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RESEARCH OF THE INFLUENCE OF VIBROACTIVATED LIME ON THE HYDRATION OF PORTLAND CEMENT AND ITS HARDENING

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The influence of vibro-activated lime additive on the hydration processes of Portland cement and the nature of changes in the strength of cement stone at different stages of its hardening were studied. It was established that long-term storage of vibro-activated lime in a wet state does not weaken its properties as a modifying additive. The methods of determining the heat release of cement dough during hardening and X-ray phase analysis show that the addition of vibro-activated lime at the initial stages of hardening accelerates the physicochemical processes of hydration of calcium silicates of clinker minerals.

Key words: vibro-activated slaked lime; Portland cement; early strength of cement stone; cement hydration temperature.

Introduction

In the construction materials industry, Portland cement has been and remains the most common binder in the last century and a half, which makes it possible to manufacture concrete products with high mechanical strength. The strength of concrete is determined by the features of the structure of cement stone, the formation of which, in turn, depends on a complex of technological factors and the presence of additives of various composition and nature in the composition of the binder [1–5]. Additives in the cement-water system can have different effects and affect the course of physicochemical hydration processes of clinker minerals and crystallization of the products of this hydration.

In the practice of using cements, the issues of reducing their clinker factor and reducing the total cost of cement per unit of manufactured products are important. The first task is solved by partially replacing clinker in cement warehouses with mineral components, and the second by searching for new technological additives that help increase the mechanical strength of hardened cement stone, which, in turn, makes it possible to reduce the consumption of cement in a cement mortar or concrete mixture. Reducing the cost of clinker in cement warehouses, as well as the total cost of cement, makes it possible to solve two important issues that have arisen before humanity in connection with the rapid progress of scientific and technical progress: reducing the use of energy carriers for burning cement clinker (energy saving) and reducing emissions into the atmosphere carbon dioxide (environmental friendliness). It is known that the cement industry produces more than 6 % of CO_2 emissions from the total annual emissions of this greenhouse gas by the entire industry.

Another important task of construction production is accelerated strengthening of cement stone in the early stages of hardening, which is an important condition for the intensification of construction work. This task is also solved by the introduction of various technological additives, among which additives of activated slaked lime are promising [6–9]. To date, the issue of obtaining activated lime and its use as an additive in the composition of cement mixtures, despite a significant number of scientific works, has not yet been sufficiently studied, which determines the relevance and practical importance of research.

The positive effect of the addition of slaked lime in small quantities on increasing the operational performance of compositions based on Portland cement is indicated in works [10–16]. At the same time, the action mechanism of hydrated lime according to [2, 3] is caused by its acceleration of the hydration of calcium silicates of clinker minerals, as well as the initiation of formation processes of crystallization centres of CH-phases. However, the rate of interaction of the slaked lime additive with the hydration products of clinker minerals is largely restrained by the large size of $Ca(OH)_2$ aggregates after quenching and, as a result, the increase in physical and mechanical parameters of hardened cement stone is relatively small. Therefore, at this stage, research is being conducted in the direction of developing methods of dispersing slaked lime and studying its effect on the processes of hydration and formation of the cement stone structure during the hardening process [10; 12–16].

In works [17–20], the method of obtaining activated slaked lime by the method of mechanical dispersion in a hopper-type vibro activator is given and the influence of the structural features of the unit on the speed and degree of dispersion is described. It has been confirmed that the addition of 1 % of vibro-activated lime based on dry matter significantly increases the mechanical strength of cement samples. At the same time, an increase in the strength of cement beams is noted already at the early stages of hardening of cement samples, which is especially important for modern construction technologies. A vibration method for determining the viscosity of colloidal systems has also been developed and proposed [18, 19], which enables continuous control of numerical values of dynamic viscosity and the process of dispersing slaked lime in general. With the help of modern methods of analysis, it is shown that the effect of a small amount of activated hydrated lime additive is based on its interaction with the hydration products of calcium silicates of clinker minerals and the intensification of the crystallization processes of newly formed calcium hydro silicates. The obtained results generally confirmed the effectiveness of the preliminary vibro-activation of slaked lime for the purpose of its further use as part of cement compositions. Therefore, it is advisable to continue such research in the direction of developing and optimizing the compositions of binders modified with the addition of vibro-activated lime, and in-depth research of its influence on the physicochemical processes of hydration of clinker minerals.

The aim of the study was to study the influence of vibro-activated lime as a modifying additive on the properties of binding compositions.

Materials and research methods

As a binder, Portland cement of general construction purpose was used by CEM I 42,5 PJSC –Ivano-Frankivskcement" (Ukraine). The chemical composition of Portland cement clinker is given in the table 1. Mineralogical composition of CEM I 42.5 % (wt.): C_3S – 61.92; C_2S – 16.86; C_3A – 6.64; C_4AF – 14.58. According to the results of the tests, Portland cement meets the requirements of DSTU B V 2.7-46:2010 regarding grinding depth, hardening time, early and standard strength.

Vibro-activated lime was used as a modifying additive to the cement mixture, which was obtained by mixing hydrated lime of the Lhoist brand (Republic of Poland) with water to achieve a system humidity of 48 % and further vibro-activation in the hopper of the vibro-activator. Vibro activation parameters: the frequency of harmonic circular oscillations of the hopper is 50 Hz, the amplitude of oscillations is 7 mm. Characteristics of the blades in the bunkervibro activator: solid non-perforated vibrating blades fixed at an angle of 86° to the direction of oscillation. The optimal duration of mechanical processing of hydrated lime was 30 minutes.

The chemical composition of hydrated lime is given in Table. 1. The content of free water in hydrated lime is 1.3 %.

Table 1

Chemical composition of materials

Materials	Oxide content, % (wt.)							
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	R_2O	CO_2
Portland cement clinker	21.44	5.22	4.84	66.18	0.95	0.72	0.65	–
Hydrated lime	–	–	–	97.20	0.70	0.40	–	0.40

Physical and mechanical tests of Portland cement and the modified Portland cement system were carried out in accordance with DSTU B V. 2.7-185:2009, DSTU B V. 2.7-187:2009, DSTU EN 196-1:2007.

The study of the phase composition of hydration products of binder systems was carried out using diffractograms obtained on a modernized DRON-3M diffractometer using copper Kα radiation (λ = 1.54185 Å).

Results and discussion

An important characteristic of Portland cement is its strength after 28 days and accelerated strength gain in the early stages of hardening. The study of the influence of vibro-activated lime on the hardening processes of Portland cement was carried out by adding vibro-activated hydrated lime to Portland cement CEM I 42.5 in the amount of 1 % in terms of dry matter with subsequent mechanical mixing. The research was carried out at W/CEM = 0.27, which ensures obtaining a cement dough of normal thickness. The following compositions were prepared for the tests:

– CEM I 42.5 without additives;

– CEM I 42.5 with the addition of lime, vibro-activated immediately before mixing with Portland cement (VALI additive);

– CEM I 42.5 with the addition of vibro-activated lime, which was stored in a wet state (humidity 48 %) in a tightly closed container for 1 year (VALY addition).

The results of determining the compressive strength of cement stone on the basis of the proposed binding compositions at different times of hardening are given in Table 2 and in Fig. 1.

Table 2

The effect of vibro-activated lime on the strength of Portland cement CEM I

Day of congelation	CEM I 42.5	CEM I 42.5with VALI additive		CEM I 42.5 with VALY addition	
	strength, MPa	strength, MPa	increase strength, %	strength, MPa	increase strength, %
1	15.5	21.9	41.3	21.5	38.7
3	32.0	39.7	24.1	39.5	23.4
7	36.8	47.0	27.7	45.4	23.4
14	44.8	54.0	20.5	52.3	16.7
28	55.3	60.2	8.7	58.9	6.5

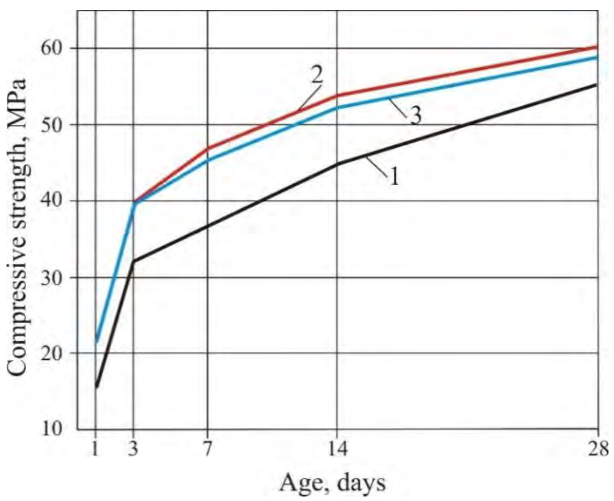

Fig. 1. Effect of addition of vibro-activated lime on compressive strength test samples during hardening under normal conditions: 1 – CEM I 42.5 without additive; 2 – CEM I 42.5 with VALI additive; 3 – CEM I 42.5 with VALY addition

A comparative analysis of the research results showed that the significant shelf life of vibro-activated lime has little effect on its activity – at all stages of hardening, both additives of vibro-activated lime lead to a significant increase in the strength of the binding composition. At the same time, it is worth noting that on the 1st and 3rd days of hardening, the addition of vibro-activated lime, both freshly prepared and aged for 1 year, leads to approximately the same increase in the strength of the binding composition. Thus, the strength of cement stone based on Portland cement without an additive after 1 day of hardening is 15.5 MPa, while the modified binding composition with the VALI addition is 21.9 MPa (increase of 41.3 %), and with the VALY addition, – 21.5 MPa (increase of 38.7 %). A similar effect of additives of vibro-activated lime on the strength of samples is observed on the 3rd day of hardening.

Later, after 7, 14, and 28 days of hardening, a somewhat smaller increase in strength is observed for binder compositions modified with the VALY addition, compared to compositions modified with freshly prepared lime. At the same time, it should be noted that the decrease in growth is relatively insignificant (Table 1). Thus, on the 28th day, for compositions modified with freshly prepared lime, the increase in strength compared to cement stone based on Portland cement without an additive was 8.7 %, while for compositions modified with the addition of lime aged for 1 year, it was 6.5 %.

This nature of the influence of different lime additives over time is obviously since during long-term storage some minor micro coagulation of small $Ca(OH)_2$ aggregates occurs. However, it is worth noting that this process does not significantly affect the reduction of the activity of vibro-activated lime, and this is an important prerequisite for its use as a modifying additive in the composition of cement mixtures, since some time passes from the moment of vibro-activation to the realization and use of the final product.

From a physico-chemical point of view, it is advisable to analyze these regularities considering the hydration processes of clinker minerals. At the initial stages of hardening of Portland cement, the processes of interaction of clinker minerals, mainly C_3S, with water are decisive. Subsequently, the processes of transformation of gel-like hydration products into calcium hydrosilicates and their crystallization reveal a more significant influence on the formation of the structure of cement stone and the increase in strength. Since $Ca(OH)_2$ is characterized by a rather high solubility in water and rapid saturation of the solution with Ca^{2+} ions, which speed up the hydration processes of calcium silicates [3], in the initial stages of hardening, the size of hydrated lime aggregates is of less significant importance, and their influence on the change in strength in the first days after mixing cement with water is less noticeable. Over time, when the influence of the processes of formation of centers of crystallization of calcium hydrosilicates and their growth becomes decisive, the influence of the size of $Ca(OH)_2$ particles becomes more significant.

The effect of $Ca(OH)_2$ (Ca^{2+} ions) on the course of cement hydration (clinker minerals) can be assessed by measuring the amount of heat released from the cement dough at the initial stage of hardening. The results of determining the heat release of cement with and without the addition of vibro-activated lime are presented in Fig. 2.

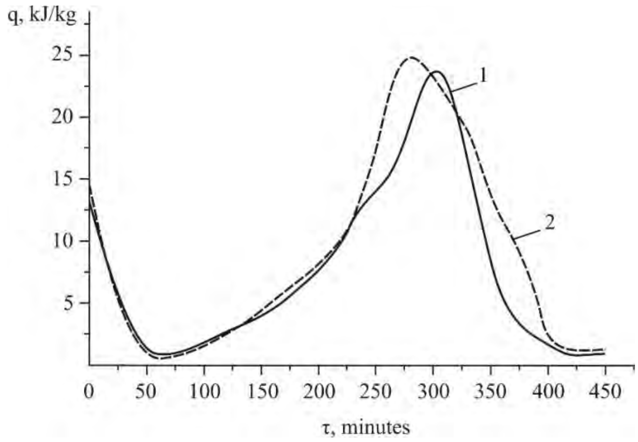

Fig. 2. Heat release of cement dough during the hardening process: 1 – CEM I 42.5 without additives; 2 – CEM I 42.5 with VALI additive

The analysis of the obtained dependencies showed that the course of the heat release process is consistent with the known data of the theory of cement hydration [4, 5]. The given curves (Fig. 2) clearly record all the characteristic periods of exoteric physico-chemical hydration processes: initial sharp heat release, induction, acceleration and deceleration of heat release, and monotonous decay, which is consistent with data [5]. However, at the stage of acceleration of heat release, a significant difference is recorded in the exotherm of cement dough with the addition of vibro-activated lime (Fig. 2, curve 2) and without it (curve 1). Addition of lime for about 30 minutes accelerates the onset of intense heat generation in the post-induction period and causes slightly more heat to be produced. This is a confirmation of the action of the addition of vibro-activated lime as an accelerator of the hydration processes of clinker minerals at the initial stage of hardening and explains the higher strength values of samples based on Portland cement, especially in the early stages of hardening.

The results of determining the strength of samples based on Portland cement and measuring the heat release of the cement dough are fully consistent with the data of the X-ray phase analysis of the test samples (Fig. 3).

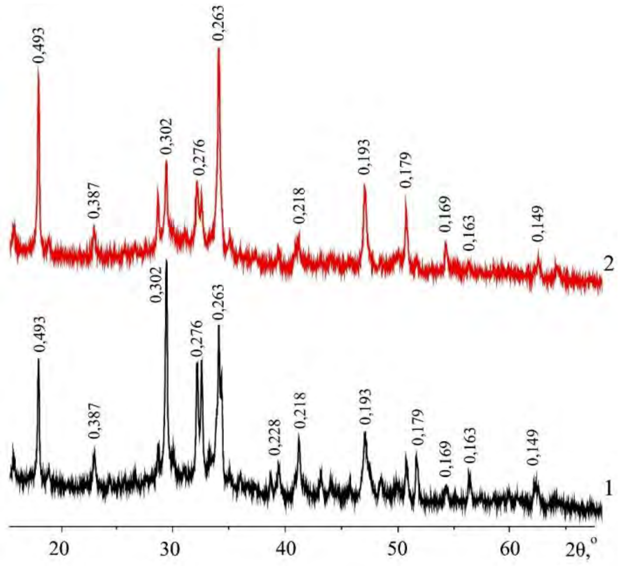

Fig. 3. Diffractograms of stone based on Portland cement on the 3rd day of hardening:
1 – CEM I 42.5 without additives; 2 – CEM I 42.5 with VALI additive

According to X-ray phase analysis data, it can be concluded that in the early stages of cement stone hardening, the presence of even a small amount of calcium hydroxide additive in the cement-water system significantly intensifies the hydration processes of calcium silicates, the amount of which is the maximum of the clinker minerals in the cement composition. Thus, on the diffractogram of cement stone without the addition of lime (Fig. 3, curve 1), the presence of significantly more intense diffraction maxima of non-hydrated alite and belite phases (d/n = 0.302; 0.276; 0.218 nm) is observed compared to the corresponding maxima of the sample with the addition of vibro-activated lime (Fig. 3, curve 2). In addition, the acceleration of the physico-chemical processes of hydration due to the introduction of a small amount of vibro-activated slaked lime additive is evidenced by the diffraction maxima of portlandite (d/n = 0.493; 0.263; 0.193; 0.179 nm), which are significantly more intense for samples of cement stone with the addition of lime. than for a sample based on Portland cement.

Conclusions

The conducted studies established that the storage of vibro-activated lime in a wet state for 1 year does not lead to a significant weakening of its properties as a modifying additive in the composition of binding compositions, which is an important condition for its use in the construction industry. Determining the strength of cement stone at different stages of hardening showed that in the early stages of hardening (up to 3 days), freshly prepared and long-term vibro-activated lime increase the strength of cement stone based on the developed binding compositions to the same extent. The effect of the vibro-activated lime additive on the hydration processes of Portland cement was studied and it was shown that in the early stages after mixing it with water, calcium hydroxide accelerates the interaction of calcium silicates of clinker minerals with water.

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ДОСЛІДЖЕННЯ ВПЛИВУ ВІБРОАКТИВОВАНОГО ВАПНА НА ГІДРАТАЦІЮ ПОРТЛАНДЦЕМЕНТУ ТА ЙОГО ТВЕРДНЕННЯ

Досліджено вплив добавки віброактивованого вапна на процеси гідратації портландцементу та тип зміни міцності цементного каменю на різних етапах його твердіння. Встановлено, що тривале зберігання віброактивованого вапна у вологому стані не призводить до послаблення його властивостей як модифікуючої добавки. Методами визначення тепловиділення цементного тіста під час тверднення та рентгенофазового аналізу показано, що добавка віброактивованого вапна на початкових стадіях тверднення прискорює фізико-хімічні процеси гідратації силікатів кальцію клінкерних мінералів.

Ключові слова: віброактивоване гашене вапно; портландцемент; рання міцність цементного каменю; температура гідратації цементу.