Alternative approach to the organization of hardening of dolomite binding materials

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Abstract. The results of experimental studies to determine the possibility of organizing the carbonate hardening of the dolomitic binder resulting from calcination of dolomite are presented. The optimum temperature of calcination of this type of raw material for obtaining a dolomitic binder with a high reactivity is established. The physicomechanical characteristics of the test samples that have been hardening in the medium ofhigh carbon dioxide concentration are determined. A forecast regarding the possibility of applying the results obtained in the production of building materials and carbonization hardening productsis made.

1. Introduction

One of the priority directions of development of science and technology is rational nature management, as well as resource and energy saving. This direction can be fully realized in the construction materials industry due to the use of less energy-intensive binders in the production from available raw materials and products based on them. Such raw materials include dolomite rocks which are one of the most widespread and insufficiently mastered varieties of mineral raw materials.They can be used for the production of various types of magnesia binding materials and building materials and products based on them. However, at present such binders are practically not manufactured by industry. Features of obtaining high-quality mineral binders from high-magnesia raw materials – magnesites and brucites, are known, but these rocks are a strategic raw material for the production of refractories. Therefore, it is of interest to develop a binding substance of carbonate hardening based on dolomite raw materials, deposits of which are widely distributed.

2. Analysis of publications, materials, and methods

Depending on the firing temperature, it is possible to obtain from dolomite binders of various composition and purpose:

   - caustic dolomite consisting of MgO and $CaCO_3$ obtained by calcining dolomite at temperatures up to 750°C;

   - dolomitic cement consisting of MgO, $CaCO_3$ and CaO obtained by calcining dolomite at temperatures up to 850°C;

   - dolomitic lime consisting of MgO and CaO obtained by soft calcining of dolomite at temperatures up to 950°C.

   At present, domestic [1, 2] and foreign [3, 4] scientists are conducting scientific research on the development of quality mineral binding materials from dolomite raw materials by obtaining caustic

dolomite and studying the characteristics of chemical processes that occur during its hardening in the presence of solutions of magnesium salts. The studies have shown that for this it is needed to decompose the magnesium component of the raw material ($MgCO_3$) to MgO at certain temperatures and exclude the formation of CaO in it. Such binders have high mechanical strength and rapid growth in the initial period of hardening, an increased bending strength index, compared with other binders, high adhesion strength with fillers in the manufacture of magnesian concretes and solutions, and also a sufficiently high corrosion resistance [1, 2]. However, this material also has disadvantages which are expressed in insufficiently high water resistance and the appearance of internal stresses in the solidified material which cause the destruction of products.

The properties of magnesian binders obtained by magnesian rocks (magnesite, brucite, dolomite) and subsequent grinding are determined by the activity of magnesium oxide (periclase). In this case, magnesium oxide obtained at low temperature (up to 600°C), the so-called underburner, is a loose, rapidly hydrating powder. With an increase in the firing temperature above 800°C, magnesium oxide exhibits crystal growth and an increase in density, then MgO passes into a low-active form, an overburner, and the rate of hydration of such a binder decreases drastically. That is why, such binders, both of highly active and low-active forms cannot be used in the production of building materials and products because of the propensity of the magnesian stone to crack. In addition, the material consisting of an underfired binder has a very low water resistance and cracks already in the first few days after its mashing, and material from the binder containing an increased amount of overburns forms cracks after prolonged hardening [5, 6].

Therefore, the main objective of the technology for the production of binder from dolomitic raw materials is reduced to the selection of a strictly defined firing regime which is characterized by a fairly narrow range of temperature variation which makes it difficult to industrialize this binder (caustic dolomite) which should be based on medium-crystallized and medium-active MgO. This especially complicates the production in rotary kilns, the range of temperature fluctuations in which reaches 50-60°C.

An alternative solution to this problem may be the production of a binder from dolomitic raw materials that does not require strict temperature limits in the firing zone and the organization of hardening of products based on it in an environment with a high concentration of CO_2 (by artificial carbonization). Interest in the process of artificial carbonization of lime binders and the production of artificial carbonate stone as a result arose at the beginning of the 20th century and was actively studied in the middle of the last century [7–9]. In most cases, the scientific interest in the carbonization process was reduced to the problem of how to prevent the active carbonation of free calcium hydroxide in concrete causing carbonation shrinkage and to increase the durability of building products and structures [10, 11].

Not a lot of scientists were engaged in the study of the carbonization of dolomitic lime. Professor N.N. Mikhailov proposed using carbonization to increase the activity of the dolomitic binder [12]. As a result, the strength of the samples made from the solution on pure dolomite, after 7 days of hardening in air reached 9.2 MPa, and after carbonization – 19.5 MPa. In the solution with sand 1:3 of plastic consistency, the strength of the samples was 4.4 at natural hardening, and after carbonization – 27.8 MPa.

According to research by P.P. Budnikov and K.E. Goryainov [13] who studied the process of corrosion of mineral-cotton fibers in an alkaline medium, the carbonization of dolomitic lime is divided into two periods. The first period corresponds to the absorption of the CO_2 necessary for the carbonation of calcium hydroxide, the second period – for magnesium hydroxide. The process of carbonate hardening takes place in the diffusion region in a liquid medium and is determined by the amount of carbon dioxide flow. In this case, a pronounced reaction front arises that moves in the sample in the direction of the gas flow. Carbonization of mineral wool products on a dolomite binder at a thickness of 80-100 mm was completed within 30-45 minutes.

However, the obtained separate positive results on the artificial carbonization of dolomitic binders have not found wide distribution in the production of building materials and products, but allow judge

the presence of a significant potential of this binder for the construction industry. The analysis of literature sources led to the conclusion that studies aimed at studying the interaction of CO_2 with dolomite binders were carried out mainly on cast systems with a large amount of water. Of particular interest are systems for producing products by pressing.

3. Purpose and statement of the research task

In connection with the foregoing, the purpose of this work is to determine the possibility of obtaining high-quality construction products based on dolomite binder of carbonate hardening, by establishing the patterns of interaction of carbon dioxide with dolomite binder, the formation of physico-mechanical properties of the material after its artificial carbonization and stability of the properties obtained in time.

4. The main section with the results and their analysis

For the studies dolomite produced in the quarry 'Kamennye Bornitsy' of the Leningrad Region (OJSC 'Dolomite Quarries' with a fraction up to 10 mm was used. Chemical analysis of the raw material was carried out using X-ray fluorescence analysis on an ED spectrometer Epsilon 3XLE (PANalytical). The results of the analysis are presented in Table 1.

**Table 1.** Chemical composition of dolomite

Title	Content, %							
	CaO	MgO	SiO_2	Al_2O_3	Fe_2O_3	MnO	K_2O	TiO_2
Dolomite	25.77	20.57	10.62	2.88	0.75	0.03	0.87	0.11

The mineral composition of the initial dolomite was determined using a system of high-temperature synchronous TGA/DTA/DSC analysis of STA 8000 by Perkin Elmer in the temperature range 30-1000°C at a heating rate of 10°C/min in a nitrogen medium (see Figure 1). The mineralogical composition of the initial dolomite raw material calculated by the results of thermal analysis is presented in Table 2.

Table 2. Mineralogical composition of the initial dolomite

Losses in the temperature range 450-840°C,%	Content of $MgCO_3$, %	Losses in the temperature range 840-1000°C, %	Content of $CaCO_3$, %	Admixtures, %
22.0-23.0	42.2-44.1	20.0-21.0	45.5-47.8	up to 13

The thermal analysis data are in complete agreement with the results of X-ray fluorescence analysis in terms of the determination of calcium and magnesium oxides, which mainly determine the binding properties of this type of raw material. According to the data of the thermal analysis (see Figure 1), on the presented thermogram there are two pronounced endothermic effects at temperatures of 827°C and 880°C which correspond to decomposition of magnesite and calcite constituents of dolomite. The temperature range of dissociation of the magnesite component is 800-845°C, calcite – 845-925°C. The horizontal area on the TG curve is not observed between these two effects, which indicates that the processes of decomposition of the dolomite constituents are superimposed on each other. Consequently, it is impossible to obtain a product from this rock after firing with a fully decomposed magnesite component without decomposition of calcite.
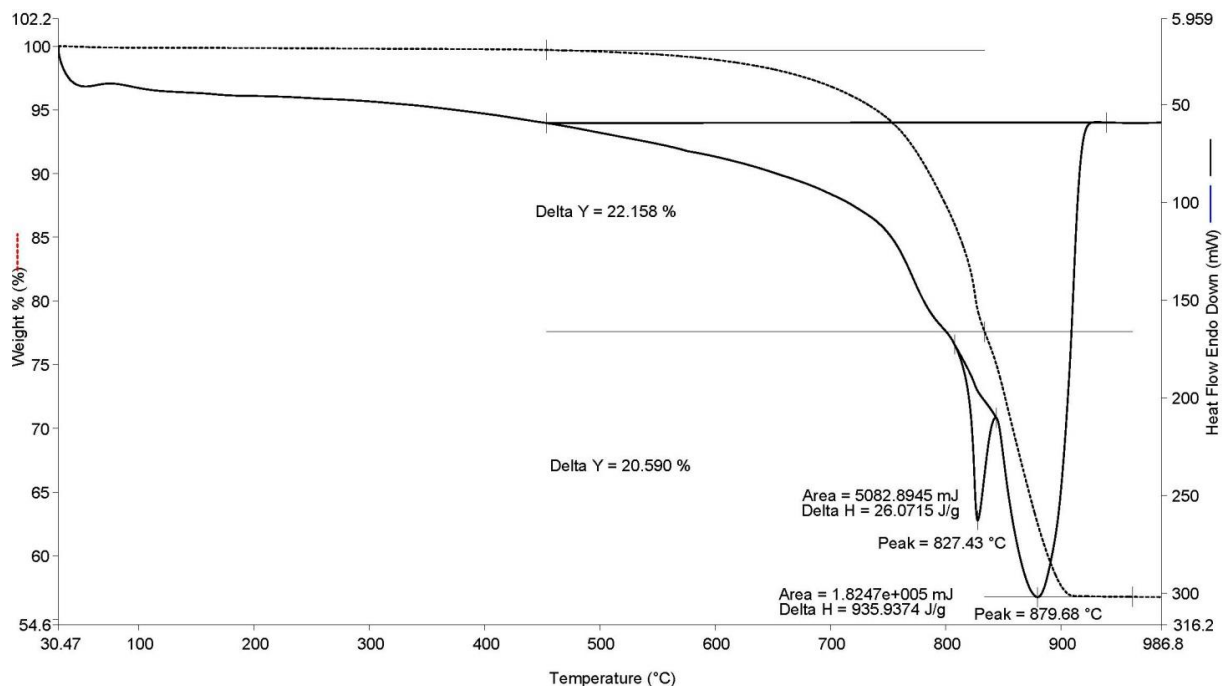
Figure 1. Thermogram of a sample of dolomite from the Bornitsy deposit

According to earlier studies [14-16], $Ca(OH)_2$ enters the active chemical interaction with carbon dioxide, while the water content of the system must be optimal. Under such conditions, the transition of $Ca(OH)_2$ to $CaCO_3$ takes no more than 3 hours, and the obtained artificial carbonate stone is characterized by considerable physical and mechanical properties and can be used for the production of various construction products, including facing products.

Due to the lack of detailed information in the literature on the mechanism of interaction of $Mg(OH)_2$ with CO_2, it was decided to fire this dolomite at the temperature corresponding to the maximum decomposition of the magnesite component, and close the resulting firing product with water to obtain a dolomite binder, followed by the organization of its carbonate hardening. The dolomite was fired in a laboratory muffle furnace of SNOL 6,7/1300 for 45 minutes.For calcination, a fraction of dolomite of 5-10 mm was used. The calcined product was ground before passing through a 1.25 mm sieve and closed with water. From the binder obtained after quenching and drying, the pressing method was used to prepare prototype cylinders. The diameter and height of the samples were 30 mm. The water content of the molding mixture ranged from 0 to 24% mac., the specific pressing pressure was 30 MPa.

According to the results of thermal analysis (Figure 1), dolomite was fired in a muffle furnace at a temperature of 820°C. Firing at a temperature of 820°C should give a material with a maximum content of MgO and a minimum of CaO, and the bulk of the calcite component should remain as $CaCO_3$. The results of the thermal analysis of such a binder after quenching and drying are shown in Figure 2.
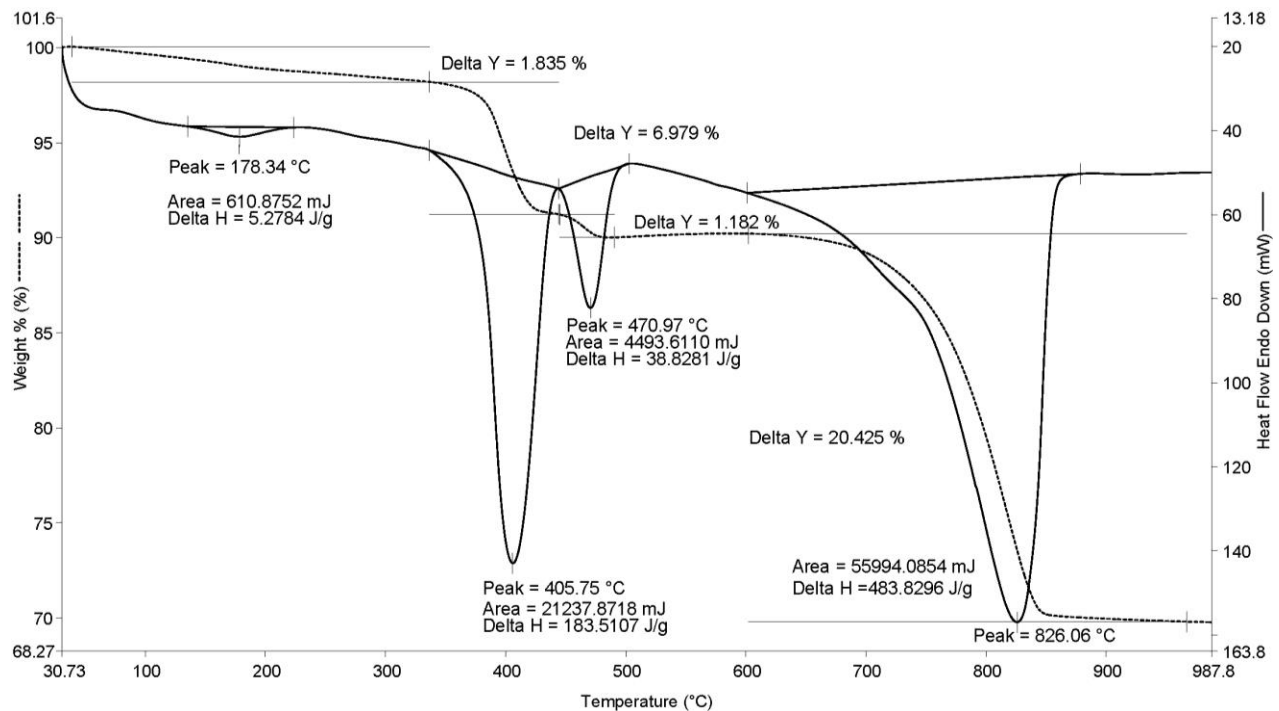
Figure 2. Thermogram of the dolomite binder obtained at 820°C after its quenching and drying

The binder, obtained at 820°C, has three pronounced endothermic effects: the first with a maximum at 406°C corresponds to the dehydration of $Mg(OH)_2$, the second at 471°C – to dehydration of $Ca(OH)_2$, the third at 826°C – to the dissociation of the carbonate calcium. The mineralogical composition of the dolomite binder obtained, calculated from the results of thermal analysis, is shown in Table 3. Minor endoeffect at 178°C with a weight loss of 1.84%, corresponds to the removal of adsorption water.

Table 3. Mineralogical composition of dolomite binder obtained at 820°C

Losses in the temperature range 350-450°C,%	Content of $Mg(OH)_2$, %	Losses in the temperature range 450-520°C, %	Content of $Ca(OH)_2$, %	Losses in the temperature range 520-980°C, %	Content of $CaCO_3$, %
6.98	22.7	1.18	4.9	20.43	46.4

Artificial carbonization of prototype cylinders obtained from this binder was carried out in a special chamber [17] without excess pressure and temperature increase. The CO_2 concentration in the carbonization chamber was maintained in the range of 30-35%. The carbonization time was 90 minutes. After the carbonization time had expired, the samples were dried to constant weight and their physical and mechanical properties were determined in accordance with regulatory standards. The mechanical characteristics of the prototypes were determined on an automatic test system based on the MCC8 (Controls) control console. The results of the tests are shown in Table 4.

**Table 4.** The physico-mechanical properties of the test samples, depending on the conditions of production

N.	Conditions for obtaining		Properties of test samples before carbonization			Properties of test samples after carbonization		
	Pressing pressure, MPa	Water content of the mixture, %	compressive strength, MPa	density, kg/m^3	water absorption, %	compressive strength, MPa	density, kg/m^3	water absorption, %
1		0	4.0	1494	24.9	4.2	1494	24.8
2		6	9.3	1535	24.1	13.3	1612	21.9
3	30.0	12	12.7	1545	23.8	26.7	1641	20.3
4		18	12.2	1551	23.0	31.7	1655	19.1
5		24	4.1	1536	24.7	4.0	1536	24.7

Analyzing the values of the compressive strength data of Table 4, it can be concluded that the active carbonization process takes place in the range of the initial water content of the mixture of 6-18 % mac., as evidenced by the increase in the strength of carbonized samples by 1.4-2.6 times in comparison with samples without carbonization. The average density of carbonized samples is also increased by 5-6%, in this case to a greater extent for samples with a water content of 12 and 18 % mac. and water absorption decreasesby mass. The graph of the change in compressive strength of the samples before and after carbonization is shown in Figure 3.
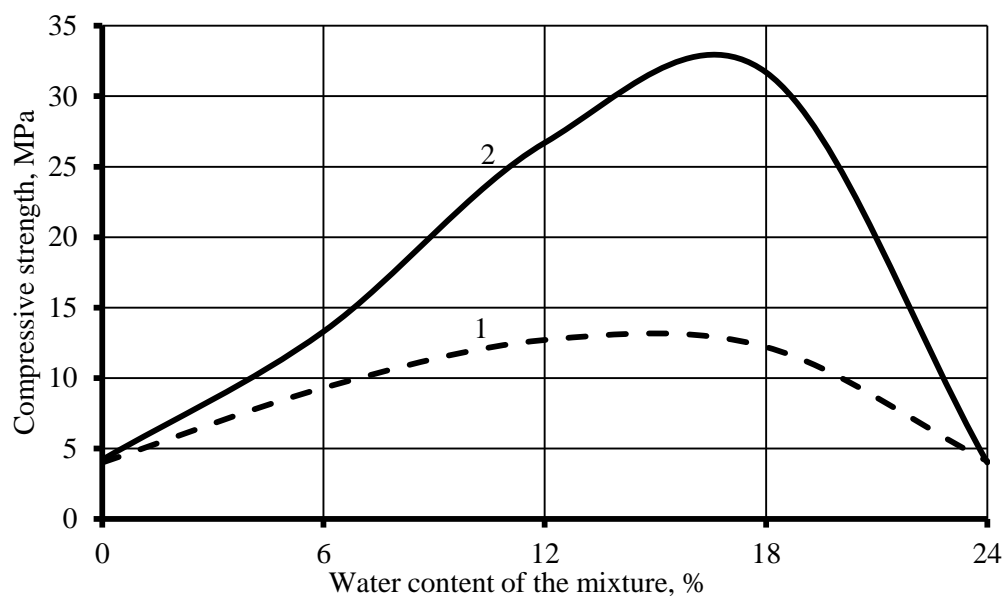
Figure 3. The change in compressive strength of the samples before and after carbonization, depending on the initial water content of the mixture: 1 – before carbonation, 2 – after carbonization

It should be noted that the characteristics of samples with zero humidity and humidity over 24% mac. do not change, which indicates that there is no chemical reaction of carbonization in the sample material. To determine the qualitative and quantitative process of the carbonization reaction, a thermal analysis of the carbonized material of samples obtained at a water content of a mixture of 18% was carried out. The results are shown in Figure 4.
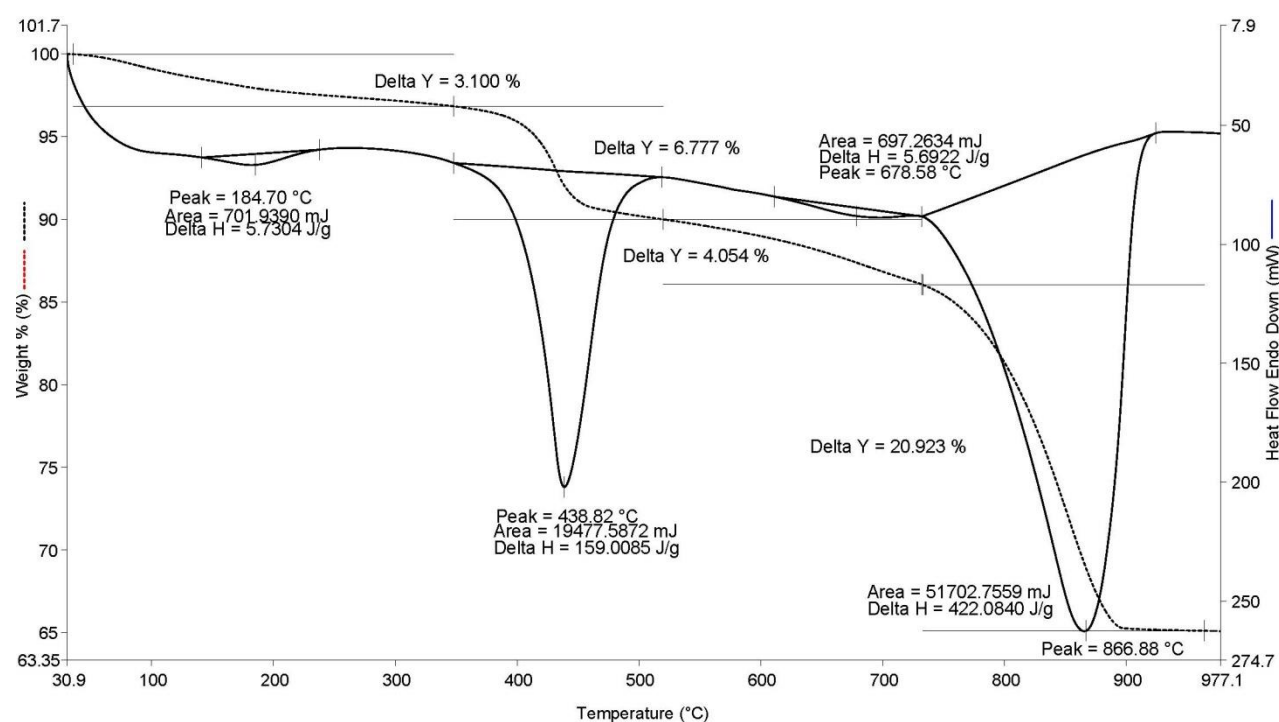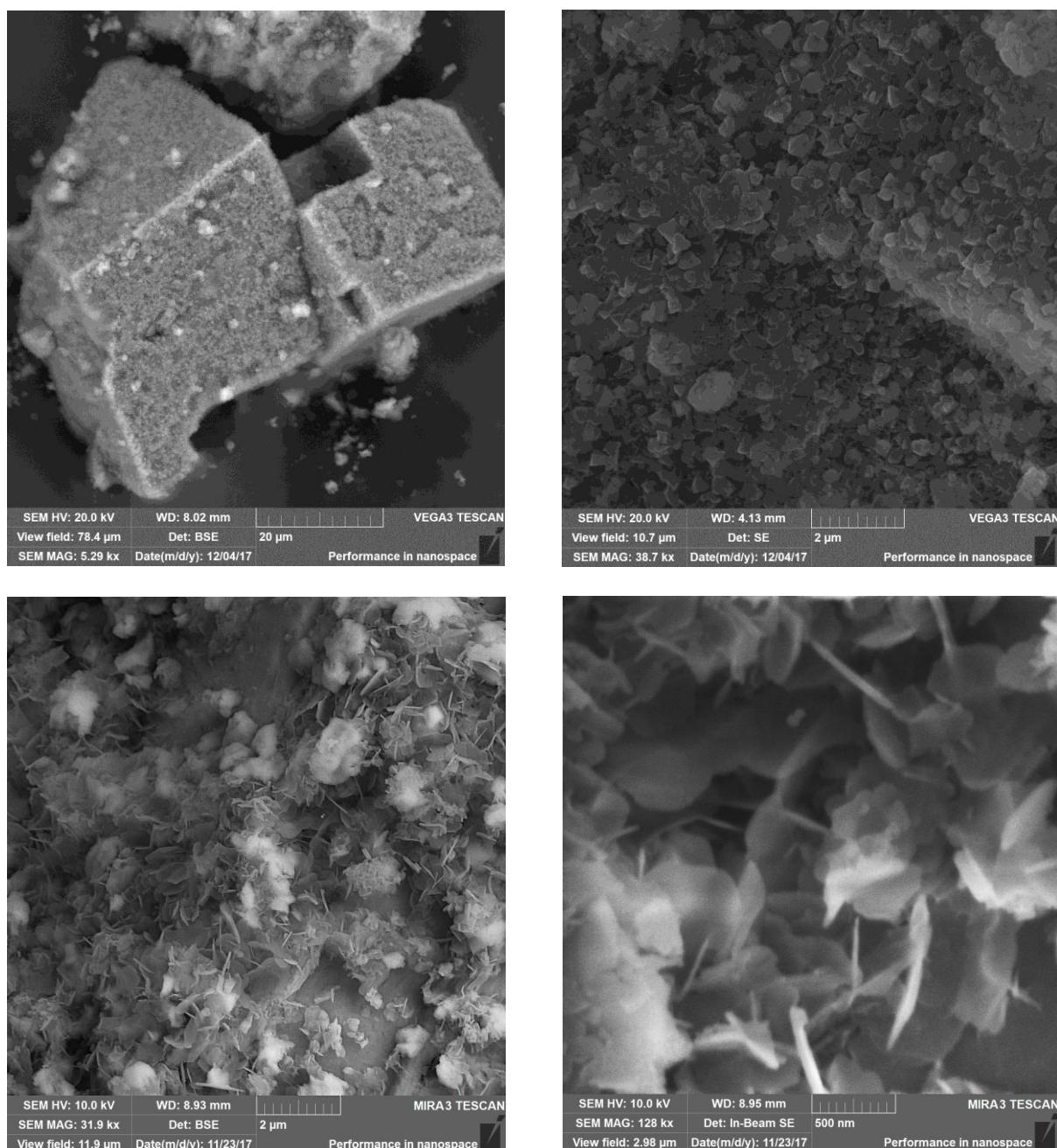

Figure 4. Thermogram of the carbonized material of the samples obtained at the initial water content of the mixture of 18%

The thermogram shown in Figure 4 is characterized by the presence of two endoeffects. The first at a temperature of 439°C corresponds to the decomposition of $Mg(OH)_2$, the second at 867°C – to $CaCO_3$. Comparing the results of the thermal analysis before and after carbonization (Figure 2 and Figure 4), it can be concluded that magnesium hydroxide practically does not enter carbonation reaction. It should be noted that the mass loss in the temperature range 370-520°C, which characterizes the dehydration of $Mg(OH)_2$, is reduced by 0.2%, which corresponds to a decrease in the magnesium hydroxide after carbonization by 0.7%. Accordingly, in Figure 4, an insignificant endoeffect appears in the temperature range 630-740°C, which characterizes the decomposition of 1.3-1.8% mac. of $MgCO_3$. At the same time, the total weight loss in the range of 520-740°C was 4.1%, which presumably indicates the presence of magnesium hydrogencarbonates in the system different in composition. The presence of the $Ca(OH)_2$ phase in the system after carbonization was not revealed, and the amount of $CaCO_3$ calculated from the mass loss in the range 740-950°C increased by an average of 2%, which agrees with the quantitative content of $Ca(OH)_2$ in the system prior to carbonation.

Thus, after carbonization of samples with an initial water content of 18% mac. within 90 minutes all of the calcium hydroxide found in the system as a result of interaction with carbon dioxide was converted to calcium carbonate. Attention is drawn to the fact that these carbonized samples have high strength at an average material density of 1655 kg/m3. The water absorption by volume characterizing the presence of open pores for these samples was 32.1%, and the softening factor was 0.6. Analyzing the amount of magnesium hydroxide reacted with CO_2, it can be concluded that under normal

conditions of this reaction, $Mg(OH)_2$ practically does not enter into a chemical reaction with the formation of the final product of the reaction – $MgCO_3$. This is apparently due to the very low solubility of magnesium hydroxide in water (0.0012 g/100 ml) compared to the solubility of calcium hydroxide (0.19 g/100 ml).

The structure of the carbonized samples was studied with a scanning electron microscope of the VEGA3 and MIRA3 series (TESCAN). The results are shown in Figure 5.

Figure 5. The microstructure of the carbonized material of the samples obtained at the initial water content of the mixture of 18%

The structure of the carbonized material is represented by plate crystals of $Mg(OH)_2$ located on a substrate of rhombohedral crystals of dolomite and calcite. The dimensions in the longitudinal and transverse directions of the $Mg(OH)_2$ crystals range from 0.2 to 1 μm. at a thickness of 20-70 nm. Dimensions of rhombohedral dolomite and calcite crystals range from 2 to 30 μm. Analyzing the data in Figure 5, it can be noted that as a result of artificial carbonization of samples from the dolomite binder obtained by burning dolomite at 820°C, a strong structure with crystals of various shapes and sizes is formed in which magnesium hydroxide probably serves as a reinforcing skeleton and calcium carbonate –as a binder matrix. In this case, the carbonized material has a sufficiently high open porosity and low density. The high compressive strengths obtained in a short time are explained by the fact that the undecomposed dolomite residues and its calcite component are probably active components that affect the structure formation of this system, acting as a 'substrate' for the oriented crystallization of the newly formed calcite on the surface of dolomite and calcite particles with the formation of strong cohesive contacts, thus creating a compact intergrown structure of calcite and dolomite crystals reinforced magnesium hydroxide crystals of unreacted carbonization.

5. Conclusions

The results obtained make it possible to conclude that the potential of dolomite raw materials in the production of building materials and products is not used to the full extent. An alternative approach to the organization of hardening of dolomitic binders in the construction industry can be the organization of hardening of products on their basis in an environment of increased concentration of carbon dioxide.The widespread introduction of such wasteless technology will reduce the environmental burden on the region with large reserves of fine-dispersed dolomite waste in dumps and reduce the emissions of CO_2 into the atmosphere, and will also contribute to the emergence of quality biopositive building products on the market for building purposes. At the same time, 800-850°C is sufficient for the production of such a binder resulting in the formation of a sufficient amount of binding phases in the form of oxides of Ca and Mg and their hydroxides, while the dolomite and calcite components that are undecomposed during firing will act as a filler. Carbonized material obtained in laboratory conditions for its physical and mechanical characteristics can be used for production of various wall products, including facing in industrial conditions.

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