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ТЕХНОЛОГІЯ НЕОРГАНІЧНИХ РЕЧОВИН ТА СИЛІКАТНИХ МАТЕРІАЛІВ

Z. I. Borovets, I. V. Lutsyuk
Lviv Polytechnic National University,
Department of Chemical Technology of Silicate Materials
iryna.v.lutsiuk@lpnu.ua

EFFECT OF SYNTHETIC CALCIUM HYDROSILICATE ON THE HYDRATION OF PORTLAND CEMENT

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The regularities of the synthesis of calcium hydrosilicates of tobermorite composition in the system “amorphous silica – calcium hydroxide – water” were investigated. The effect of calcium hydrosilicates 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 was studied. The methods of determining the heat of hydration of cement dough during hardening and X-ray phase analysis showed that the addition of calcium hydrosilicates at the initial stages of hardening accelerates the physicochemical processes of hydration of clinker minerals.

Key words: calcium hydrosilicates; tobermorite; Portland cement; early strength of cement stone; cement heat of hydration.

Introduction

Modern trends in the construction industry involve the production and use of construction materials and products with improved performance. In particular, it is of great importance to increase the strength of concrete based on Portland cements with an unchanged or lower amount of cement in the concrete mix [1–3]. This makes it possible to simultaneously solve two important problems:

– to reduce cement consumption per unit of product without compromising the physical and mechanical properties of the product and, accordingly, to reduce the cost of products;

– reducing cement consumption, which is based on clinker fired at temperatures of 1450–1500 °C, makes it possible to reduce fuel consumption and, accordingly, CO_2 emissions, which is an important factor in environmental protection [4–8].

One of the most promising ways to increase the strength of cement products is to introduce modifying agents into the mixtures when mixing with water. According to experts, the share of concrete in Ukraine using modifier additives should increase to 50 % or more in the coming years [1, 2, 5, 9].

In general, technological additives can be divided into two large groups: organic and inorganic compounds (substances). Their introduction into the concrete mix in the amount of several tenths of a percent to 1–2 percent makes it possible to increase the strength of the hardened cement stone, its density and water resistance, frost resistance, and corrosion resistance. This is achieved, in particular, by targeted regulation of the cement stone structure by intensifying the processes during its hardening [8, 9].

Among the inorganic additives-modifiers, which are represented by a large nomenclature of various chemical compounds and substances and differ in both chemical composition and mechanism of action, vibro-activated slaked lime is promising [10–13]. Its use as an additive in the amount of 1 % (by dry matter) of the cement weight makes it possible to improve the entire range of physical and mechanical properties of concrete. The mechanism of the modifying effect of the quicklime is its chemical interaction with the hydration products of clinker minerals with the subsequent formation and crystallization of calcium hydrosilicates, which provide high performance of concrete and mortars.

In this direction, it is of considerable scientific and practical interest to study the possibility of preliminary synthesis of calcium hydrosilicates in order to use them as a modifying additive for cement systems. Such an additive should act as crystallization centers for externally introduced clinker minerals, which, during the hydration of silicate clinker minerals (C_2S and C_3S), would help to intensify the processes of calcium hydrosilicates formation and crystallization.

The issue of the effect of calcium hydrosilicates additives on the cement stone hardening process is not fully understood today. Modern requirements for the quality of building materials, as well as the need for their economical and efficient use, necessitate the study of the effect of calcium hydrosilicate additives on the technological and operational properties of cement, which makes this research relevant.

The purpose of the work studying the effect of calcium hydrosilicates of tobermorite composition on the cement stone hardening processes and properties.

Materials and research methods

To obtain the modified binder compositions, Portland cement for general construction purposes CEM II/A-S 42.5 R of PJSC "Ivano-Frankivsk-cement" (Ukraine) was used as a binder. The chemical and mineralogical composition of the Portland cement clinker is given in Table 1, and the physical and mechanical properties of the cement in Table 2.

Table 1

Chemical and mineralogical composition of Portland cement clinker

Oxide content, wt. %							Mineralogical composition, wt. %			
SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	R_2O	C_3S	C_2S	C_3A	C_4AF
23.45	5.37	4.73	64.20	0.92	0.72	0.61	61.19	13.99	6.60	10.13

Table 2

Characteristics of Portland cement CEM II/A-S 42.5 R

No.	Main indicators	Requirements according to the standard EN 197-1:2011	Value
1	Composition and ingredients, additives content, %	slag 6–20	slag 15,0
2	Compressive strength, MPa:		
	2 days	≥ 20.0	29.0
	28 days	42.5–62.5	56.0
3	Setting time, min:		
	initial	≥ 60	150
	finish	no later than 10 hours	250
4	Soundness (expansion), mm	≤ 10	0
5	Standard consistency, %	–	30.2
6	Average steaming activity, MPa	≥ 32.0	37.0
7	Steaming efficiency group	–	I
8	Signs of false setting	no	no

Portland cement clinker is a high-calcium clinker by chemical composition and is classified as a high-alite clinker by mineralogical composition. This determines its high activity (52–54 MPa) and makes it possible to produce Portland cement with high early strength based on it.

For the preparation of the cement-sand mortar, sand from the Zhovkva deposit in Lviv region was used as a fine aggregate, which belongs to the medium group in terms of particle size distribution (particle size distribution 2.24), true density 2.62 g/cm^3, bulk density 1475 kg/m^3, void content 43.7 %, and the content of dusty and clay particles 0.5 %.

An artificially synthesized calcium hydrosilicates of the tobermorite type, SSN, was used as an additive-modifier of the cement system. The synthesis of the additive was carried out by grinding amorphous SiO_2 and calcium hydroxide (slaked lime) in an aqueous medium in a laboratory mill for 5 days. The molar ratio of $CaO : SiO_2 = 1 : 1$. The moisture content of the suspension was 60 %. After the synthesis, the resulting calcium hydrosilicates was dried in a laboratory dryer at a temperature of (110±5) °C.

To determine the physical and mechanical tests of Portland cement and the modified Portland cement system, generally accepted standardized methods were used in accordance with DSTU B V. 2.7-185:2009, DSTU B V. 2.7-187:2009, DSTU EN 196-1:2007.

The phase composition of artificially synthesized calcium hydrosilicates and hydration products of binding systems was studied using diffractograms obtained on a modernized DRON-3M diffractometer using copper Kα radiation ($\lambda = 0.154185$ nm).

Electron microscopic studies were performed using a scanning electron microscope REM-16I (Selmi). To increase the conductivity of the samples, a copper conductive film was applied to their surface by thermal vacuum sputtering. The film thickness was no more than 50 nm. Micrographs were processed using computer morphometry.

Results and discussion

One of the conditions for the production of artificially synthesized calcium hydrosilicates of tobermorite composition is a humid environment, which provides the necessary conditions for the chemical interaction of SiO_2 with $Ca(OH)_2$ to form calcium hydrosilicates. The constant mixing of the mixture in the laboratory mill and the presence of grinding media in it prevents the synthesized tobermorite crystal formations from growing together into large crystal splices and contributes to the production of a finely dispersed final product.

To study the structure formation processes that occur in the $CaO–SiO_2$ system during the synthesis of calcium hydrosilicates, samples were taken daily and the phase composition was determined by X-ray diffraction analysis (Fig. 1).

According to the results obtained, we can assert a gradual interaction between amorphous silica and calcium hydroxide. Thus, after 1 day of synthesis, diffraction maxima of tobermorite ($d/n = 0.308$, 0.281, 0.183 nm) appear on the diffractogram (Fig. 1, curve *a*), the intensity of which increases with further synthesis, and the intensity of $Ca(OH)_2$ maxima ($d/n = 0.492$, 0.263 nm), on the contrary, decreases (Fig. 1, curves *b*, *c*). An increase in the synthesis duration to 5 days leads to the maximum interaction of these components with the formation of only calcium hydrosilicates (Fig. 1, curve *d*), as evidenced by the absence of calcium hydroxide peaks in the diffractograms.

According to electron microscopic studies (Fig. 2), the above synthesis conditions provide a calcium hydrosilicates powder with a grain size of 0.5–2.5 μm with a predominant content of particles of about 1 μm.

The influence of the addition of synthesized calcium hydrosilicates (1 wt. %) on the physical and mechanical properties of Portland cement was studied on test specimens in the form of 20×20×80 mm beams made of cement-sand mortar at a cement: sand ratio of 1 : 2 ($W/C = 0.39$). The results of determining the compressive strength are shown in Fig. 3.

A comparative analysis of the research results showed that the addition of CSH in the amount of 1 wt. % leads to an increase in the compressive strength of the binder composition at all times of its curing. At the same time, an increase in the strength of cement stone is observed already on the 1st day of curing. For example, the strength of a stone based on Portland cement without the additive is 27.3 MPa, while that of the modified binder composition with the addition of CSH is 37.8 MPa ($\Delta R = 38.5$ %). A similar effect of the additive on the relative increase in strength of the samples is observed on days 3, 7, 14, 28 of curing and is 40.2, 37.2, 30.3, and 30.1 %, respectively.

The intensity and completeness of the hydration processes of Portland cement systems in the presence of additives is determined by the peculiarities of the hydration mechanism according to thermokinetic characteristics.

The study of temperature changes during the hydration of Portland cement showed (Fig. 4) that the maximum hydration temperature ($t = 55.5$ ºC) of

Portland cement CEM II/A-S 42.5 R is reached after 10 hours. During the hydration of CEM II/A-S 42.5 R with the addition of calcium hydrosilicates, the hydration processes were accelerated, which is manifested in the shift of the temperature maximum to 9.5 hours.

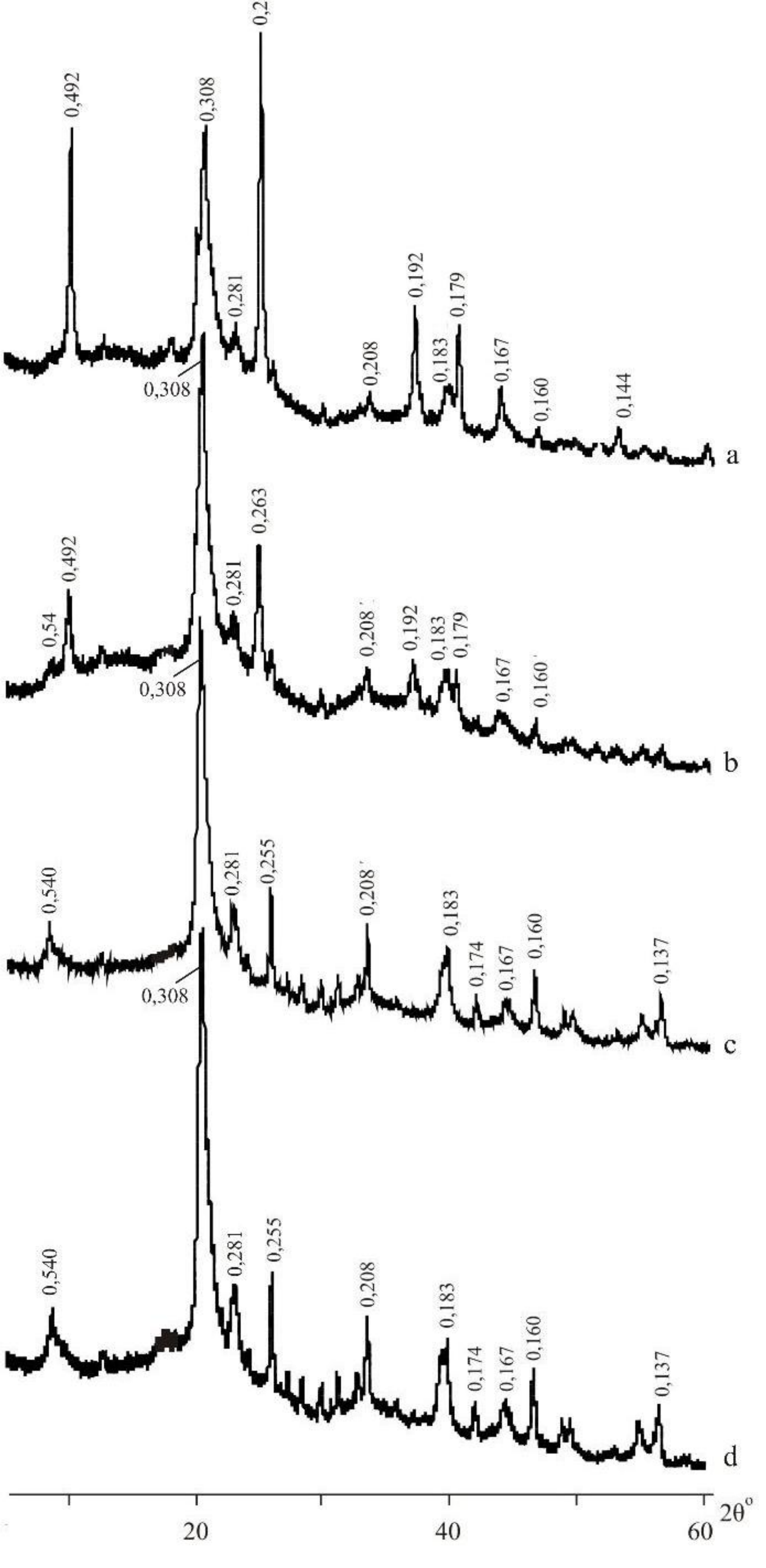

Fig. 1. Diffractograms of the $CaO–SiO_2–H_2O$ *system during synthesis, days: a – 1; b – 2; c – 3; d – 5*

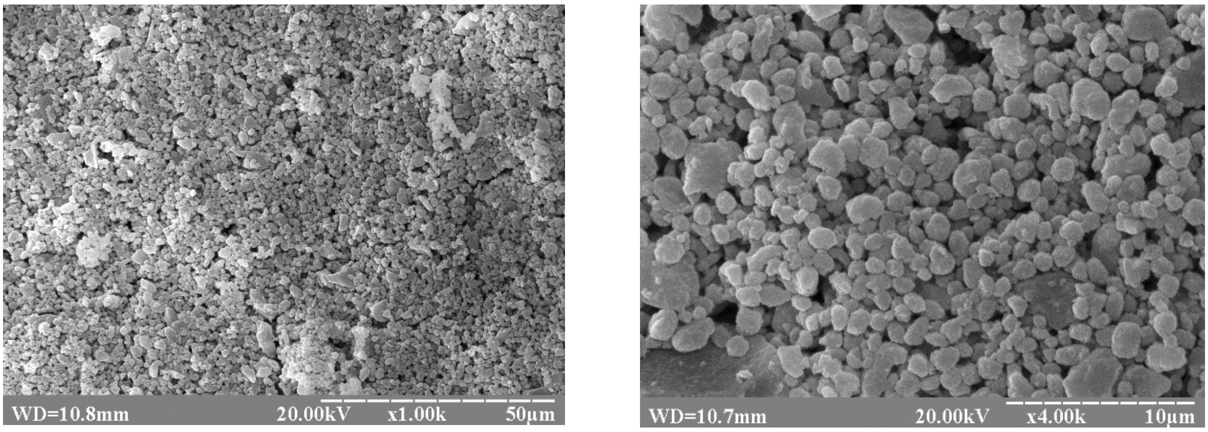

Fig. 2. Electron micrographs of calcium hydrosilicates (after 5 days)

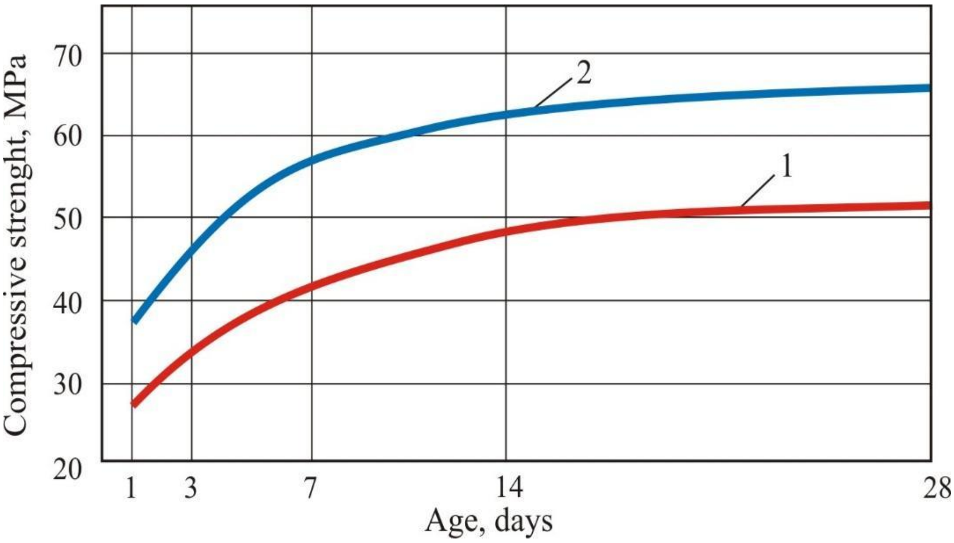

Fig. 3. The effect of calcium hydrosilicate additive on the compressive strength of cement stone:
1 – CEM II/A-S 42.5 R; 2 – CEM II/A-S 42.5 R with CSH additive

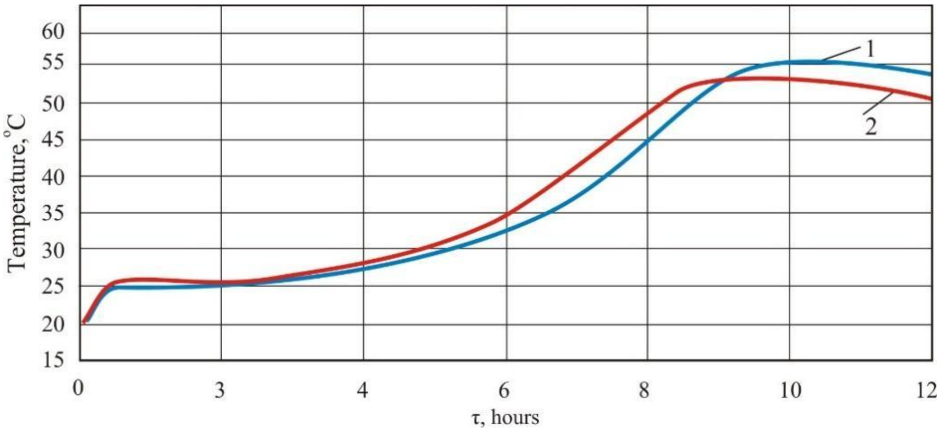

Fig. 4. Temperature change during hydration:
1 – CEM II/A-S 42.5 R; 2 – CEM II/A-S 42.5 R with CSH additive

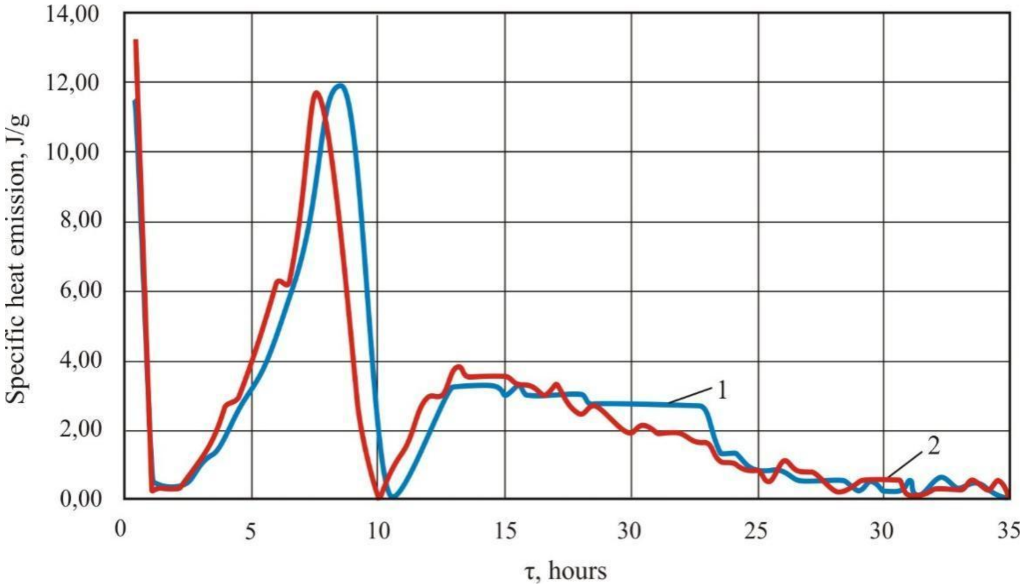

Fig. 5. Changes in heat hydration:
1 – CEM II/A-S 42.5 R; 2 – CEM II/A-S 42.5 R with CSH additive

To establish the mechanism of influence of the CSH additive on the physicochemical processes of Portland cement hydration, we studied the change in the rate of heat of hydration during the first day and a half of hardening (Fig. 5).

As can be seen from the measurement results, one of the mechanisms of action of the CSH additive is the intensification of the chemical interaction of clinker minerals with the mixing water, as evidenced by the nature of the heat of hydration curves. Thus, when CSH was added to the composition (Fig. 5, curve 2), the post-induction period and the period of diffusion-controlled hydration were accelerated by about 30 min. The maximum heat of hydration at the boundary of these periods for Portland cement is observed 8.5 h after the start of mixing with water (heat of hydration value of 11.97 J/g), while for the composition with the addition of CSH, this maximum occurs 7.5 h after mixing with water (heat of hydration value of 11.70 J/g). From a crystallochemical point of view, it can be assumed that the introduction of pre-synthesized calcium hydrosilicates causes a significant acceleration of the processes of formation of crystallization germs and growth of hydrosilicates crystals in the matrix of gel-like hydration products of clinker minerals. This, in turn, leads to an increase in the permeability of water through its thickness to the non-hydrated surface of silicate clinker minerals and, accordingly, an acceleration of their hydration. For Portland cement without additives, crystallization processes are limited by the diffusion rate of silicon oxide, while for Portland cement with artificially synthesized CSH, the processes of nucleation and crystal growth partially occurred at the stage of its synthesis.

Conclusions

The studies have established that in the process of interaction of a mixture of amorphous silica and calcium hydroxide for 5 days, the maximum interaction between its components occurs with the formation of calcium hydrosilicates of tobermorite composition. The grain size of calcium hydrosilicates is in the range of 0.5–2.5 µm with a predominant content of particles of about 1 µm. The introduction of an additive of artificially synthesized calcium hydrosilicates in the amount of 1 wt. % leads to an increase in the strength of cement stone at all curing times by an average of 30–40 %. The nature of the change in thermokinetic parameters shows that the introduction of calcium hydrosilicates activates the process of hydration of clinker minerals and the processes of crystallization of calcium hydrosilicates during the hardening of cement stone.

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З. І. Боровець, І. В. Луцюк
Національний університет “Львівська політехніка”,
кафедра хімічної технології силікатів

ВПЛИВ СИНТЕТИЧНОГО ГІДРОСИЛІКАТУ КАЛЬЦІЮ НА ГІДРАТАЦІЮ ПОРТЛАНДЦЕМЕНТУ

Досліджено закономірності синтезу гідросилікату кальцію тоберморитового складу в системі “аморфний кремнезем – гідроксид кальцію – вода”. Вивчено вплив добавки гідросилікату кальцію на процеси гідратації портландцементу та зміни міцності цементного каменю на різних етапах його тверднення. Методами визначення тепловиділення цементного тіста під час тверднення та рентгенофазового аналізу показано, що добавка гідросилікату кальцію на початкових стадіях тверднення пришвидшує фізико-хімічні процеси гідратації клінкерних мінералів.

Ключові слова: гідросилікат кальцію; тоберморит; портландцемент; рання міцність цементного каменю; тепловиділення цементу.