65.0	10.0	25.0
K9	73.5	10.0	16.5

Table 3

Chemical composition of raw mixtures

Mixture code	Content of oxides, wt. %						
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	LOI
K7	25.62	6.70	0.10	35.66	0.16	0.05	32.95
K9	16.99	6.71	0.11	40.45	0.18	0.06	35.50

Note: LOI – Loss on Ignition

indicate differences in the influence of the composition and degree of firing of the starting mixtures on the indicators of the properties of the binder material (Table 4). Thus, according to the classification of DSTU B V.27-91-99 [14], according to the speed of hardening, the binder from K7 and K9 mixtures when fired at a maximum temperature of 1100 °C belongs to the group of ultra-fast hardening (starting time no later than 15 min.), which is considered characteristic of expanding and tensioning cement.

At the same time, sample K7 differs from K9 in the slowing down of the hardening process, which is associated with a higher ratio of the quantitative content of pyloquartz and aluminum hydroxide S_{qd}/S_{ah} – 2.5 versus 1.6.

According to the specified standard, the binder samples belong to the group of reduced strength (from 10 to 30 MPa per compression), but they significantly exceed the regulated indicators of natural or Roman cement, and in terms of whiteness, they meet the requirements of the white Portland cement standard [15].

The development and practical use of cement obtained by reducing the maximum firing temperature and, accordingly, the specific fuel consumption contributes to a comprehensive solution to the issues of resource conservation and production technology of silicate building materials.

From the point of view of resource conservation and ecology, it is important that the K7 mixture, with a lower content of the natural carbonate component – chalk, is characterized by lower losses during firing – precipitates and, accordingly, lower CO_2 emissions into the atmosphere – 28.2 against 32.0 % for K9.

3.2. Phase transformations and material properties. The results of the X-ray phase analysis obtained in this work indicate certain differences in the physical and chemical transformations during firing of the studied mixtures, which are correlated with the specified chemical composition and depend on the content and ratio of the components (Fig. 5, 6). Thus, after firing to the maximum temperature of 1200 °C with approximately the same qualitative phase composition, sample K7 differs from sample K9:

– more crystalline quartz (3.34; 4.25 Å);

– in relation to calcium aluminosilicates – by greater development of C_2AS helenite (2.86 Å);

– in relation to calcium aluminates – by a greater development of CA (2.51; 4.05 Å) with a significantly smaller amount of mayenite $C_{12}A_7$ (4.92 Å);

– in relation to calcium silicates – by a greater development of C_2S (2.75; 2.77 Å).

The results of testing samples of the binder from the studied mixtures

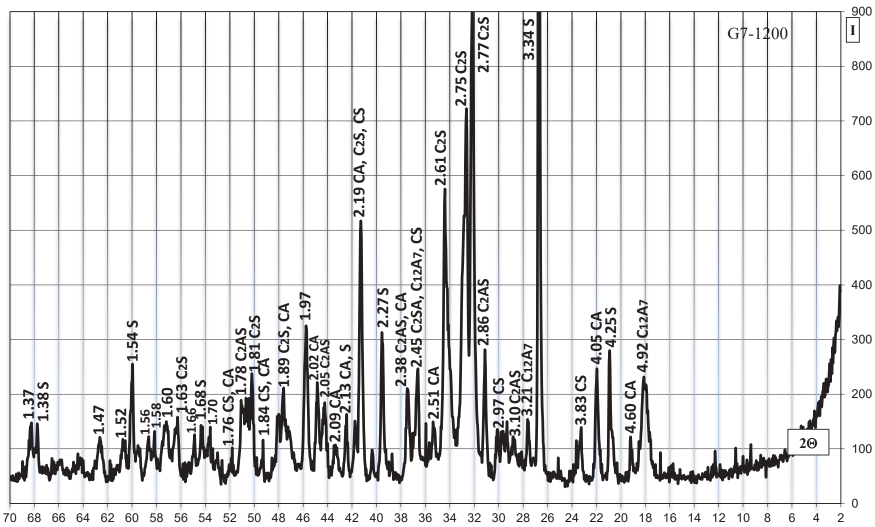

Fig. 5. X-ray diffraction of binder sample K7 after firing at 1200 °C

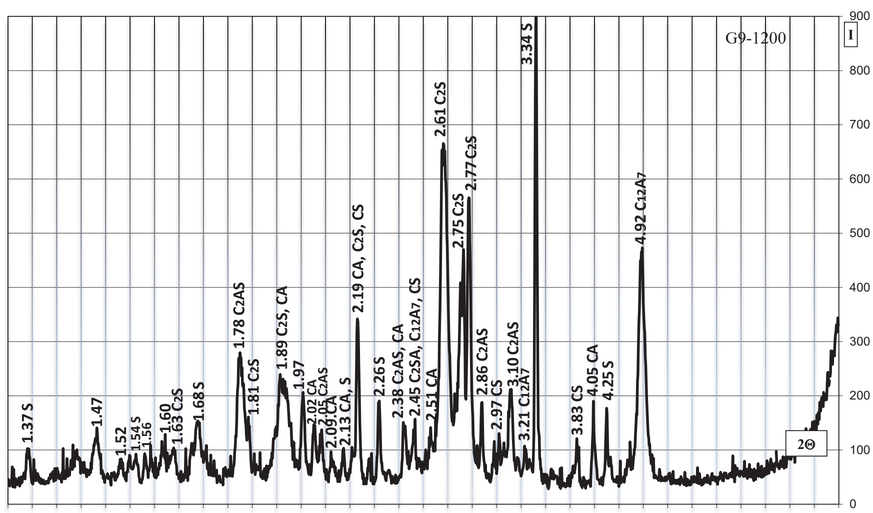

Fig. 6. X-ray diffraction of binder sample K9 after firing at 1200 °C

Table 4

Properties of the binding material

Characteristics		Sample code and firing temperature, °C			
		1100		1200	
		K9	K7	K9	K7
Grinding fineness, residue on sieve 008, wt. %		8	7	8	8
Setting time, min.	Initial	10	15	30	30
	Final	25	90	60	75
Compressive strength after 28 days, MPa		22.0	21.0	27.5	25.3
Whiteness, %		80	80	86	85

The presented results of research and development open up additional reserves for the expansion of the range and development of cement production, taking into account modern energy saving requirements. At the same time, there are no restrictions on the implementation of the results in relation to the existing enterprises for the production of white cement. Implementation of the development at new factories is expedient using the dry method of production.

Prospects for further research are related to the possibility of introducing mineralising additives into the created raw material mixtures as a factor of intensification of sintering and phase formation.

The use of the obtained results in the educational process of higher education is an example of a practical solution to the development of chemical technology of cement while reducing specific fuel consumption, which is especially important in the conditions of martial law.

4. Conclusions

When studying the silicate system chalk-aluminum hydroxide-powder quartz for the production of white cement, it was established that in the range of the quantitative ratio of aluminum and silica-containing components *Ca/Cp* from 0.4 to 0.6 to silica, the modulus of the binder changes in an inversely proportional dependence within n=3.8–2.5 with a low content of colored iron oxides at the level of C=0.14–0.17 %.

The defined compositions of the raw material mixture based on chalk with the use of an aluminum-silica-containing complex of aluminum hydroxide-powder quartz allow at the maximum firing temperature of 1100–1200 °C to obtain a mineral binder that exceeds natural or Roman cement in terms of strength (21–27 MPa vs. 10–15 MPa) and linen (80–85 % vs. 55–60 %).

Conflict of interest

The authors declare that they have no conflict of interest in relation to this research, whether financial, personal, authorship or otherwise, that could affect the research and its results presented in this paper.

Financing

The study was performed without financial support.

Data availability

The manuscript has associated data in a data repository.

Use of artificial intelligence

The authors confirm that they did not use artificial intelligence technologies when creating the current work.

References

1. Duda, W. H. (1988). *Cement Data Book. Vol. 3: Raw Material for Cement Production*. French & European Pubns, 188.
2. Ghosh, S. N. (2003). *Advances in Cement Technology: Chemistry, Manufacture and Testing*. Taylor & Francis, 828.
3. Chatterjee, A. K. (2018). *Cement Production Technology. Principles and Practice*. CRC Press, 439.
4. Moresová, K., Škvára, F. (2001). White cement – Properties, manufacture, prospects. *Ceramics Silikaty, 45 (4)*, 158–163.
5. Dorohan, N. O., Sviderskyy, V. A., Cherniak, L. P. (2018). *Bilyi portlandtsement*. Kyiv: KPI im. Ihoria Sikorskoho, vyd-vo «Politekhnika», 204.
6. Varas, M. J., Alvarez de Buergo, M., Fort, R. (2005). Natural cement as the precursor of Portland cement: Methodology for its identification. *Cement and Concrete Research, 35 (11)*, 2055–2065. doi: https://doi.org/10.1016/j.cemconres.2004.10.045
7. Miras, T., Markopoulos, E. G. (2007). *Natural cements for constructions applications*. XXVII Reunion de la sociedad espaniol de mineralogia.
8. *ASTM C10/C10M-14. Standard Specification for Natural Cement – ASTM International* (2014). West Conshohocken.
9. Hughes, D. C., Jaglin, D., Kozłowski, R., Mucha, D. (2009). Roman cements – Belite cements calcined at low temperature. *Cement and Concrete Research, 39 (2)*, 77–89. doi: https://doi.org/10.1016/j.cemconres.2008.11.010
10. Shelonh, H., Sanytskyi, M. A., Kropyvnytska, T. P., Kotiv, R. M. (2012). Romantsement – v'iazhuche dlia oporiadzhuvalnykh robit v budivnytstvi. *Stroytelnie materyali y yzdelyia, 1 (72)*, 7–12.
11. Sviderskyy, V. A., Cherniak, L. P., Dorogan, N. O., Nudchenko, L. A. (2017). Pidvishchennia pokaznikiv vlastivostei v'iazhuchogo materialu tipu romantcementu. *Stroitelnye materialy i izdeliia, 5-6 (96)*, 20–22.
12. Berezhnoi, A. S., Pytak, Ya. M., Ponomarenko, O. D., Sobol, N. P. (1992). *Fizyko-khimichni systemy tuhoplavkykh, nemetalichnykh i sylikatnykh materialiv*. Kyiv: NMK VO, 172.
13. Sviderskyy, V. A., Cherniak, L. P., Sanhinova, O. V., Dorohan, N. O., Tsybenko, M. Yu. (2017). Prohramne zabezpechennia tekhnolohii nyzkotempe-raturnykh viazhuchykh materialiv. *Budivelni materialy ta vyroby, 1-2 (93)*, 22–24.
14. DSTU B V.2.7-91-99. *V'iazhuchi mineralni*. Klasyfikatsiia. Vved. 01.03.1999 (1999). Kyiv: Derzhbud Ukrainy, 26.
15. DSTU B V.2.7-257:2011. *Portlandtsementy bili*. Tekhnichni umovy. Vved. 01.12.2012 (2012). Kyiv: Minrehion Ukrainy, 20.

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