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SUBSTANTIATION OF PRINCIPLES OF LIME ARTIFICIAL CARBONATION IN THE TECHNOLOGY OF SOLIDPHASE CONSTRUCTION MATERIALS

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Summary. Due to the theoretical and empirical research, it has been proved that the formation process of secondary calcium carbonate under the carbonation of lime putty is the complex one and associated with the formation of various intermediate compounds: hydrated calcium carbonate with different degrees of hydration and hydrogen carbonate. These processes can occur in the carbonating system simultaneously or can alternate according to the concentration of carbon dioxide as well as availability of free water in the system. The links formed between these compounds and calcium hydroxide and calcium carbonate provide high endurance of structure of the material to be derived.

Key words: lime, carbon dioxide, carbonation, calcium carbonate, hydrate of calcium carbonate, hydrogen carbonate, structure

INTRODUCTION

Current tendencies of the most effective combination of environmental friendliness and economic feasibility for the manufacturing of final products concern all production industry including construction. Under Kyoto Protocol to the United Nations Framework Convention on Climate Change, anthropogenic emissions of greenhouse gases in equivalent of carbon dioxide within the period of the years 2008-2012 should not exceed the rate of the above-mentioned emissions in the year 1990, otherwise the charge for emission of one (1) ton of CO_2 to the atmosphere in excess of quota may amount to 87USD. The largest source of CO_2 emission is energy-consuming production of cement that is the original material for the manufacturing of structural stones. Reduction of cement consumption and transition to less energy-intensive production ma greatly y reduce carbon pollution.

Resolution of global ecological problems and problems of effective use of resources requires more than optimization of traditional process of materials structure formation at the current stage. It would be reasonable to develop new breakthrough technologies and principles for the production of non-cement artificial construction materials. In this context, it would be more reasonable to study the issues of artificial portlandite stone formation on the basis of alternative approaches to the organization of process for high-calcium lime curing – carbonation of goods in CO_2 environment.

This method will allow the producers to reduce emissions of carbon dioxide evolving from burning by 2/3 and use it as the key raw component.

ANALYSIS OF PUBLICATIONS

Lime carbonation has always been regarded as the secondary process of lime mortar curing. When dealing with environment, lime carbonation process is very slow and takes centuries. This is caused by low concentration of CO_2 in the air and formation of blocking film of calcium carbonate on the surface of lime particles. There are various points of view about importance of carbonation in the process of sand-lime mortar curing. According to the research of V.Rodt [Rodt 1936] the role of carbonation in the curing process should be regarded as the minor one. The sample of sand-lime mortar that had been cured by V.Rodt within four weeks contained only 0,03% of carbon dioxide that was on the surface layer of the sample. Works of Donath and Hint [Donath 1926, Hint 1960] proved that the carbonation affected the process of sand-lime mortar curing at the initial stage. N. Zalmanoff [Zalmanoff 1956] thought that to make the reaction of calcium hydroxide carbonation faster, a larger part of lime putty surface should be subjected to the reaction. Furthermore, the access of CO_2 should be provided to the surfaces where carbon dioxide reacts with the lime by means of permanent expulsion and closure of water released as the result of reaction.

Origin and structure formation of the products derived as the result of artificial carbonation of lime is also the issue in dispute. D.Mendeleyev [Mendeleyev 1906] described calcium carbonate derived at the initial stage of carbonation as having jelly-like state and believed its chemical composition to be unclear. V. Kosman [Kosman 1920] and Fuks [Fuks 1940] considered the product of carbonation at an early stage to be very similar to $CaCO_3 \cdot n\,Ca(OH)_2$ (hydroxide carbonate). N. Mikhaylov [Rozenfeld 1955] supposed that the products derived as the result of lime carbonation process shall fall into the category of colloids with the crystallization in the form of carbonate of submicroscopic size.

GOALS AND OBJECTIVES OF THE RESEARCH

According to the analysis of the above-mentioned publications, there is no unequivocal opinion about the role of carbonation period in the process of lime curing as well as structure formation of calcite crystals and process of chemical transition from $Ca(OH)_2$ into $CaCO_3$. The process of artificial stone production by means of lime putty carbonation depends mainly on CO_2 concentration, humidity of mortar to be molded and the temperature of the process, that can hardly be optimized due to insufficient study of this process.

The reason for the more intensive research on lime carbonation principles is the wide application and availability of raw materials for the production of lime that allow manufacturers to easily develop a high production of materials on the basis of lime by means of curing, without complex autoclave equipment and at the least cost. New knowledge about non-autoclave manufacturing of waterproof materials on the basis of lime systems has the primary importance for the construction industry as well as for the production of construction materials.

The objective of the present research is to substantiate the principles of lime artificial carbonation in the technology of solidphase construction materials by the determination of formation structures mechanisms and phase transformations in lime systems under carbon dioxide gas treatment.

RESULTS AND THEIR ANALYSIS

For the study of the structure formation process of lime systems subjected to carbonation, cylindrical samples with diameter of 0,03 m were manufactured by means of contact moulding of lime putty with various humidity of moulding mortar (*W*) 12,5 – 22,5 % of mas. under unit moulding pressure of (*P*) 5 – 25 MPa. The samples were manufactured from the slaked lime with the intensity of 68 %. According to the chemical analysis and DTA the composition of the slaked lime was as indicated in Tab. 1, 2.

Table 1. Chemical composition of slaked lime, % of mas

SiO_2	Al_2O_3	Fe_2O_3	FeO	CaO	MgO	MnO	K_2O	Na_2O	P_2O_5	SO_3	CO_2	H_2O+
2,1	1,2	0,4	< 0,05	71,2	0,59	0,02	0,16	0,08	0,05	0,15	3,73	20,3

Table 2. The composition of slaked lime as (according to the results of DTA), % of mas

$Ca(OH)_2$	$CaCO_3$	H_2O	The rest
86,00	7,00	3,00	4,00

The samples were subjected to carbonation in CO_2 environment. During the process constant 100 % gas concentration was maintained.

Carbonation of slaked lime is the heterogeneous reaction where solid, liquid and gas components react with one another. This reaction can be described by general chemical equation indicated below:

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

According to the chemical equation of reaction of calcium hydroxide carbonation and difference between molecular weights of $Ca(OH)_2$ and $CaCO_3$, weight of solid residue $CaCO_3$ in case of complete carbonation of lime putty shall be more than $K = 100/74 = 1{,}35$ times. Therefore, weight increase, i.e. ratio between actual weight of carbonated samples and theoretical weight of samples under complete carbonation, allow us to determine the degree and rate of artificial carbonation of lime putty. The degree of lime putty carbonation can be calculated under the following equation:

$$\eta = \frac{(m_2 - m_3)}{\left[(\boldsymbol{m_1} - \boldsymbol{W}) - \boldsymbol{m_3}\right] \times K} \times 100\%, \tag{2}$$

$\boldsymbol{m_2}$ – weight of carbonated sample dried up to constant weight; $\boldsymbol{m_3}$ – weight of additional substances in lime; $\boldsymbol{m_1}$ – weight of as-molded lime sample; $\boldsymbol{W}$ – quantity of water in the as-moulded lime samples.

Some estimate indexes of carbonation degree are presented at Fig. 1.

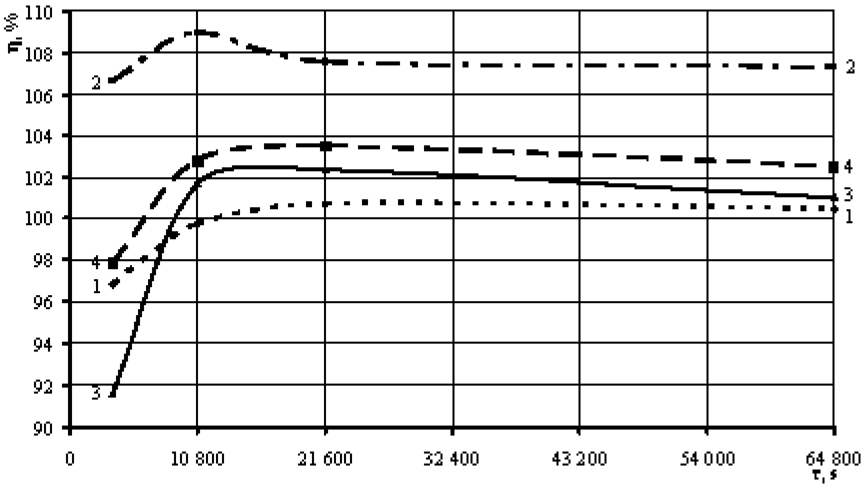

Fig. 1. Indexes of carbonation degree of samples in cost of time and according to the initial humidity of lime putty and unit moulding pressure: 1 – *P* = 5MPa, *W* = 15% of mas., 2 – *P* =5 MPa, *W* = 25% of mas., 3 – *P* = 20 MPa, *W* = 15% of mas., 4 – *P* = 20 MPa, *W* = 25% of mas

As follows from the results stated above, the carbonization degree of samples is more than 100% , which cannot be possible. It is obvious that the process of $CaCO_3$ formation in the system under research occurred according to the scheme different from that described in equation (1). $CaCO_3$ is formed in several stages with the release of various intermediate soluble compounds.

As the above-mentioned chemical reaction is impossible without water, it is reasonable to assume that the formation of calcium carbonate occurs also as the result of hydration process with the release of hydrated compounds.

According to Le Chatelier theory, the basic requirement for getting high mechanic durability is oversaturation of the solution by primary products surrounding stable part of the system during its collapse. Taking this theory into account it may be supposed, that calcium carbonate is present in the solution during the reaction in two forms of different equation degrees: hydrated and non-hydrated [Zalmanoff, 1956]. With the supply of CO_2 into the chamber with the lime samples, carbon dioxide enters chemical reaction with the lime test and on the surface of $Ca(OH)_2$ grain $CaCO_3$ forms, which possessing high reaction activity mutually dissolves in $Ca(OH)_2$ with the formation of hydrated $CaCO_3{:}xCa(CO)_2yH_2O$. The dissolubility of $CaCO_3$ causes saturation of hydrated calcium carbonate and simultaneously the solution becomes oversaturated in relation to converted waterless $CaCO_3$ Setting of the temporary stable state in the solution leads to crystallization of calcium carbonate and its collapse, leaving the solution unsaturated in relation to hydrated calcium carbonate. This process is accompanied by the isolation of free water. For the saturation of the system by hydrates of carbonate more hydrated $CaCO_3$ dissolves and finally, having passed the continuous process of two stages, it turns into the final product – crystalline calcium carbonate.

The research on this process shows that it has a nature contrary to that which exists in the circle of hydrate compounds. If equation of other astringent substances draws the transformation of compounds from the lowest degree of equation to the highest, then the medium of the carbonate is characterized by the conversion of more hydrated compounds into less hydrated. This difference between carbonic medium and the medium of other known hydraulic materials, by which water molecules enter chemical reaction allows to determine carbonate-crystallization as a "hydraulic system", as water in both cases plays the integrating role and enters into the compounds on one of the reaction stages.

The additional theoretical research is well-founded and is possible due to low concentrations of carbonic gas in the environment. By enlarged concentrations of CO_2 in the humid lime test, as a result of dissolution of carbon dioxide in the water invariably carbonate acid will form, which being two-based by the interaction with calcium hydroxide gives two salts: middle – calcium carbonate $CaCO_3$ and acid – calcium hydrocarbonate $Ca(HCO_3)_2$ [Doronin 1962, Karapetyanc 1994]. Calcium carbonate is formed in relation to the lack of carbonate acid (carbonic gas), calcium hydrocarbonate is formed in relation to the excess of carbonate acid (carbonic gas) by the reaction:

$$CaCO_3 + CO_2 + H_2O = Ca\left(HCO_3\right)_2 . \tag{3}$$

As far as the experiments were carried out by us in relation to 100 % of concentration of CO_2 with the aim of confirmation of the supposition of the forming of calcium hydrocarbonate in the studied system, the chemical analysis by the method [Kremkov 1976] determined possible contents of the present new formation in carbonated samples (Tab. 3).

Table 3. Contents of calcium hydrocarbonate in carbonated samples

Conditions of getting samples		Contents of $Ca(HCO_3)_2$, %, by carbonization during, s			
P, MPa	*W*, %	3600	10800	21600	64800
15	15	35,5	38,0	36,5	32,0
15	22,5	32,5	40,0	25,0	22,0

The data of the chemical analysis of calcium hydrocarbonates contents in carbonized samples conform to the results of calculation of carbonization degree. The maximum amount of $Ca(HCO_3)_2$ is formed in the system during three hours of carbonization, which is expressed by the noticeable growth of mass of experimental samples. With the increase of duration of carbonization of lime test the amount of new formation of $Ca(HCO_3)_2$ is reduced.

The research of carbonization products of lime test were carried out with the help of differential-thermal analysis. As the carbonization process goes from the outward layers of test lime and gradually moves deeper, the experimental samples are not similar in their structure and show the outward carbonated one as well as the inner one containing a significant amount of not over-carbonated lime. Over-carbonated layer and not over-carbonated part, determined by the way of drifting on the spirits solution phenolphthalein on cracks of experimental samples are shown in Fig. 2. In relation to this, the content of calcium carbonate was determined in different zones of the sample – on border of layers and in thec central part of experimental samples cylinders. The data of quantitative contents of $CaCO_3$ on border of layers and in the center of experimental carbonated samples are given in Tab. 4.

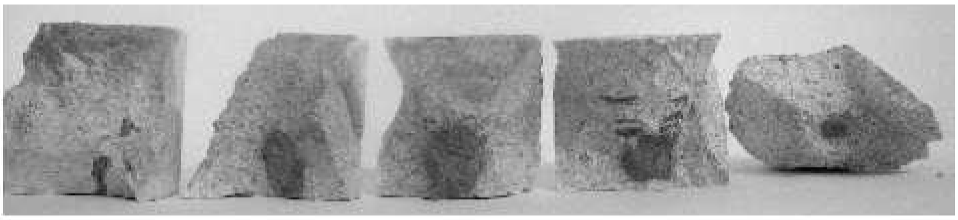

Fig. 2. The example of determination of carbonated (not coloured part) and not over-carbonated (coloured part) layers on cracks of experimental samples cylinders, got at $P = 5$ MPa from lime test by humidity (from left to right) 15,0, 17,5, 20,0, 22,5, and 25,0 % of mas.

It is determined that with the increase of time of carbonization of samples from lime test, contents of second calcium carbonate grows and by 64800 s of keeping reaches, depending on conditions of formation of sample cylinders, 80 %/ . It is most likely, that the lowering of contents of calcium hydrocarbonate in the system happens because of its transformation into calcium carbonate.

Table 4. Contents of calcium carbonate in experimental samples (by data of DTA)

Conditions of getting samples		Contents of $Ca(HCO_3)_2$, %, in samples carbonated during tests					
P, MPa	*W*, % of mas.	3600		21600		64800	
		border layer	center	border layer	center	border layer	center
15	5	59	64	68	75	77	77
15	20	70	71	80	77	80	75
25	5	73	36	80	75	80	80
25	20	65	10	68	46	71	71

So, the process of getting secondary calcium carbonate by the way of artificial carbonization of lime test by heightened concentrations of carbon dioxide may be introduced in such way. With the supply of carbonic gas into the carbonic chamber, instantaneous carbonization of lime test happens because the growth of temperature is fast in the carbonic chamber (from 293 to 345 K). This process is accompanied by the abundant isolation of water. As long as carbon dioxide is in excess, a part of it dissolves in the isolated water, as a result carbonic acid isolates, which enters the chemical reaction with newly-formed calcium carbonate and so calcium hydrocarbonate appears in the system. Calcium hydroxide present in the system also dissolves in the isolating water, forming solution of strong base, which by the known equation of chemical reaction of lowering of inflexibility of water neutralizes calcium hydrocarbonate. It decomposes with the collapse of calcium carbonate into unsoluble sediment:

$$Ca\left(HCO_3\right)_2 + Ca\left(OH\right)_2 = 2CaCO_3 + 2H_2O. \tag{4}$$

From the carried out theoretical and practical researches it may be seen that the process of formation of secondary calcium carbonate by artificial carbonization of lime test is not monosemantic and is connected with the formation of different intermediate compounds: hydrated calcium carbonates of different hydration degrees and of calcium hydrocarbonate. These processes may proceed in the carbonated system at the same time or take turns in relation to concentration of carbon dioxide and also to the presence of free water in the system. So, the structure of material, obtained from lime test of carbonic firmness, may include $Ca(OH)_2$ $CaCO_3 \cdot xCa(CO)_2 \cdot yH_2O$ and $Ca(HCO_3)_2$ molecules, connected with calcium carbonate.

The similarity of $CaCO_3$ calcite and $Ca(OH)_2$ portlandite in the sense of their belonging to the same crystal grid brings an assumption of similarity of their fields of force, which leads to an increase of durability of the carbonated system. The durability to pressure of experimental samples after keeping them in the medium of carbonic gas during 3600 s exceeds the durability of samples before carbonization by 3 times on average, during 10800 s – in 5,5 time, during 21600 s – in 7 times, during 64800 s – in 8,5 times and reaches 35 MPa in relation to the initial humidity of lime test and unit pressure of pressing. The ratio of softening reaches 0,8–0,9, which allows us to classify the derived materials as waterproof.

CONCLUSIONS

1. The process of curing of lime test in the medium of carbon dioxide for an account of carbonate-crystallization at the determined stage of structure formation may be considered as hydratational, because it is accompanied by formation of hydrate carbonate of different degree of hydration and calcium hydrocarbonate with their gradual transformation into calcium carbonate.

2. The structure of material obtained on the basis of carbonated lime firming includes $Ca(OH)_2$, $CaCO_3 \cdot xCa(CO)_3 \cdot yH_2O$ and $Ca(HCO_3)_2$ molecules, connected with calcium carbonate. The connections formed between these compounds with calcium hydroxide and calcium carbonate determine high durability of the obtained material's structure.

3. The artificial carbonization of lime test allows to get durable and waterproof artificial stone with the durability to pressure of 35 MPa and ratio of softening more than 0,8 in short terms.

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UDOWODNIENIE ZASAD SZTUCZNEGO UWĘGLANIA WAPNA W TECHNOLOGII STAŁOFAZOWYCH MATERIAŁOW BUDOWLANYCH

Streszczenie. Badania teoretyczne oraz empiryczne dowodzą, że powstawanie wtórnego węglanu wapnia podczas karbonatyzacji kitu wapiennego jest procesem złożonym i wiąże się z powstawaniem różnych związków pośrednich: uwodnionionego węglanu wapnia o różnych stopniach hydratyzacji oraz wodorowęglanu. Procesy te mogą zachodzić symultanicznie podczas karbonatyzacji lub naprzemiennie w zależności od stężenia dwutlenku węgla oraz od dostępności niezwiązanej wody w systemie. Powiązania powstałe pomiędzy tymi związkami a wodorotlenkiem wapnia i węglanem wapnia zapewniają wysoką wytrzymałość struktury otrzymywanego materiału.

Słowa kluczowe: wapno, dwutlenek węgla, karbonatyzacja, węglan wapnia, wodzian weglanu wapnia, wodorowęglan, struktura