# CHEMISTRY AND CHEMICAL ENGINEERING

Volume 2024 | Number 3

Article 3

September 2024

# INFLUENCE OF THE GRANULOMETRIC COMPOSITION OF CARBONATE ROCKS ON GLASS FORMATION PROCESSES IN FLOAT GLASS TECHNOLOGY

Sergey P. Grechuha Belarusian State Technological University, Minsk, Belarus Minsk, Belarus, spgrechuha@yandex.ru

Yury G. PAVLIUKEVICH Belarusian State Technological University, Minsk, Belarus, pavliukevitch@belstu.by

Ludmila F. PAPKO Belarusian State Technological University, Minsk, Belarus, papko@belstu.by

Olesya M. Mozhdzher Belarusian State Technological University, Minsk, Belarus, mozhdzher.olesya@mail.ru

Aleksandr P. Kravchuk Belarusian State Technological University, Minsk, Belarus, kravchuk@belstu.by

Follow this and additional works at: https://cce.researchcommons.org/journal

Part of the Materials Science and Engineering Commons

#### **Recommended Citation**

Grechuha, Sergey P.; PAVLIUKEVICH, Yury G.; PAPKO, Ludmila F.; Mozhdzher, Olesya M.; and Kravchuk, Aleksandr P. (2024) "INFLUENCE OF THE GRANULOMETRIC COMPOSITION OF CARBONATE ROCKS ON GLASS FORMATION PROCESSES IN FLOAT GLASS TECHNOLOGY," *CHEMISTRY AND CHEMICAL ENGINEERING*: Vol. 2024: No. 3, Article 3. DOI: https://doi.org/10.70189/1992-9498.1634 Available at: https://cce.researchcommons.org/journal/vol2024/iss3/3

This Article is brought to you for free and open access by Chemistry and Chemical Engineering. It has been accepted for inclusion in CHEMISTRY AND CHEMICAL ENGINEERING by an authorized editor of Chemistry and Chemical Engineering. For more information, please contact zuchra\_kadirova@yahoo.com.

## INFLUENCE OF THE GRANULOMETRIC COMPOSITION OF CARBONATE ROCKS ON GLASS FORMATION PROCESSES IN FLOAT GLASS TECHNOLOGY

Sergey P. GRECHUHA (spgrechuha@yandex.ru) Yury G. PAULIUKEVICH (pavliukevitch@belstu.by) Ludmila F. PAPKO (papko@belstu.by) Olesya M. MOZHDZHER (mozhdzher.olesya@mail.ru) Aleksandr P. KRAVCHUK (kravchuk@belstu.by) Belarusian State Technological University, Minsk, Belarus

The aim of this work is to study the influence of the granulometric composition of dolomite and limestone of 0.1-1.0 mm, 1.0-1.6 mm, 1.6-2.5 mm fractions on the rate of glass formation processes in the synthesis of float glass. The dependence of the degree of decarbonization of dolomite and limestone on the dispersion of particles and the time of heat treatment has been established. According to the study of the influence of the granulometric composition of carbonate rocks on the melting characteristic of float glass, it can be concluded that it is possible to use the 1.0-1.6 mm fraction of limestone or dolomite. The combined introduction of coarse-grained carbonates reduces the homogeneity of the batch and slows down the glass melting process.

Keywords: carbonate rock, decarbonation kinetics, glass formation, float glass

## ИССЛЕДОВАНИЕ ПРОЦЕССА ПЕНООБРАЗОВАНИЯ ПРИ АЗОТНОКИСЛОТНОМ РАЗЛОЖЕНИИ ДОЛОМИТОВОГО СЫРЬЯ

Сергей П. ГРЕЧУХА (spgrechuha@yandex.ru) Юрий Г. ПАВЛЮКЕВИЧ (pavliukevitch@belstu.by) Людмила Ф. ПАПКО (papko@belstu.by) Олеся М. МОЖДЖЕР (mozhdzher.olesya@mail.ru) Александр П. КРАВЧУК (kravchuk@belstu.by) Белорусский государственный технологический университет, Минск, Беларусь

Целью работы является проведение исследования влияния гранулометрического состава доломита и известняка фракций 0,1–1,0 мм, 1,0–1,6 мм; 1,6–2,5 мм на скорость процессов стеклообразования при синтезе листового стекла. Установлена зависимость степени декарбонизации доломита и известняка от дисперсности частиц и времени термической обработки. По результатам исследования влияния еранулометрического состава карбонатных пород на варочные свойства листового стекла можно заключить о возможсности использования известняка либо доломита фракции 1,0–1,6 мм. Совместное введение крупнозернистых карбонатов снижает однородность инхты и замедляет процессы стекловарения.

Ключевые слова: карбонатная порода, кинетика декарбонизации, стеклообразование, листовое стекло

### DOLOMIT XOM ASHYOLARINING NITRAT KISLOTALARIDA PARCHALANISHIDAN KO'PIK HOSIL BO'LISH JARAYONLARINI O'RGANISH

Sergey P. GRECHUHA (spgrechuha@yandex.ru) Yuriy G. PAVLYUKEVITCH (pavliukevitch@belstu.by) Lyudmila F. PAPKO (papko@belstu.by) Olesya M. MOZHDZHER (mozhdzher.olesya@mail.ru) Aleksandr P. KRAVCHUK (kravchuk@belstu.by) Belarus davlat texnologiya universiteti, Minsk, Belarusiya

> Ishning maqsadi dolomit va ohaktoshning granulometrik tarkibi 0,1-1,0 mm, 1,0-1,6 mm, 1,6-2,5 mm bo'lgan fraksiyalarining listli shisha sintezida shisha hosil bo'lish jarayonining tezligiga ta'sirini o'rganishdir. Dolomit va ohaktoshning dekarbonizatsiya darajasi zarrachalarning tarqalishiga va issiqlik bilan ishlov berish vaqtiga bog'liqligi aniqlangan. Karbonatli jinslarning zarracha kattaligi taqsimotining pishirish xususiyallariga ta'sirini o'rganish natijalariga ko'ra, ohaktosh yoki 1,0-1,6 mm fraktsiyali dolomitdan foydalanish mumkin degan xulosaga kelish mumkin. Dag'al donali karbonatlarning birgalikda kiritilishi omixtaning bir xilligini pasaytiradi va shisha erish jarayonini sekinlashtiradi.

Kalit soʻzlar: karbonat jinsi, dekarbonizatsiya kinetikasi, shisha hosil bo'lishi, qatlamli shisha

#### DOI: 10.34920/cce202433

3'2024

#### Introduction

The characteristics of raw materials – chemical and phase composition, dispersion – have a profound effect on the glass melting processes: the sequence and kinetics of phase transformations, the melting point of eutectic compositions, the thermal conductivity of the batch, the heat-absorbing capacity of the glass melt [1, 2].

In industrial glassmaking, much attention is paid to the energy efficiency in production, which

is influenced by many factors, including the choice of raw materials. The batch formulation should ensure the reduced energy consumption in the glass synthesis. Technological and economic aspects of glass production are also important [3–6].

Rational selection of the granulometric composition of raw materials is among important tasks of glass melting. The grain size of the batch components affects the rate of silicate and glass formation processes, and the processes of mixing

LI M YOU UNIT

the batch and its homogeneity [7-11].

The problem of choosing the granulometric composition of raw materials most relates to silica sand, while, however, there is no uniform approach to choosing grain composition of carbonate rocks. A common practice in industrial glass melting is the use of fine particle fractions of dolomite and limestone (0.1–1.0 mm). At the same time, it is known that these materials are used in larger sizes (coarse-grained materials 1–3 mm), and they are known to have a positive effect on the process of homogenization of glass melt. The use of coarse-grained carbonate rocks is however possible with a limited content of siliceous impurities [7, 8].

The grain size of carbonate rocks can influence the rate of processes in the batch, in particular, the rate of phase transformations. In case of solid-phase reactions, the packing of the batch particles is important, since reactions occur on the surface of grains and an increase in their size can have a negative impact on the rate of silicate formation processes.

Carbonate grain size can also affect the rate of decarbonation. The rate of carbonate decomposition, in turn, affects the reactivity of decarbonized particles. In addition, the temperature range of carbon dioxide emissions can influence the processes of melt homogenization.

To assess the influence of the granulometric composition of carbonate rocks on the melting characteristic of float glass, the study of the kinetics of the decarbonization process of dolomite and limestone was carried out, which included determining the decomposition rate and activation energy of the process, study of the influence of the granulometric composition of carbonate rocks on the processes of silicate and glass formation and quality of float glass synthesized using carbonate rocks of various granulometric compositions.

#### **Research methods**

The following materials were used in the study:

- carbonate rocks - dolomite and limestone of various fractional compositions (0.1-1.0 mm; 1.0-1.6 mm and 1.6-2.5 mm);

- a batch of float glass composed using the specified carbonate rocks, silica sand (OBC-030-B), soda ash (grade A) and feldspar (Table 1).

Heat treatment of the batch was carried out in a batch-type gas furnace at a rate of temperature rise of 250 °C/h at temperatures between 700 °C and 1500 °C in increments of 100 °C at exposure for 0.5 hours. The gas environment is oxidizing with an excess air ratio of 1.08–1.13. The crucibles were removed from the furnace, and, after their cooling, the quality of the weld was visually assessed. At a heat treatment temperature of 1500 °C, a homogeneous melt was obtained, which was produced by casting in the form of plates.

Chemical analysis of carbonates performed by using LEA-S500 laser analyzer. For analysis, the sample was ground to a powdery state in a PUL-VERISETTE 5 Classic line planetary mill and pressed into tablets.

The differential scanning calorimetric (DSC) measurements have been performed by METTLER TOLEDO Instruments TGA/DSC-1/1600 HF. The heating range was up to 1000 °C at a speed of 10 K/min.

The gasometric method was used to study

Table 1

No. of glass batch	Granulometric composition of carbonates, mm		Glass batch calculation		
	Dolomite	Limestone	parts by weight per 100 parts by weight of glass		
1	0.1 - 1.0	0.1 - 1.0			
2	1.0 - 1.6	0.1 - 1.0			
3	1.6 - 2.5	0.1 - 1.0	Silica sand + Soda ash +	97.24	
4	0.1 - 1.0	1.0 - 1.6	Feldspar		
5	0.1 - 1.0	1.6 - 2.5	Limestone + Dolomite	23.58	
6	1.0 - 1.6	1.0 - 1.6	]		
7	1.6 - 2.5	1.6 - 2.5			

Granulometric composition of samples and composition of the glass batch

the kinetics of the decarbonization process of dolomite and limestone. The studies were carried out under isothermal conditions at temperatures of 900 and 1000 °C. Carbonate rocks were placed in a ceramic boat-like container and installed in a quartz reactor in a tubular laboratory furnace SNOL 0.25.1/12. The rate of carbonate decomposition was determined by the rate of carbon dioxide emission.

Optical microscopy was performed by using Nikon H600L microscope, designed for studying the microstructure and texture of objects in reflected light.

SEM/EDS measurements have been performed by JED-2201 system, working with JSM-5610 LV (JEOL) scanning electron microscope.

Raman spectroscopy was performed using a Confotec MR350 3D scanning laser microscope and 532 nm laser.

### **Results and Discussion**

Chemical composition of carbonate rocks is presented in Table 2.

The chemical composition of dolomite does not reveal a pronounced influence of the granulometric composition on the content of the main components. In a finely dispersed dolomite (fraction 0.1-1.0 mm), there is a higher content of impurity components – SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>. The influence of the granulometric composition of limestone on its chemical composition is as follows: as the grain size increases, the content of the main substance decreases, while the content of SiO<sub>2</sub> in samples of the 1.6–2.5 mm – before 3.72 wt.% fraction increases significantly. The insoluble residue in HCl is 9% for this sample, which indicates an increased content of silica materials. Limestone of the 1.6–2.5 mm fraction is consequently characterized by a high content of refractory inclusions and does not meet the requirements specified for its chemical composition.

According to the dolomite thermal analysis, there is no influence of the granulometric composition on the temperatures of the maximum endo-effects and the loss of mass of the material during decomposition. There is an increase in the rate of mass loss, determined from the differential curve during the decomposition of MgCO<sub>3</sub>, with increasing grain size.

An experimental study of the kinetics of the decarbonization process of dolomite and limestone was carried out to assess the influence of temperature and grain composition on the rate of their decomposition.

To describe the kinetics of the decomposition reaction of calcium carbonate, the B.V. Erofeev equation was used [12, 13]:

$$\alpha = 1 - e^{-kt^n}$$

where  $\alpha$  is the conversion, t is time from the start of the reaction, n is empirically determined exponent, k is reaction rate constant.

$$k = A \cdot e^{-\frac{E}{RT}} , \qquad (2)$$

Limyo texnologiyasi 3'2024

where A is preexponential factor; E is the activation energy, kJ/mol; R is the gas constant, 8.31 J/(mol<sup>+</sup>K)

Carbonate conversion ( $\alpha$ ) for different time intervals were determined graphically using Figure 1.

The kinetics of the decomposition process is influenced by such factors as the genesis of samples, grain dispersion, imperfection of the lattice structure, the presence of defects, impurity

Fraction	Oxide content, wt.%					IOI			
	SiO <sub>2</sub>	$Al_2O_3$	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	LOI			
Dolomite									
0.1-1.0	0.65	0.3	0.081	31.91	20.33	47.18			
1.0-1.6	0.38	0.11	0.053	33.17	19.69	47.10			
1.6-2.5	0.46	0.078	0.052	32.58	20.06	47.15			
Limestone									
0.1-1.0	0.82	0.06	0.023	53.07	1.76	43.59			
1.0-1.6	1.83	0.044	0.015	51.64	1.98	43.71			
1.6-2.5	3.72	0.045	0.026	48.54	2.3	40.48			

Chemical composition of carbonate rocks

Table 2

#### content, etc. [14-19].

According to modern concepts, the process of decomposition of calcium carbonate in limestone is heterogeneous and proceeds in several successive stages, namely, the crystal chemical transformation of CaCO<sub>3</sub> to CaO; CO<sub>2</sub> desorption is distinguished from the reaction surface; CO<sub>2</sub> diffusion into the core of the gas flow. According to the mechanism of these elementary stages, they can be combined into two groups: diffusion and adsorption-chemical or kinetic.

The reaction  $CaCO_{3(solid)} = CaO_{(solid)} + CO_{2(gas)}$  does not begin on the entire surface of the original solid, but at individual points, lines and areas, the so-called potential reaction centers, from where the reaction gradually spreads deep into the crystal. Reaction centers are places on the surface of the CaCO<sub>3</sub> where bonds with nearby particles are weakened. Such active places include the vertices of corners, edges and some points on the faces of the crystal. Areas with various types of surface defects are particularly reactive [13–19].

Since the process occurs only at the phase boundary, which is initially small, the speed of the process is low. As the nucleus is completed with new formations of calcium oxide, the phase interface at each nucleus increases and, consequently, the rate of the process also increases. The reaction front at each nucleus increases and then merges into a single reaction front. At this time, the speed of the process reaches its maximum. However, in so far as the pieces of calcium carbonate have finite sizes, the surface area begins to decrease down to zero from a certain point in time.

As already noted, the decomposition of

K I M YO va kimyo texnologiyasi

3'2024

calcium carbonate includes adsorption and chemical stages and diffusion stages, which occur sequentially. The observed speed of the process will be determined by the speed of its slowest stage. At low temperatures, when the energy of the reacting molecules is low, the slowest stage is the crystal chemical transformation, which occurs with considerable activation energy. At high temperatures, when the energy of the reacting molecules is significant, the slowest stage is the diffusion of  $CO_2$ from the reaction zone. This change in the rate ratio is implied by the different degree of influence of temperature on the rate of crystal chemical transformation and the rate of the diffusion process.

The effect of dispersion and firing temperature on the dissociation of carbonates in limestone is given in Figure 1.

The dependence of the degree of limestone decarbonization on the dispersion of particles and temperature indicates a different influence of temperature on different fractions of the material: for particles of 1.6-2.5 mm in size, the degree of decomposition, other things being equal, is lower than for fractions of 0.1 mm. For fractions of 0.1-1.0 and 1.0-1.6 mm, the process of particle decomposition looks like being controlled by both kinetic factors and the rate of heat supply. For large particles of 1.6-2.5 mm, the process is probably limited only by the supply of heat to the zone of the endothermic reaction, which proceeds frontally from the surface of the particle to its center. At the same time, under conditions of rapid heating of large particles of the 1.0-1.6 and 1.6-2.5mm fraction, an increase in the defectiveness of CaO crystals can be observed, which is associated



Figure 1. The effect of dispersion and firing temperature on the dissociation of carbonates in limestone.

CHEMISTRY AND CHEMICAL ENGINEERING

ХИМИЯ И ХИМИЧЕСКАЯ ТЕХНОЛОГИЯ



Figure 2. The effect of dispersion and firing temperature on the dissociation of carbonates in dolomite.

with the instantaneous dissociation of carbonates during thermal shock, during which the crystal lattice of the resulting calcium oxide does not have time to form a stable structure and has increased reactivity.

The thermal decomposition of dolomite occurs stepwise to form, at the first stage, calcite  $(CaCO_3)$  and magnesite  $(MgCO_3)$ , which immediately decomposes at a high rate into MgO and CO<sub>2</sub> with the formation of a mechanical mixture of magnesium oxide and calcium carbonate, the dissociation of which occurs at more high temperature [13, 20–28]:

 $CaMg(CO_3)_2 \rightarrow CaCO_3 + MgCO_3 \rightarrow CaCO_3 + MgO + CO_2 \rightarrow CaO + MgO + 2CO_2.$ 

Modern concepts of the mechanism of decomposition of magnesium and calcium carbonates do not significantly differ and are described using the example of  $CaCO_3$  above.

The dependence of the degree of dolomite

decomposition on the treatment time at a temperature of 900 °C and 1000 °C is given in Figure. 2.

A characteristic inflection in the decomposition curves of dolomite of the 0.1-1.0 mm fraction indicates a multi-stage process; for fractions of 1.0-1.6 and 1.6-2.5 mm, the effect is less pronounced, since as the dolomite grain warms up, the processes in the volume of the grain and on the surface may differ. The overall rate of the process will be determined by both the intensity of heat supply and the rate of thermal decomposition. In a certain temperature range, the rate of decomposition turns out to be commensurate with the rate of heat supply, and then the resulting value of the kinetics of the process is determined by the ratio of these factors.

The activation energy of the carbonate dissociation process was calculated using thermogravimetric curves of thermal analysis based on the formulas [29]

3'2024



$$\ln m - 2 \cdot \ln T = K_0 - \frac{E}{R \cdot T}, \quad (3)$$

where E is activation energy, kJ/mol; R is the gas constant, J/(mol·K); T is temperature, K; m – decrease in the mass of a substance determined by the TG curve, % (mg).

Graphs characterizing the kinetic parameters of the decomposition process of limestone and dolomite of different granulometric compositions, plotted in coordinates  $ln m - 2 \cdot lnT = f(1/T)$ are given in Figure 3.

The tangent of the angle of inclination of the resulting straight lines corresponds to the value of the activation energy.

Activation energy (E, J/mol), was calculated using:

$$E = K \cdot R \cdot 10^{-3} , \qquad (4)$$

where K is slope of curve.

It has been established that the activation energy level of limestone is within the range of 215–250 kJ/mol, while the higher the grain size, the higher the activation energy during dissociation. A similar dependence is seen for dolomite. The activation energy is in the range of 87–182 kJ/mol. The highest values of activation energy for the decarbonization process are typical for the 1.0–1.6 mm fraction.

Thus, during the heat treatment of the batch at temperatures close to the cooking temperature, almost instantaneous thermal dissociation of carbonates occurs. The resulting calcium oxide has a fine-crystalline defective structure and is characterized by increased activity.

According to the study of the influence of the fractional composition of carbonate rocks on glass melting processes, there is no influence of the granulometric composition on glass melting processes during heat treatment of the batch, and the grains of carbonate rocks visually retain their

3'2024 Kaimyo texnologiyasi

sizes. It is known that the liquid phase in the batch appears in the temperature range of 780–880 °C as a result of the melting of sodium carbonate, double carbonates  $Na_2Mg(CO_3)_2$  and  $Na_2Ca(CO_3)$  and eutectics between these compounds and  $Na_2CO_3$  [30–32].

In the temperature range of 1100–1400 °C, active dissolution of silica grains occurs; on the surface of the melt of all samples, there is a continuous siliceous crust. A larger crust volume is characteristic of samples in which a 1.6–2.5 mm limestone fraction is used, as well as with the combined introduction of large grains of limestone and dolomite. When the batch was heat treated in a gas furnace at a temperature of 1500 °C, regardless of the fractional composition of the carbonates, a homogeneous melt containing a gas phase was obtained.

According to electron microscopy data, the original dolomite grains have a dense structure. When the dolomite decomposes, a porous structure is formed, and the pore size increases with the sequential decomposition of MgCO<sub>3</sub> and CaCO<sub>3</sub>. Microcracks appear that divide the grain into separate zones. Grains of limestone are loosened during heat treatment.

The results of studying the structure of batch 2 (dolomite fraction 1.0–1.6 mm, Table 1), as obtained by heat treatment at temperatures of 900 °C and 1000 °C using electron microscopy, are given in Figure 4.

The structure of the samples contains dolomite grains with a size of about 700–1000  $\mu$ m, which have a porous structure due to the decomposition of carbonates. At 900 °C at the grain boundary, the interaction of the batch components occurs with the formation of sodium silicate or Na<sub>2</sub>O×2CaO×3SiO<sub>2</sub>. According to microprobe analysis, the formation of calcium and magnesium silicates of non-stoichiometric composition is also



Figure. 4 – SEM images of Batch 2.

СНЕМІSTRY AND CHEMICAL ENGINEERING ХИМИЯ И ХИМИЧЕСКАЯ ТЕХНОЛОГИЯ



900 °C



1000 °C

Figure 5. SEM images of Batch 4.

recorded. Melting of eutectic mixtures leads to the formation of a glass phase. In the structure of samples processed at a temperature of 1000 °C, at the grain boundary CaO and MgO, the formation of magnesium and calcium silicates (light grains surrounding the grain of decarbonized dolomite) is recorded. Active melting of eutectics between silicates and the initial components causes an increase in the volume of the glass phase. Grains of decarbonized dolomite are preserved in the structure of the samples up to a temperature of 1100 °C. When the heat treatment temperature increases to 1200 °C and 1300 °C in the structure of the samples, the crystalline phase is represented only by residual silica grains. Using Raman spectroscopy, it was established that up to a temperature of 1200 °C silica is represented by quartz, at 1300 °C cristobalite, along with quartz, is recorded. At a temperature of 1400 °C, the crystalline phase is represented only by cristobalite.

The results of studying the structure of samples of batch 4 (limestone fraction 1.0-1.6 mm, Table 1), obtained as a result of heat treatment at temperatures of 900 °C and 1000 °C, are given in Figure 5.

The composition of grains at points 1 and 2 corresponds to CaO. Analysis at point 3 reveals the following grain composition, wt.%: 49.24SiO<sub>2</sub>; 32.80CaO; 18.51Na<sub>2</sub>O . At a heat treatment temperature of 1000 °C, the structure contains loose CaO grains with a size of about 1000 µm. Calcium silicate (light grains) is formed at the grain boundary; in particular, point 3 corresponds to the following composition, wt.%: 21,77SiO<sub>2</sub>; 78,23CaO. This composition may correspond to the formation of sodium calcium silicate of non-stoichiometric composition.

According to Raman spectroscopy data,

the phase composition of grains distributed in the glassy and gaseous phases corresponds to quartz (up to 1200 °C), which turns into cristobalite at a temperature of 1300 °C.

To assess the influence of the granulometric composition of carbonates on the quality of glass, the volume fractions of phases in samples synthesized in a gas furnace at a temperature of 1500 °C were determined. The sizes of gas inclusions vary within 0.1–0.3 mm. The volume fraction of the gas phase varies within 2.4–6.9 vol.%.

The relationship between the fractional composition of carbonate raw materials used for glass synthesis and the proportion of the gas phase in them is ambiguous. It must be taken into account that the temperature factor, and not the fractional composition of carbonates, has a decisive influence on the quality of glass melt in terms of gas phase content. It however seems possible to establish general trends in the influence of the granulometric composition and type of carbonate raw materials on the proportion of gas inclusions in the glass melt. The combined introduction of coarse-grained limestone and dolomite (fractions 1.0-1.6 and 1.6-1.25 mm) leads to an increase in the volume of gas inclusions (5.5-6.9 vol.%) in comparison with the base batch (5.4 vol.%). For glass based on batch into which only one coarsegrained material was introduced - dolomite or limestone of 1.0–1.6 and 1.6–2.5 mm fractions – a decrease in the proportion of the gas phase to 2.4-3.8 vol.% is observed. The antagonistic effect of the introduction of coarse-grained raw materials is probably associated with the packing density of particles in the powder mixture. Apparently, the use of dolomite and limestone of different fractional compositions makes it possible to increase the packing density of grains in the batch, in com-

3'2024

parison with a batch containing only coarsegrained carbonates, which increases the contact area of the reacting particles and the rate of reactions in the batch.

#### Conclusion

To rationally select the granulometric composition of carbonate rocks used in the production of float glass, studies of the technological properties of dolomite and limestone of the following fractional composition were carried out: 0.1-1.0 mm; 1.0-1.6 mm and 1.6-2.5 mm. Coarse -grained carbonate rocks were introduced into the mixture both separately and in combination with each other. In dolomite of the 0.1-1.0 mm fraction, traditionally used in industrial glassmaking, a higher content of impurity components (Fe<sub>2</sub>O<sub>3</sub>,  $SiO_2$ ,  $Al_2O_3$ ) was revealed. In the chemical composition of limestone, with increasing grain size, the content of the main substance decreases and the content of  $SiO_2$  to 3.72 wt.%. It has been established that during heat treatment, dolomite and limestone grains retain their sizes after the decarbonization process. According to electron microscopic research, a porous grain structure is formed, and microcracks appear that divide the

grain into separate zones. Based on the results of a study of the kinetics of the processes of decarbonization of dolomite and limestone it has been established that at temperatures of 900 and 1000 °C the thermal dissociation of carbonates occurs in 100-300 s. There is dependence of the degree of decarbonization on the particle dispersion and heat treatment time.

According to electron probe microanalysis at heat treatment temperatures of 900 °C and 1000 °C at the grain boundary containing CaO and MgO, the components of the batch interact with the formation of sodium, magnesium and calcium silicates of non-stoichiometric composition. At processing temperatures of 1200, 1300 and 1400 °C, the crystalline phase is represented only by quartz and cristobalite, glass formation processes are completed in the temperature range of 1400-1500 °C. Based on the study of glass formation processes and the quality of float glass, we can conclude that it is possible to use limestone or dolomite of the 1.0-1.6 mm fraction in float glass technology. The combined introduction of coarsegrained carbonates can reduce the homogeneity of the batch and, although to a small extent, slow down the glass melting process.

#### REFERENCES

- Schaeffer Helmut A. Allgemeine Technologie des Glases: Grundlagen des Schmelzens und der Formgebung. Institut für Werkstoff wissen-1. schaften III (Glas und Keramik), Universität Erlangen-Nürnberg, 1995. 306.
- 2. Li H. Alumina and silica sources for E-glass fiber manufacturing-melting energy aspect. Glass Tech.: Eur. J.Glass Sci. Tech. A, 2014, 55, 7 -13
- 3. Pierro S. D. Raw Materials for Glassmaking: Properties and Constraints, in: P. Richet, R. Conradt, A. Takada, J. Dyon (Eds.), Encyclopedia of Glass Science, Technology, History, and Culture, The American Ceramic Society, 2021, 39–51. DOI: 10.1002/9781118801017.ch1.2.
- ERAMIN Research Agenda. Available at: https://hal-insu.archives-ouvertes.fr/insu-00917653. (accessed May 2024) 4.
- Varshneya A.K., Mauro J.C. Fundamentals of Inorganic Glasses, 3rd ed, Elsevier Inc., 2019. 1-18. DOI: 10.1002/9781118801017.ch1.2 Hrma P., Schweiger M.J., Humrickhouse C.J., Moody J.A., Tate R.T., Rainsdon T.T., TeGrotenhuis N.E., Arrigoni B.M., Marcial J., Rodri-guez C.P., Tincher B.H. Effect of glass-batch makeup on the melting process. *Ceramics- Silikäty*, 2010, 54, 193. 6.
- 7. Manevich V.E., Subbotin K.Yu., Efremov V.V. Syrevye materialy, shihta i steklovarenie [Raw materials, batch and glassmaking]. Moscow, Strojmaterialy Publ., 2008. 224. (In Russ.).
- 8. Pankova N. A., Mihajlenko N. Yu. Stekolnaya shihta i praktika ee prigotovleniya [Glass batch and the practice of its preparation]. Moscow, Mendeleev Russian University of Chemical Technology Publ., 1997. 80. (In Russ.).
- Pankova N. A., Mihajlenko N. Yu. Teoriya i praktika promyshlennogo steklovareniya [Theory and practice of industrial glassmaking]. Moscow, Mendeleev Russian University of Chemical Technology Publ., 2000. 102. (In Russ.). 9
- 10. Guloyan Yu.A. Fiziko-himicheskie osnovy tehnologii stekla [Physicochemical foundations of glass technology]. Vladimir, Tranzit-IKS Publ., 2008. 736.
- 11. Tereshenko I.M. Tekhnologiya listovogo stekla [Float glass technology]. Minsk, BSTU Publ., 2009. 360.
- 12. Kinetika geterogennoj himicheskoj reakcii (raschet kineticheskih harakteristik reakcii razlozheniya karbonata kalciya) [Kinetics of a heterogeneous chemical reaction (calculation of kinetic characteristics of the calcium carbonate decomposition reaction)]. Available at: https:// studfile.net/preview/5862240/page:4/. (accessed 23.06.2024). (In Russ.).
- 13. Belousov M.V., Selivanov E.N., Gulyaeva R.I., Tyushnyakov S.N., Rakipov D.F. Termodinamika i kinetika protsessa termicheskoy dissotsiatsii dolomita [Thermodynamics and kinetics of dolomite thermal dissociation]. Izv. vuzov. Tsvet. Metallurgiya, 2016, 2, 18-25. DOI: 10.17073/0021-3438-2016-2-18-25.
- 14. Karunadasa K.S.P., Manoratne C.H., Pitawala H.M.T.G.A., Rajapakse R.M.G. Thermal decomposition of calcium carbonate (calcite polymorph) as examined by in-situ high-temperature X-ray powder diffraction. Journal of Physics and Chemistry of Solids, 2019, 134, 21-28.

15. Vasilevich S.V., Malko M.V., Degterov D.V., Asadchyi A.N. Influence of dolomite particle size on the kinetics of its thermal decomposition process Proceedings of the National Academy of Sciences of Belarus, Physical-technical series, 2022, 67(2), 204-213.

- 16. Bajkov A.A., Tumashev A.S. Razlozheniye prirodnýkh uglekislyhk soley pri nagrevanii [Dissociation of natural carbonates when heated]. *Izvestija Akademii Nauk SSSR. OTN*, 1937, 4, 565–592. (In Russ.).
   Samtani M., Dollimore D., Alexander K.S. Comparison of dolomite decomposition kinetics with related carbonates and the effect of proce-
- dural variables on its kinetic parameters. Thermochim. Acta. 2002, 392-393, 135-145.
- 18. Burnham A.K, Braun R.L. Global kinetic analysis of complex materials. Energy Fuels. 1999, 13, 1-22.
- 19. Hills A.W.D. The mechanism of the thermal decomposition of calcium carbonate. Chemical Engineering Science. 1968, 23(4), 297-320.

- Belousov M.V., Rakipov D.F., Nikonenko E.A., Kolesnikova M.P. Issledovaniye mekhanizma razlozheniya dolomita Srednego Urala [The research of dolomite decomposition in the Middle Urals]. *Tsvetnyye Metally*, 2012. 4, 50–52.
- Criado J.M., Ortega A. Kinetic study of thermal decomposition of dolomite by controlled transformation rate thermal analysis (CRTA) and TG. J. Thermal Analys. 1991, 37, 2369–2375.
- 22. Olszak-Humienik M., Mozejko J. Kinetics of thermal decomposition of dolomite. J. Thermal Analys. Calorimetr, 1999, 56, 829-833.
- 23. Olszak-Humienik M., Jablonski M. Thermal behavior of natural dolomite. J. Thermal Analys. Calorimetr. 2015, 119. 2239–2248. DOI: 10.1007/s10973-014-4301-6.
- Rodriguez-Navarro C., Kudlacz K., Ruiz-Agudo E. The mechanism of thermal decomposition of dolomite: New insights from 2D-XRD and TEM analyses. *American Mineralogist*, 2012, 97, 38-51. DOI: 10.2138/am.2011.3813 38
- 25. Hartman M. Trnka O. Vesely V, Svoboda K. Predicting the rate of thermal decomposition of dolomite. Chem Eng Sci., 1996, 51, 5229-32.
- L'vov BV. Mechanism and kinetics of thermal decomposition of carbonates. *Thermochim Acta*, 2002, 386, 1–16.
  McIntosh, R.M., Sharp J.H., Wilburn F.W. The thermal decomposition of dolomite. *Thermochimica Acta*. 1990, 165 (2), 281–296.
- McIntosh, R.M., Sharp J.H., Wildum F.W. The mermal decomposition of dolomite. *Inermochamica Acta*, 1990, 165 (
  Gunasekaran S. Anbalagan G. Thermal decomposition of natural dolomite. *Bull Mater Sci.*, 2007, 30, 339–44.
- Papko L.F., Kravchuk A.P. Fiziko-khimicheskiye metody issledovaniya neorganicheskikh veshchestv i materialov [Physicochemical meth-
- Papko L.F., Kravenuk A.P. Fiziko-knimicneskiye metody issiedovaniya heorganicneskikh vesicneski i materialov [Physicochemical methods of studying inorganic substances and materials]. Minsk, BSTU, 2013. 100.
  Verheijen O.S., Hubert M. Batch Chemistry and Reactions: In the book Handbook of Glass / Editors J.D. Musgraves, J. Hu, L. Calvez.
- 30. Verheijen O.S., Hubert M. Batch Chemistry and Reactions: In the book Handbook of Glass / Editors J.D. Musgraves, J. Hu, L. Calvez. Springer: Cham, Switzerland, 2019, 1231–1256.
- 31. Bourhis E. L. Glass. Mechanics and Technology. Weinheim: Wiley-VCH Verlag GmbH & Co., 2014, 211-234.
- 32. Hujová M., Vernerová M. Influence of fining agents on glass Melting. Ceramics-Silikáty. 2017. 61(2), 119-126.