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OPTIMIZATION OF THE PROCESS OF LIME SYSTEMS CARBONIZATION AS AN EFFICIENT WAY OF REDUCING ENERGY INTENSITY OF CARBONACEOUS CONSTRUCTION MATERIALS PRODUCTION

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Summary. By means of a kinetic analysis of lime carbonization reaction, it is established that the speed of carbon dioxide absorption by lime systems depends on temperature and humidity factors. By changing these factors one can control the process of lime putty carbonization and obtain strong and water-resistant lime putty based on artificial carbonate stone. Lime carbonization does not require additional energy consumption and gives an opportunity of reducing the amount of carbon dioxide emissions into the atmosphere.

Key words: lime, carbon dioxide, carbonization, calcium carbonate, kinetics.

INTRODUCTION

The fundamental conception of development of modern materials science and technology is energy and resource saving. Resolving the energy and resource saving issue may be connected both with an improvement and optimization of existing technologies and processes of material structure formation and development of new non-conventional lines of obtaining artificial construction materials. The investigations aimed at reducing carbon dioxide emissions into the atmosphere by using lime process as raw component in a technological process are of specific interest.

Air-setting lime is the material that provides potential opportunities of saving both energy and raw resources. One can create efficient technologies of making constructional goods of an available and less energy intensive product, i.e. lime.

ANALYSIS OF PUBLICATIONS

Despite the fact that lime-based solutions have been used for thousand of years, the issue of speeded carbonized hardening of lime putty, which many investigators and builders were concerned about, has not been solved. And since ancient times till the present moment, the classification of lime as “air-setting binder” has been defining only the limited sphere of its application. The first published experiments of obtaining secondary calcium carbonate were run by James Galley in 1804. Later, similar experiments were held by Buchgolz, Werner Siemens, Mitscherlich. The heteromorphism of lime carbonate with the development of methods of obtaining “lime carbonate in all its heteromorphic states” was studied in the middle of the XIXth century by the investigator G. Roze, who obtained lime carbonate of aqua solutions at different temperatures. This issue was also researched by M. Tolstopyatov 1867, H. Credner, M. Bauer, H. Vater and others.

The issues of chemistry and technology of obtaining secondary calcium carbonate were raised by A.A. Baykov for the first time in the beginning of XX century. In the first part of the XXth century, the artificial carbonization of lime and lime solutions were investigated in the USSR in Communal Service Academy (1938 – 1948) and in the RDE of Stroyneft (1948 – 1950) [Zatsepin 1952]. Similar works were held in the USA in the middle of the XXth century [Zalmanoff 1956]. However, the achieved scarce positive results did not lead to mass production of artificially carbonized lime products.

The carbonization of slaked lime is a heterogenic reaction expressed by the following general chemical equation:

$$\boldsymbol{Ca(OH)_2 + CO_2 + H_2O = CaCO_3 + 2H_2O + 82{,}0\ kJ}. \tag{1}$$

Following ionic nature of the process, the main reaction of $CaCO_3$ solid residue formation will run in fluidal component of the system. Before being involved into the complex carbonization reaction mechanism, CO_2 gas should go through the solution process. Simultaneously, solid hydrate should deliquesce by dissolving in liquid before the ionic reaction happens.

According to the investigations [Zalmanoff 1956], the process of obtaining $CaCO_3$ artificial stone by means of lime carbonization depends much on lime putty hydrometer, CO_2 concentration and process temperature which are quite hard to be optimized due to lack of studies of the process so far.

AIM OF RESEARCHES AND SPECIFICATION OF THEIR OBJECTIVE

Analyzing the works of foregoers, one can come to a conclusion that the theoretical obviousness of the lime carbonization process in relation to the chemical reaction equation is hard to achieve in practice since one encounters many factors impacting the course of the process, and it is difficult to achieve positive final results, namely to obtain secondary calcium carbonate, without taking control over these factors. In previous works [Fedorkin 2006, Lyubomirskiy 2007], scientific and practical objectives, representing the system of principles, were formulated. The implementation of these principles will give an opportunity to obtain strong and ecologically clean construction products based on lime of carbonized hardening, and also to solve a number of ecological and resource problems such as reduction of CO_2 emissions into the atmosphere and utilization of carbonate co-products of stone output by using them in a technological process. In relation to carbon dioxide utilization in production of construction goods, the investigation of speed of lime putty carbonization is of certain interest.

In connection with this, the work is aimed at the development of technology of obtaining strong and water-resistant artificial stone based on lime of contact-carbonized type of hardening by specifying natural influence of different technological factors on the kinetics of lime putty carbonization process and formation of main physical and mechanical characteristics of carbonized hardening lime based samples.

RESULTS AND THEIR ANALYSIS

Cylinder samples of 0,028 m diameter, obtained by contact molding of the lime putty structure with different humidity *(W)* of molding sand (12,5 – 22,5 % of mas.), were exposed to the artificial carbonization at press-molding pressure of 7,5 MPa. The samples were made of lime obtained by slaking of non-slaked lime, the activity of which reached 62 %. The test samples were carbonized in CO_2 environment by maintaining constant 100 % concentration of gas in the designed plant with automatic control [Lyubomirskiy 2007]. The carbonization of lime samples was run at different temperatures *(T)* in the interval of 295...323 K. During the carbonization process, the amount of carbon dioxide absorbed by the samples in time was determined. The carbonized cylinder samples were put to tests with determination of the following coefficients: compression strength, softening and depth of carbonization right after the carbonization. Softening coefficient was determined after keeping the samples in water for 172800 s. The carbonization depth *(δ)* was determined by applying the phenolphthalein on the chips of the samples.

The investigations have shown that lime samples carbonization starts from the moment of supplying carbonization chamber with CO_2 gas. The temperature in chamber rises up to 345 K. The curves of absorption of CO_2 by the test samples, depending on humidity of lime putty and carbonization conditions, have the same character (Fig. 1) and depend on humidity of lime putty and carbonization temperature.

Speed graphs of absorption of carbon dioxide by the volume unit of the test samples cylinders, drawn in logarithmic coordinates of time, come to straight lines (Fig. 2). The angle of inclination of straight lines to abscise axis indicates the decrease of speed of interaction of $Ca(OH)_2$ with CO_2 with constant values of coefficient (constants) of carbonization reaction speed.

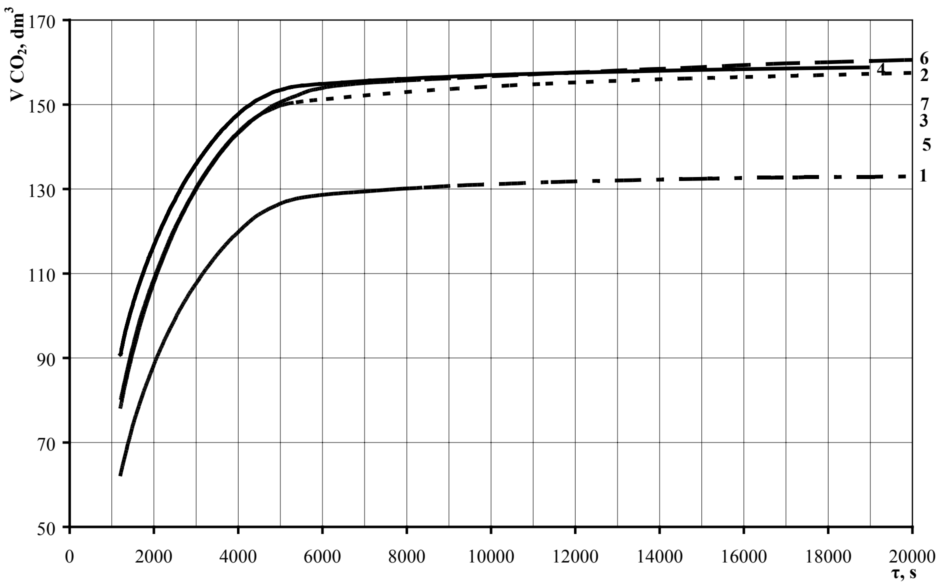

Fig. 1. The curves of absorption of CO_2 by the test samples, obtained at specific pressure of compression being 7,5 MPa, depending on humidity of lime putty and carbonization temperature: 1, 2, 3 – W = 12,5, 17,5, 22,5 %, T = 313 K; 4 and 5 – W = 15 %, T = 303 and 323 K; 6 and 7 – W = 20 %, T = 303 and 323 K

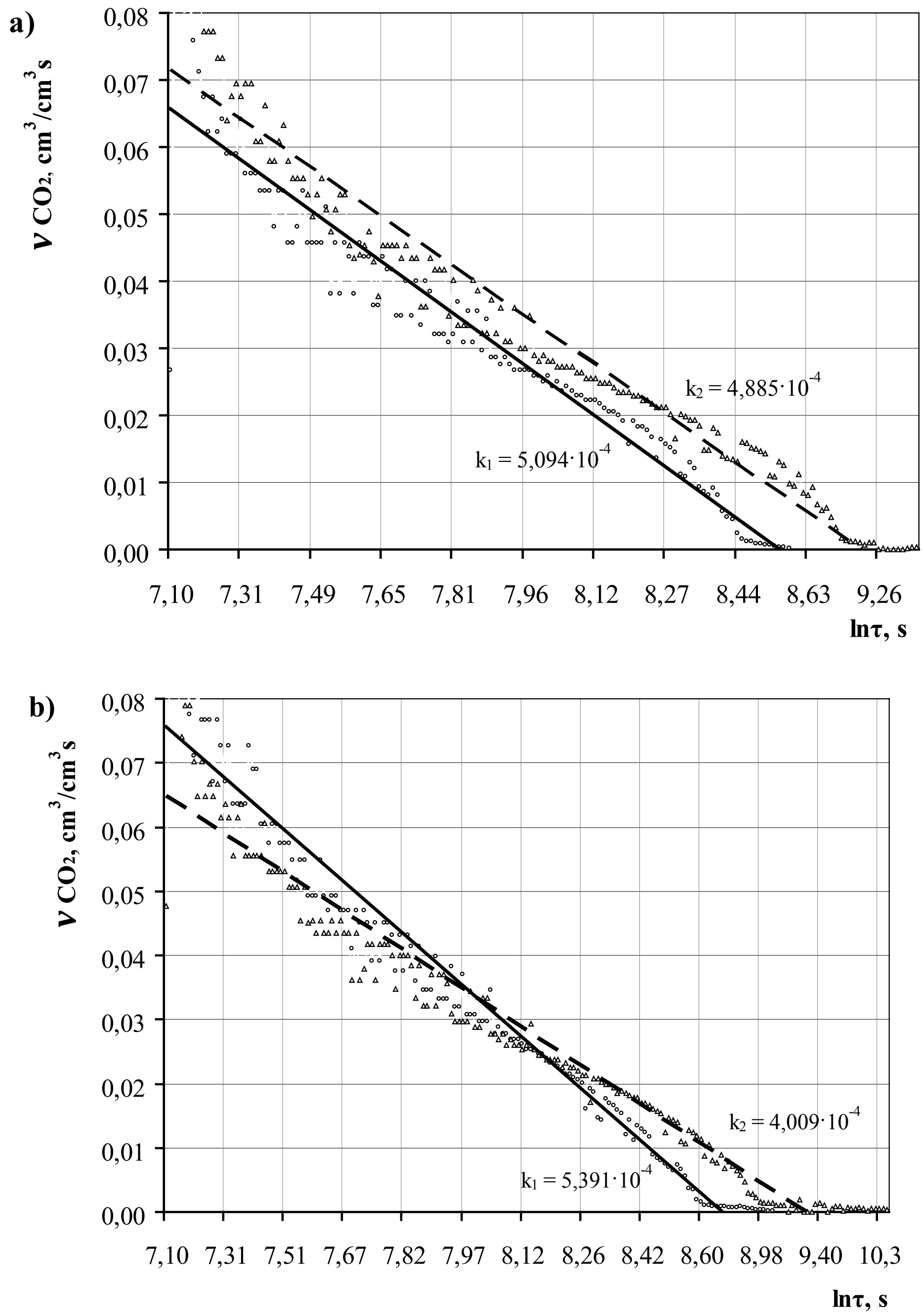

Fig. 2. The speed of absorption of dioxide carbon by the samples depending on *W* of lime putty and *T* of carbonization: a) – W = 15 % of mas.; b) – W = 20 % of mas.; – T = 303 K; – T = 323 K

The speed of absorption of carbon dioxide by the test samples significantly depends on the humidity of lime putty and initial temperature of carbonization. At W = 15 % of mas. with the increase of T from 303 to 323 K, the speed of absorption of CO_2 by the test samples increases and carbonization continues for a longer time (active absorption of CO_2 by the samples at temperature of 303 K continues for 52000 s, and at 323 K, it continues for 114000 s). Upon the increase of samples humidity up to 20 % of mass, carbonization speed decreases with the increase of temperature. However, the time of active carbonization increases: at temperature of 303 K carbonization speed stabilizes to 6600 s, and at temperature of 323 K, it stabilizes to 12000 s.

According to the obtained values of hydrate lime constants of carbonization reaction speed and the well-known equation of Arrhenius, it is possible to determine the values of activation energy of the studied process.

For the calculation of activation energy, the transformed equation of Arrhenius was used, taking into consideration the change of speed of reaction constants at two different temperatures [Kuznetsova 1989]:

$$E_a = \frac{4{,}576 \cdot T_1 T_2}{T_2 - T_1} \cdot \frac{k_2}{k_2}. \tag{2}$$

where Ea is the energy of activation, kJ·mol-ą·K-ą.

T_1 and T_2 is the temperature of proceeding of carbonization, K; constants of reaction speed (at the temperature T_1 and T_2 in K);

4,576 – multiplier allowing for the gas constant in the equation of Arrhenius and recalculation of natural logarithms into decimals.

The results of calculation of activation energy of lime carbonization process in the investigated temperature interval are as follows: 16,65 kJ·mol-ą·K-ąat the humidity of lime putty being 15 and 20 %, correspondingly.

Low values Ea indicate high reactive property of lime to interact chemically with CO_2. Upon the increase of humidity of lime putty up to 20 %, the value of activation energy decreases. Thus, the humidity of lime putty influences the proceeding of carbonization $Ca(OH)_2$ reaction most of all. One can control the process of lime putty carbonization by changing its humidity.

The observations have shown that carbonization continues not over the whole volume of lime putty simultaneously, but by layers (Fig. 3). The conversion of $Ca(OH)_2$ into $CaCO_3$ happens by means of diffusion.

Fig. 3. Change of thickness of carbonized layer of lime samples depending on molding humidity of lime putty (t = 10800 s), % of mas.: 1 – 12,5; 2 – 17,5; 3 – 22,5

Knowing the thickness of carbonization layer and the amount of CO_2 gas absorbed by lime samples, by means of the developed methods [Lyubomirskiy 2007], one can calculate the efficient coefficient of carbon dioxide diffusion *D* in the test samples (Table 1).

From Table 1, one can see that the coefficient of CO_2 diffusion in lime putty is the highest during the first period of carbonization, it gets lower with time. Upon an increase of *W* and *T* the diffusion coefficient increases, however, upon an increase of *T* and longer keeping of lime samples in the carbon dioxide environment, *D* decreases. Upon the carbonization temperature increase, at the same humidity of the lime putty, the diffusion coefficient clearly decreases. That is explained by a decrease of lime samples humidity due to their drying. Thus, the defining factor of lime putty carbonization is its humidity.

Table 1. Diffusion coefficient of CO_2 diffusion in the test samples

№ п/п	Conditions of test samples carbonization		Diffusion coefficient, D, 10-5 cm2/s, within time, s			
	W, % of mas.	T, K	3600	10800	21600	32400
1	15	303		4,94		2,06
2	20			6,03		3,20
3	15	323		5,06		2,63
4	20			6,13		2,44
5	17,5	291			3,83	
6		295			2,79	
7		313	14,79		2,04	
8		330			1,52	

The artificial carbonization of the lime samples significantly improved their physical and mechanical characteristics (Fig. 4): strength at compression increased 3 times, water-resistance increasedby 60 – 110 % depending on carbonization conditions.

The properties of carbonized test samples significantly depend on humidity and temperature of carbonization and indicate that by means of artificial carbonization one can obtain sufficiently strong and water-resistant products based on air-setting lime.

When test samples carbonized at normal temperature are compressed, the strength increases upon an increase of humidity of lime putty up to 18 %. At that, water-resistance of these samples decreases slightly while softening coefficient does not decrease more than 0,7. Upon an increase of carbonization temperature up to 303 K, the strength increases at an increase of humidity up to 20 %, and at a further temperature increase, up to 323 K, it decreases. It should be noted that the strength of lime samples of contact-carbonized type of hardening, when compressed, does not correspond to the thickness of carbonization layer. It would be logical to assume that the more carbonized a layer is, the higher is the strength, however, such dependence is not observed. In our opinion, it is connected both with creation of initial density of test samples structure based on the lime putty, when pressed, and with formation of different forms of secondary $CaCO_3$. At a temperature higher than 303 K, calcium carbonate exudes in form of aragonite crystals [Brauns 1904], the strength of which is lower than that of calcite. Water-resistance of the test samples depends more on the thickness of the carbonized layer.

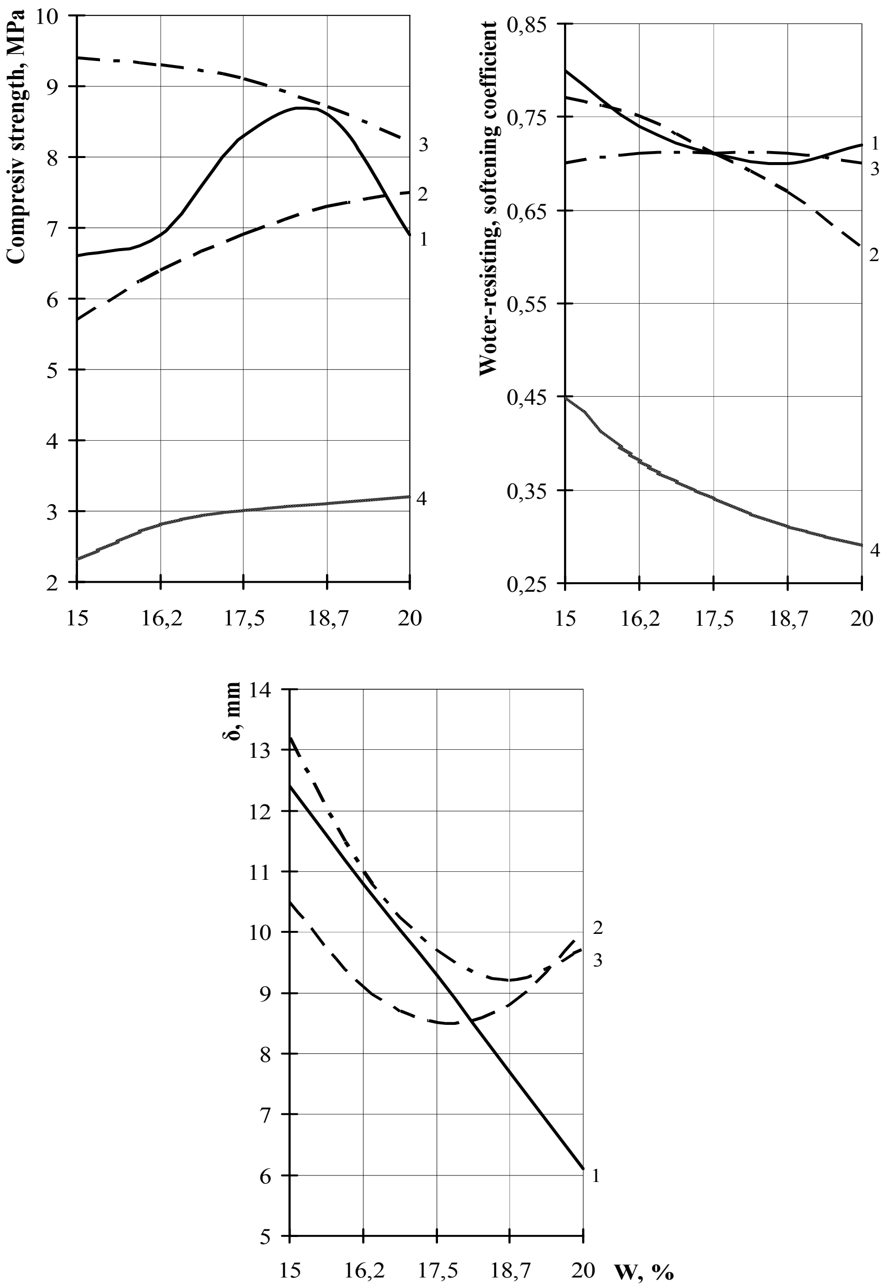

Fig. 4. Physical and mechanical coefficients of test samples obtained by compression strength of 7,5 MPa, carbonized for 10800 s, depending on the humidity of raw putty and carbonization temperature: 1 – 295 K; 2 – 303 K; 3 – 323 K; 4 – non-carbonized sample

CONCLUSIONS

1. Temperature and humidity parameters of lime carbonization process when obtaining artificial carbonate stone were investigated. The samples maximum strength were obtained at W = 17,5 – 18,5 % and T = 295 K.
2. The kinetics of carbonization process were investigated, the activation energy and carbon dioxide diffusion coefficient were calculated at different temperature and humidity parameters. The opportunity of controlling the process of lime carbonization was shown.
3. Temperature parameters of test samples carbonization process are similar to the temperature conditions of environment, which predetermines low energy intensity of the carbonized materials production process.
4. Obtaining artificial stone based on carbonized lime is an efficient method of reducing the energy intensity of wall construction materials.

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