Temperature Influence on Forced Carbonation Speed of Half-Dry Pressure Lime Stone

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Summary. We have researched the temperature influence on the forced carbonation speed of the half-dry pressure limestone as function of different technological factors. It has been demonstrated that the maximum carbonation speed is reached at a temperature of 293 K. The increase of temperature reduces the carbonation reaction speed. To control the speed of interaction between lime and carbon dioxide in carbonizing reactors, it is necessary to provide low-temperature zones and removal of water produced by the chemical reaction.
Key words: building materials, lime, carbon dioxide, forced carbonation, temperature, half-dry pressure.

INTRODUCTION

The major technical and economical aspect of resource saving and enriching the market with construction goods is development and implementation of new processes of producing construction composites able to harden and acquire the needed properties, for example, by carbon dioxide absorption. Among such materials are those based on lime.

In recent years, scientific research and practice have clearly shown that the contact shaping of the initial structure with use of half-dry pressing is an effective way of controlling the properties of artificial stone materials.

The problem of slow lime carbonation under normal conditions with low CO_2 concentration in the atmosphere can be solved by forced lime carbonation with CO_2 produced in the process of lime burning. Recycling of carbon dioxide obtained in lime burning will enable creation of closed-cycle resource-saving technology of producing carbonized lime-based items, having autonomous operation without extra energy and resource expenses.

Today, the issues of producing half-dry pressure materials based on carbonized lime lack scientific substantiation; there is no comprehensive research of how various technological factors affect carbonation of the lime-cementing agent.

ANALYSIS OF PUBLICATIONS

Lime refers to the group of binders whose hardening is based on the physical phenomena of crystallization that occurs due to mixing-water evaporation, and only then, in process of hardening, carbonization takes its part [Syichov, 1970]. The reaction of lime mixture carbonation is a complex mechanism consisting of carbon dioxide diffusion through the porous structure and its dissolution in the water of the capillary pores, the reaction with calcium hydroxide solution causing deposition of calcium carbonate crystals.

Many scientists assign a secondary role to the period of carbonation hardening of calcareous binders, mainly because of the long time the lime takes for its transition into calcium carbonate under natural conditions. Nevertheless, the reaction of carbonation of calcium hydroxide in solutions is highly important from the technical point of view, since it is a reaction that improves, depending on the binder composition, the mechanical properties of the material and therefore its structure.

The analysis of scientific publications made by many scientists [2, 3, 4, 5, 7, 8, 9, 10, 22] and studies of our own [11, 12, 13, 14, 15, 16] have led to the conclusion that the chemical reaction of lime carbonation depends on many process factors: the moisture and water content of lime paste, carbonization temperature, pressure and concentration of carbon dioxide, lime particle fineness, carbonization time, etc. A number of scientists studying the kinetics of lime carbonation [17, 18] have come to the conclusion that to accelerate the carbonation, the products need some predrying. However, the effect of the elevated

temperature on forced carbonation of the lime binder has not been studied.

AIM OF RESEARCHES AND SPECIFICATION OF THEIR OBJECTIVE

The purpose of this article is to establish the mechanisms of the temperature effect on the carbonation speed of dry-pressed limestone with its forced carbonation under elevated CO_2 concentration and as function of different technological factors.

This purpose has been realized through studies of the carbonation kinetics of dry-pressed lime samples as function of their initial water content, temperature and pressure.

RESULTS AND THEIR ANALYSIS

The carbonation kinetics of lime samples has been investigated by a specially developed static technique in a closed system (Fig. 1).

The operation principle of the plant is based on detection of the lime sample mass change by reacting the sample with carbon dioxide at predetermined CO_2 pressure and temperature. The pressure increase is produced by adjusting the pressure regulator on the CO_2 cylinder. The pressure decrease is created by the vacuum pump. The set pressure in the reactor (carbonization chamber) is supported by the tracking pressure-and-vacuum gage that, when the pressure in the chamber changes, sends a corresponding signal, in case a higher pressure is to be maintained, for opening the electric valve, and, in case the experiment is performed under vacuum, for starting the vacuum pump. The reaction chamber has a water jacket to maintain the temperature desired for the experience. The buffer capacity also has a water jacket and is designed to condense therein water vapor, while CO_2 is sucked through the reactor.
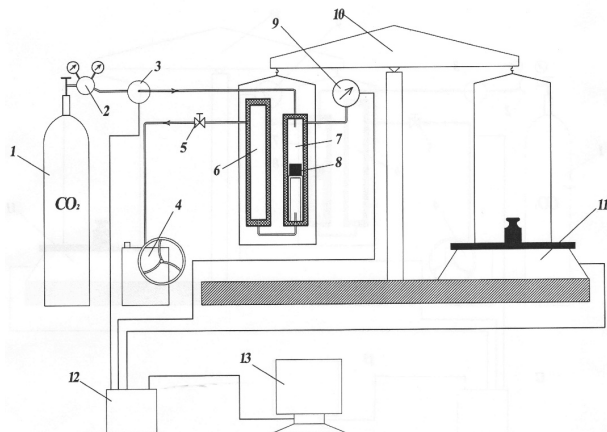

Fig. 1. The apparatus for studying lime carbonation kinetics: 1 – CO2 gas cylinder; 2 – pressure regulator; 3 – electric valve; 4 – vacuum pump; 5 – tap;6 – buffer vessel; 7 – reactor; 8 – sample; 9 – trackingpressure-and-vacuum gage;10 – shoulder scales; 11 – electronic scales; 12 – control unit; 13 – computer

Thus, the system is closed. The mass change is registered by the electronic scale signals produced by a specially developed computer program that is plotting the corresponding graphs of the kinetics of lime paste carbonation.

The speed of conversion of $Ca(OH)_2$ into $CaCO_3$, or the lime carbonation speed, was determined by the ratio of the calcium hydroxide mass to the theoretical mass gain of $Ca(OH)_2$ during its transformation into $CaCO_3$ according to the chemical reaction equation:

$$Ca(OH)_2 + CO_2 + H_2O \rightarrow CaCO_3 + 2H_2O,, \quad (1)$$
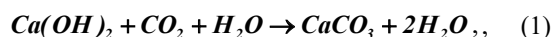
by the formula:

$$\alpha = \frac{m_{Ca(OH)_2} + \Delta m}{1.351 \cdot m_{Ca(OH)_2}} \times 100\% , \quad (2)$$

where:

$m_{Ca(OH)_2}$ is the mass of $Ca(OH)_2$ in the sample, g;

Δm is the system massincrement at any moment of carbonization g,

1.351 is the factor reflecting the change in the mass of the system at 100% of $Ca(OH)_2$ conversion into $CaCO_3$.

The experiments were carried out on dry-pressed lime cylinders30 mm in diameter. To determine the mass and molding pressure values at which it is possible to minimize testing errors, preliminary experiments were made, owing to which we established that the utmost similarity of the results was provided with 20-g samples obtained with a compression force of 10 MPa.

The sample carbonization kinetics was studied in100%-concentration carbon dioxide at a temperature of 293–333 K under low pressure and excessive pressure values, within a CO_2 pressure range of 0.02 MPa to 0.2 MPa and different initial water contents of the lime binder ranging from 1 to 25 mass %. The variable factors were selected on the basis of theoretical investigations of forced lime carbonation [Lyubomirskiy N., 2010; Lyubomirskiy N., 2011].

The data about the temperature effects upon the changes in the degree of lime binder carbonation in compressed samples as function of the initial water content and the CO_2 pressure in the carbonization chamber are shown in Fig. 2.

Fig.2 shows that the carbonization degree indices reduce with the temperature in crease. With an increase of the initial water content of the lime samples and the carbon dioxide pressure, the temperature effect on the **C** value becomes less significant (see Fig.2, III-c and III-d).

With CO_2 pressure in crease, the temperature effect on the carbonization process becomes less expressed; the curves of $Ca(OH)_2$ conversion into $CaCO_3$ at temperatures of 293 K to 313 K and 333 K at initial stages start coinciding, and here, with thepressure increase, this period grows. Thus, for the samples with an initial water content of 10 mass % at 0.02 MPa there is no such period, whereas at a pressure of 0.05 MPa and 0.08 MPa it is 400 s and 1000 s respectively, and at a pressure of 0.1 MPa the curves of the carbonation degree practically coincide throughout the studied time period (3600 s), and with further increase in pressure above
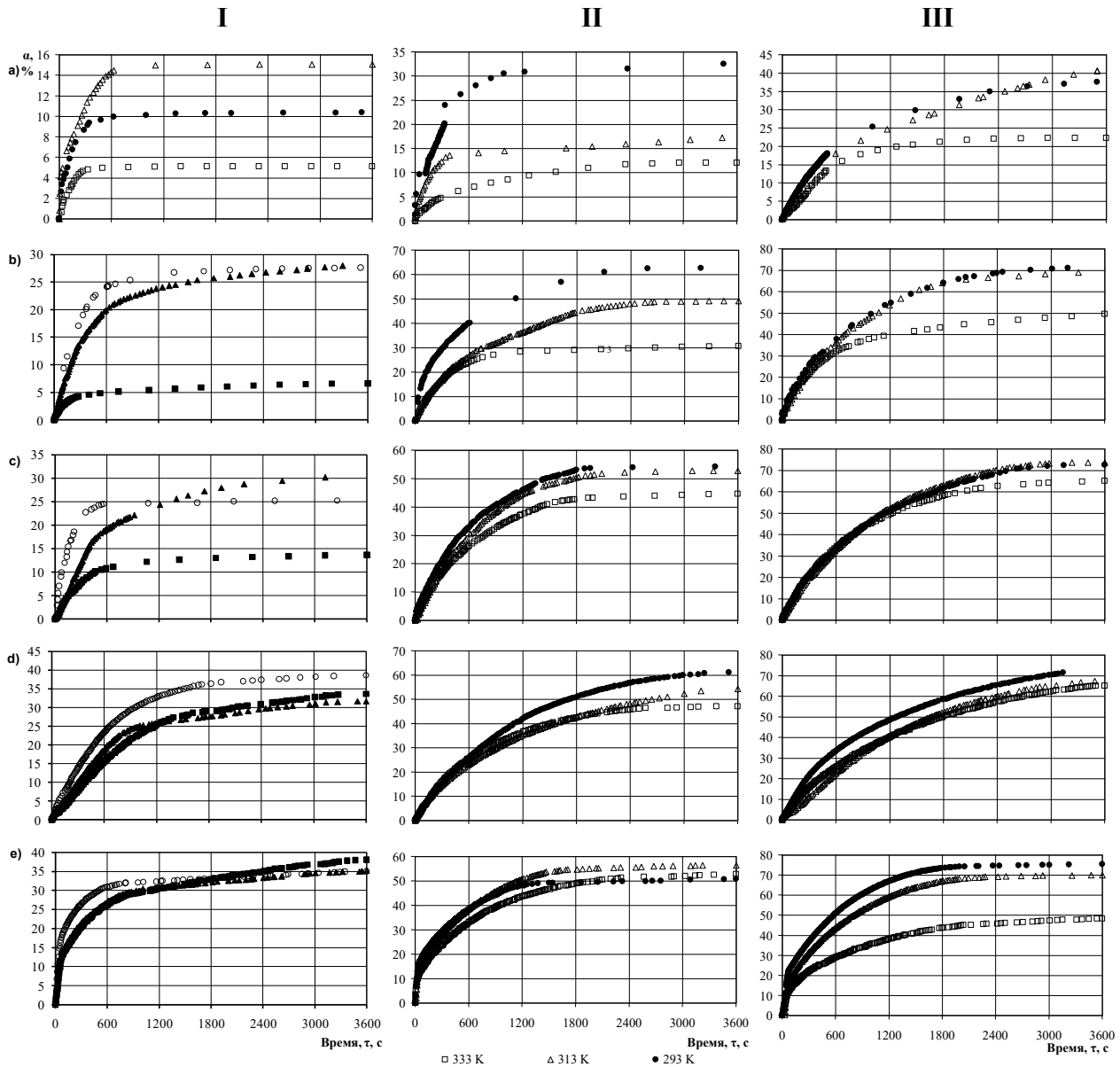
Fig. 2. Temperature effect upon the change in the carbonation degree of lime samples as function of the water content, mass percent: I – 1; II – 5; III – 10, and carbon dioxide pressure, MPa: a) – 0.02; b) – 0.05; c) – 0.08; d) – 0.1; e) – 0.2

the atmospheric value the temperature influence becomes more noticeable.

With increasing CO_2 pressure in the carbonation chamber above the atmospheric value, there is a significant increase in the speed of transformation of $Ca(OH)_2$ into $CaCO_3$ within the first 100 seconds of forced carbonation. The graphs of the carbonation speed of the experimental lime samples as function of the factors under investigation are presented in Fig. 3.

The data in Fig. 3 show that the carbonation process of half-dry pressed lime samples corresponds to the instant engagement of lime into chemical reaction with the carbon dioxide, which is immediately followed by a period of decrease and stabilization of the carbonation speed, and here, both the carbonization speed values and the carbonation change features depend on the temperature. The carbonation speed decreases with increasing temperature,

regardless of other process factors. An increase of the initial water content in the experimental samples from 1 mass % to 5 mass % within a pressure range of up to 0.1 MPa accelerates the carbonization process, and with further increase in the water content up to 10 mass % the speed of lime reaction with CO_2 is reducing. With pressure increasing above 0.1 MPa, the lime carbonation speed, as compared to carbonization at a pressure of 0.1 MPa, is increasing 2 or 3 times, and in the graphs, we can see a well-pronounced induction period (as it is called) of reaching maximum carbonation speed values of the lime samples. With an increase of the initial water content in the samples, the duration of this period increases.

Thus, the initial water content being 1 mass %, the maximum speed is reached within 3 to 15 seconds, with the content being 5 mass % – within 6 to 30 s, and with the content being 10 mass % – averagely within 50 seconds. The
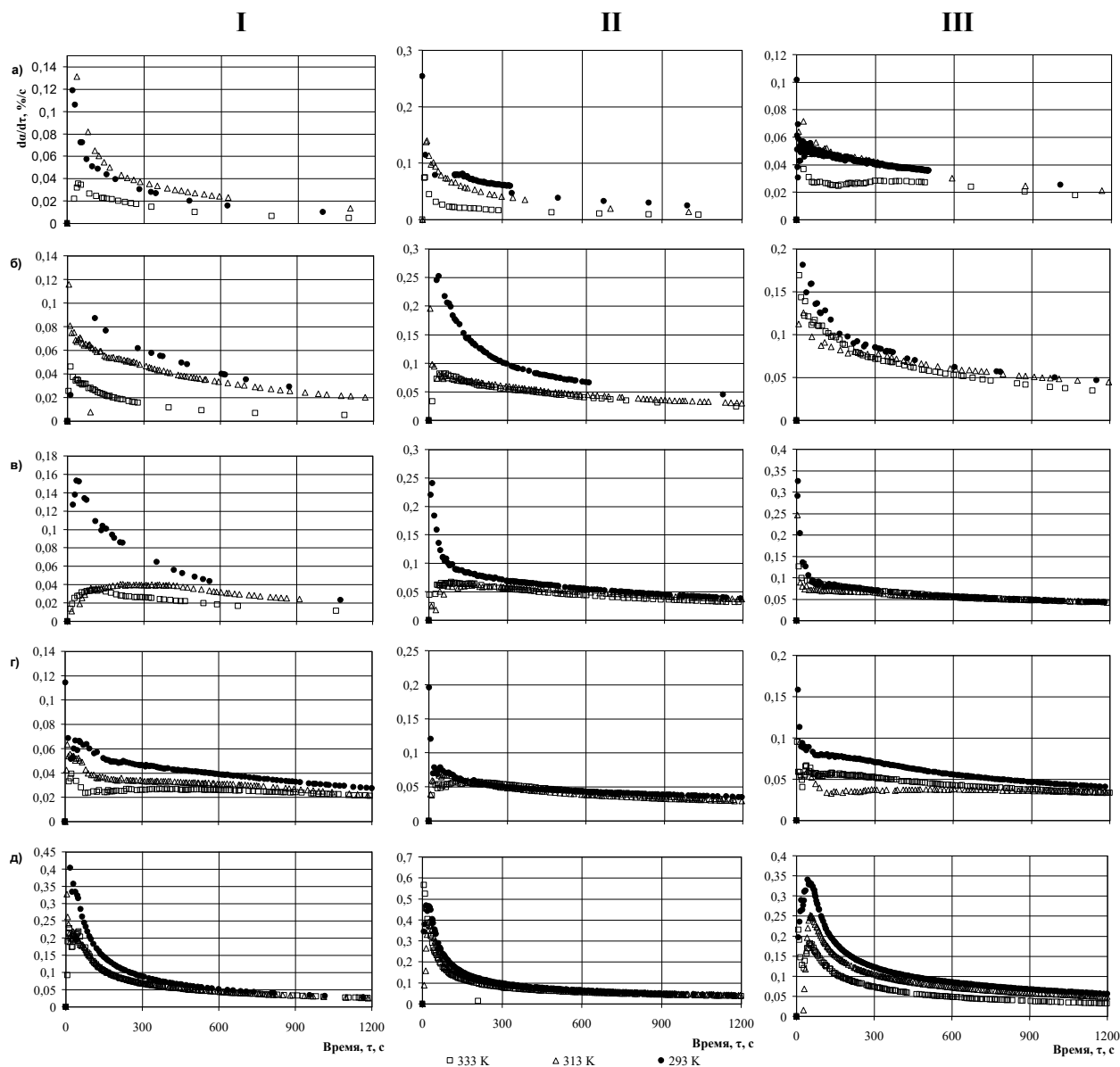
Fig. 3.The carbonation speed change in lime samples as function of the temperature, water content and pressure of carbon dioxide: I, II, III, a), b), c), d) and e) are the same as in Fig. 2

presence of the period of gradual carbonation speed growth can be explained by the fact that under high pressures the amount of CO_2 adsorbed on the surfaces of lime particles increases, which causes a sharp increase in the speed of interaction of $Ca(OH)_2$ with CO_2. Accordingly, engagementof a larger amount of lime into the chemical interaction causes immediate formation of a large amount of water in the system, forming a barrier film on the surface of lime particles, which prevents free access of CO_2 to $Ca(OH)_2$. Over time, CO_2diffusion decreases due to formation of a carbonized layer on the surface of lime particles, and the carbonation speed, having reached its maximum, begins to gradually decrease.

Carbonation of calcium hydroxide relates to heterogeneous reactions of the type

„solid.1 + liquid.1 + hetero = solid.2 + liquid.2",

where solid.1 is calcium hydroxide; solid.2 is calcium carbonate; liquid.1 is water; liquid.2 is a saturated solution of calcium carbonate, calcium bicarbonate and calcium hydroxide in water.

The water layer, rather a layer of the liquid phase, is a saturated water solution of calcium carbonate and calcium hydroxide that can be viewed as a barrier-type yet permeable obstacle at the surface of Ca (OH)$_2$ crystals being carbonized. In addition, the features of the kinetic curves gives a basis to assign the process either to the reactions whose kinetics obeys the laws characteristic of instant engagement of the entire surface into the reaction, followed by reduction of the solid reactant volume, or to the to pochemical transformations.

Based on the foregoing, to process the kinetic curves, we used three kinetic equations [6, 20, 21]: Avrami – Yerofeyev equation, the diminishing volume equation, and the diminishing area equation.

Processing of the primary array of the experimental data has showed that a slightly better agreement with the

measurement results was provided by Avrami – Yerofeyev equation, for which the correlation factor was 0.9977.

The reaction of calcium hydroxide with carbon dioxide is a process whose development at elevated temperatures can be complicated by dehydration of crystalline calcium hydroxide that formsin process of mixing lime with water. This means that at elevated temperatures, in presence of a temperature gradient, along with carbonation of calcium hydroxide hydrate, its dehydration will occur, accompanied by transfer of the water vapor into to the cold part of the system.

A study of the temperature effect upon the carbonation speed of lime binder has shown that, for given values of the initial water content and pressure, the reaction speed is weakly dependent on the temperature, which can mean that the apparent activation energy of the process approximates zero. This is understandable, since it is known that the neutralization reactions, which the transformation of $Ca(OH)_2$ and $CaCO_3$ can be attributed to, occur as non-activation processes whose reaction speed is limited only by transport of reactants to the interaction zone.

The apparent activation energy was estimated by the conventional method: through determining the temperature dependence of the maximum process velocity [20, 22]. With the whole surface instantly engaging into the reaction, the maximum velocity conforms to the slope of the curves, $\alpha = f(\tau)$, at the initial stage.

As an example, Fig. 4 shows fragments of the kinetic curve of lime binder carbonation with an initial water content of 10 mass %. The curve characterizes the process development for 60 seconds at different temperatures and pressures (in vacuum, under conditions of the atmospheric pressure and overpressure). Fig. 5 shows the dependences of the speed logarithm on the reverse temperature at different carbon dioxide pressures and the initial water content of lime samples.

As can be seen, the reaction speed decreases with the temperature increasing, i.e. the apparent activation energy value will be negative. It is believed that in this case the speed of the process depends only on CO_2 delivery to the surface of $Ca(OH)_2$ not protected by the presence of a barrier layer. With temperature increase, the CO_2 delivery process can be complicated by overcoming another obstacle: the water vapor pressure increasing with the temperature. In addition, with the temperature increasing, dissolution of $Ca(OH)_2$ and CO_2 in water decreases, which limits the process speed. It is obvious that by changing the geometry of the reactor, or arranging it with the low-temperature zones, we can manage the process of removing water from the reaction system and thereby control the speed of $Ca(OH)_2$ carbonation.

The corresponding data about the speed constants for the initial stage of carbonization (τ = 300 s) at 293 K and 333 K and the calculated values of the apparent activation energy are given in table 1.
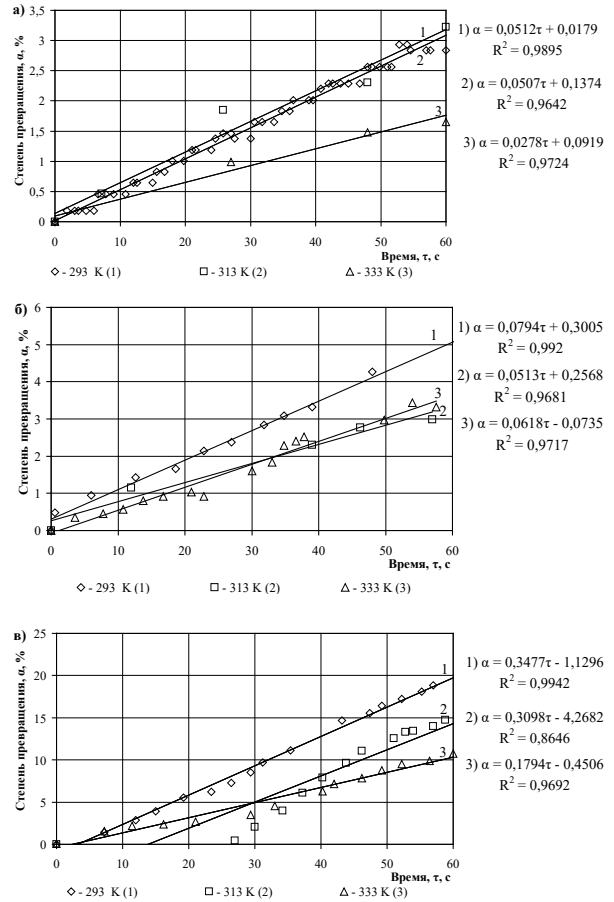

Fig. 4. The initial portions of the kinetic curves characterizing the process development at different temperatures and pressures, MPa: a) – 0.02; b) – 0.1; c) – 0.2.
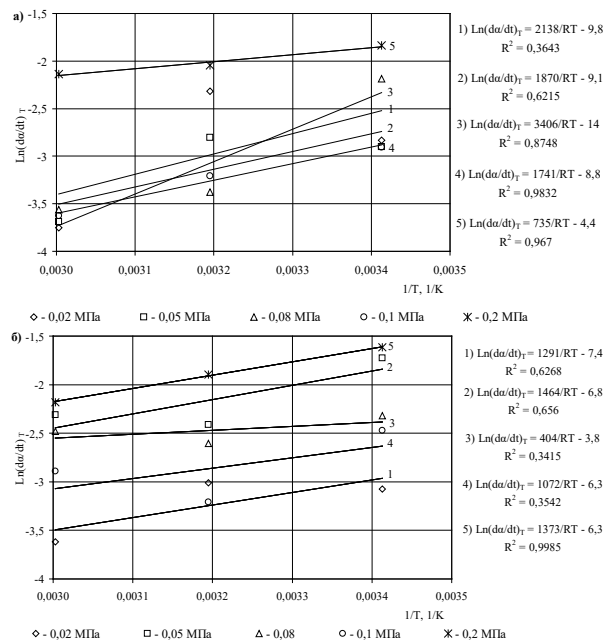

Fig. 5. Temperature dependence of the carbonation speed of lime binder with a water content of 1 mass % (a) and 10 mass % (b) at different pressures of carbon dioxide

Table 1. Speed constants and calculated values of apparent activation energy of carbonation of lime samples

$E_a = \dfrac{R \cdot T_1 \cdot T_2}{T_2 - T_1} \, Ln \dfrac{K_2}{K_1}$ [Kuznetsova T., Kudryashov I., Timashev V., 1989]

CO$_2$ pressure, MPa	Initial water content in lime samples, mass %	Speed reaction constants at temperature, K		Apparent activation energy, E_a, kJ/mol
		293, K$_1$	333, K$_2$	
0.02	1	0.03052	0.01716	-11.68
	5	0.0618	0.0165	-26.81
	10	0.0410	0.0280	-7.60
0.05	1	0.0619	0.0155	-28.14
	5	0.0992	0.0554	-11.83
	10	0.0850	0.0715	-3.50
0.08	1	0.0855	0.0261	-24.05
	5	0.0689	0.0554	-4.41
	10	0.0718	0.0689	-0.82
0.1	1	0.0466	0.0260	-11.85
	5	0.0495	0.0531	1.43
	10	0.0704	0.0524	-5.98
0.2	1	0.0880	0.0677	-5.31
	5	0.0973	0.0803	-3.89
	10	0.1223	0.0741	-10.16

The calculated values of the apparent activation energy indicate a high reactivity of the lime binder for CO$_2$ and confirm that the speed-limiting factor is the diffusion of CO$_2$ to grains of Ca(OH)$_2$. With increasing the water content and pressure, the values of E_a reduce.

CONCLUSIONS

1. It has been found that the process of forced carbonation of calcium hydroxide corresponds to the case of entry into an instant reaction of the entire surface of the reagent without forming the barrier layer of the reaction product at the initial period.
2. It has been proved that both temperature and pressure of CO$_2$ do not produce a decisive effect on the degree of lime carbonation at a constant value of one of the factors; however, they are important and mutually complementary parameters governing the speed of Ca(OH)$_2$conversion into CaCO$_3$. The most important factor affecting the degree of lime carbonation is the initial water content in the system.
3. It has been shown that the maximum speed of carbonation may be achieved at temperatures up to 293 K; the limiting factor is dissolution of CO$_2$ followed by its diffusion to the surface of the solid reactant, as well as dissolution of Ca(OH)$_2$, and diffusion of hydroxyl ions to the surface of contact with the gas phase. It has been found that for controlling the carbonization speed, it is necessary to ensure water drainage by providing a low-temperature zone in the carbonation chamber.

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ВЛИЯНИЕ ТЕМПЕРАТУРЫ НА СКОРОСТЬ
ПРИНУДИТЕЛЬНОЙ КАРБОНИЗАЦИИ
ИЗВЕСТКОВОГО КАМНЯ ПОЛУСУХОГО
ПРЕССОВАНИЯ

Аннотация. Исследовано влияние температуры на скорость карбонизации известкового камня полусухого прессования при его принудительной карбонизации в зависимости от различных технологических факторов. Показано, что максимальная скорость карбонизации достигается при температурах до 293 K, с повышением температуры скорость реакции карбонизации снижается. Установлено, что для управления скоростью процесса взаимодействия извести и углекислого газа в карбонизационных реакторах необходимо предусматривать низкотемпературные зоны и отвод выделяющейся в результате химической реакции карбонизации воды.

Ключевые слова: Строительные материалы, известь, углекислый газ, принудительная карбонизация, температура, полусухое прессование.