This paper reports a study into the influence of temperature and gas consumption on the carbonization kinetics (saturation with carbon dioxide) of sodium carbonate-bicarbonate solution. The study also examined the quality and speed of crystal formation in this process. This research is predetermined by the environmental problems faced by modern enterprises that produce purified sodium bicarbonate—an insufficient degree of carbonization and, as a result, excessive air pollution with carbon dioxide, which did not participate in the reaction during the process. This study addresses these particular issues. As a result of using specialized laboratory equipment, it was found that an increase in the absorbent temperature from 79 to 83 °C leads to a decrease in the maximum degree of carbonization of the solution from 64 to 59%. In contrast, the quality of the resulting sodium bicarbonate crystals improves but only in the range from 79 to 82 °C. With a further increase in temperature, the quality stabilizes. It is shown that the carbonization rate increases with increasing specific consumption of the absorbent (carbon dioxide) and is characterized by a negative correlation with the value of over-saturation of the absorbent in terms of NaHCO₃. The quality of sodium bicarbonate crystals decreases with increasing gas velocity. Thus, it was reasonable to assume that the established dependence of the kinetics of carbonization of Na₂CO₃ and NaHCO₃ solution on the gas velocity in the apparatus is explained by the inhibition of CO₂ absorption, which is caused by the diffusion resistance of sodium bicarbonate crystallization. To improve the quality of crystals and the productivity of carbonization by reducing the supersaturation in terms of NaHCO₃, it is recommended to introduce a seed crystal in the zone of binding of crystals in the carbonization columns.

Keywords: sodium bicarbonate, sodium bicarbonate production, carbonization, carbon dioxide absorption, absorption kinetics

1. Introduction

The production of refined sodium bicarbonate is characterized by high consumption of materials and energy resources, as well as a significant impact on the environment. For example, carbon dioxide emissions reach 270 kg per 1 t of NaHCO₃, and the volume of liquid waste formation is 0.6–0.7 tons per 1 t of NaHCO₃. Keeping the latter in storage facilities requires significant areas of land, and filtration pollutes groundwater [1]. Therefore, reducing the amount of waste produced by purified sodium bicarbonate against the background of a significant increase in environmental safety requirements is becoming an increasingly relevant task [2]. One of the directions to solve it is to increase the degree of CO₂ disposal during the carbonization of the solution containing carbonate and sodium bicarbonate [3].

Thus, it is a relevant scientific task to identify those factors that affect the carbonization kinetics and to devise, on this basis, recommendations for reducing CO₂ emissions into the atmosphere.

2. Literature review and problem statement

Carbonization of technical soda ash solution is one of the main stages in the production of purified sodium bicarbonate. Despite the more than a century of existence of this technology, the kinetics of the process of absorption of carbon...
dioxide by a sodium carbonate-bicarbonate solution has not yet been fully investigated. Thus, it was established in one of the fundamental works that studied this process [4] during experiments on the tube with irrigated walls that the rate of absorption of carbon dioxide with a solution of sodium carbonate does not depend on the speed of the gas flow. The increase in irradiation intensity from 0.3 to 1.4 m²/(m²·h) had a relatively small effect on the kinetics of CO₂ absorption. That has made it possible to conclude that the limiting factor of the process is the rate of chemical reaction or, in any case, it is comparable to the rate of diffusion.

It has also been found that the absorption rate of carbon dioxide significantly depends on its concentration in the gas and has a maximum depending on the concentration of Na₂CO₃. However, no recommendations were given on the use of the data obtained under industrial conditions.

In [5], the authors explored the possibilities of CO₂ recycling, which did not react during the carbonization process. Based on the results, a mathematical model of the carbonization process using secondary CO₂ was built. A significant disadvantage of that work was the study of the process only at the absorbent temperature (50 °C), which is significantly different from actual production conditions (80–82 °C).

Much attention was paid to the kinetics and the mechanism of carbonization of the sodium carbonate and bicarbonate solution in [6]. It has been proven that the CO₂ chemisorption with Na₂CO₃ solution proceeds in the kinetic region, and, therefore, in order to intensify the process, it is necessary to increase the volume of liquid in the apparatus and the size of the phase contact surface. In order to implement the latter, it was proposed to use a nozzle in carbonization columns. It should be noted that the reliable operation of the device with the nozzle under the conditions of crystallization of the solution is debatable. Moreover, similar to previous works, the cited study was carried out at too low a temperature that does not correspond to actual industrial conditions.

The authors of [7] managed to build a mathematical model and obtain the results of modeling a bubbling carbonization column, which reflect the change in process parameters for the height of the apparatus, in particular, the rate of origin and growth of crystals. Significant effect of temperature on the kinetics of the process and the quality of the product was noted. However, the authors only planned to check the adequacy of the mathematical model by comparing with the results of operation of industrial devices.

A study into the impact of gas consumption on the CO₂ absorption process was reported in [8]. Thus, the authors proved the existence of three main factors affecting both the absorption rate of CO₂ and the crystallization processes of the product. These are gas consumption, solution temperature, and molar ratio of absorbent components. The cited study found that the efficiency of CO₂ capture is reduced by 10 % with an increase in gas consumption from 0.7 to 2.3 dm³/min, which was explained by a decrease in the time of the absorbent’s stay in the reactor and, consequently, a decrease in the reaction rate. However, paper [9] found that an increase in gas consumption and, accordingly, its speed, causes an increase in the absorption efficiency and reaction rate. However, the authors could not warrant an increase in the formation of the final product. The reason is that increasing the rate of gas containing CO₂ can reduce the contact time between CO₂ and absorbent, as well as affect the reaction temperature and pressure at the top of the absorber.

A positive correlation between the absorption rate and the increase in gas consumption was also established by the authors of [10], which was explained by the increase in the interphase surface of the gas–liquid. Thus, the total absorption of carbon dioxide can be divided into two stages: physical and chemical absorption. Physical absorption, in terms of film absorption theory, proceeds by diffusion of CO₂ from the gas phase to the surface of the gas-liquid interface, dissolution, and subsequent diffusion deep into the liquid. Chemical absorption is associated with a chemical reaction between dissolved carbon dioxide and solution components [11]. Thus, the kinetics of CO₂ absorption is determined by the ratio of the velocity of its diffusion from gas to the interphase surface, diffusion deep into the liquid, and the chemical reaction in it. If the reaction rate is high enough, then the absorption kinetics is determined by diffusion processes and increases with an increase in the size of the interphase surface and the thickness of the diffusion layers of gas and liquid near it. As regards carbonization process, this is achieved by increasing the irrigation density of the absorber with liquid, increasing the speed of gas and crushing bubbles. If the reaction rate is small, then it determines the kinetics of the absorption, which, in this case, depends on the volume of the liquid and the concentration of reagents in it [12].

Crystallization of sodium bicarbonate during the interaction of sodium carbonate and sodium bicarbonate solution with gas containing carbon dioxide further complicates the analysis of the carbonization mechanism making the experiment the main tool for obtaining reliable information about this process.

To summarize, we can note certain inconsistencies in the impact of gas velocity in a carbonization column on the quantity and quality of the resulting product, as well as insufficient investigation of the effect of absorbent temperature on the kinetic characteristics of the process. Thus, the unresolved issue is the search for directions to reduce the man-made impact of the production of purified sodium bicarbonate by reducing carbon dioxide emissions.

3. The aim and objectives of the study

The purpose of this study is to find directions of intensification of the process of carbonization of sodium carbonate and bicarbonate solution through experimental study into the dependences of the process speed and the quality of sodium bicarbonate crystals on the gas velocity and temperature.

To accomplish the aim, the following tasks have been set:
- to analyze the effect of the temperature of the sodium carbonate and bicarbonate solution on the degree of CO₂ absorption and the quality of the resulting product crystals;
- to investigate the impact of gas velocity on the degree of CO₂ absorption and the quality of the resulting product crystals.

4. The study materials and methods

The main hypothesis of this study assumed the existence of dependence of the kinetics of CO₂ absorption and the quality of the crystals in the resulting sodium bicarbonate on the specific gas consumption.

We studied the carbonization of sodium carbonate-bicarbonate solution in two stages. At the first stage, the dependence
of the degree of carbonization of the solution and the quality of the obtained sodium bicarbonate crystals on the temperature of the process was investigated. This work was carried out at one of the enterprises that produce purified sodium bicarbonate by monitoring the carbonization column regime.

The device worked under a standard mode, which did not make it possible to vary in a wide range of gas and liquid consumption and their ratio. Therefore, at the second stage – investigating the impact of gas consumption on carbonization kinetics and the quality of crystals – the study was carried out under laboratory conditions. To this end, an installation was developed, the scheme of which is shown in Fig. 1.

![Diagram](Image)

**Fig. 1. Laboratory set-up: a — structural diagram: CO₂ — CO₂ cylinder; R — carbonizer reactor; GA — gas analyzer; T — water laboratory thermostat; b — photograph of the laboratory set-up**

The main element in the installation was a carbonizer reactor, which was a glass pipe with a diameter of 50 mm and a height of 1,000 mm with a water jacket. The installation was provided with a CO₂ gas cylinder with a reducer, pressure gauge, flow meter, gas analyzer, and thermostat.

A soda solution (absorbent) was prepared by dissolving sodium carbonate and bicarbonate in distilled water when stirring the suspension with a stirrer and heating. The total alkalinity of the solution was ≈ 4.5 mol/l. The soda solution was introduced into the reactor; heated to the predefined temperature, and subjected to carbonization with carbon dioxide (99.5 % CO₂). Carbon dioxide was fed into the carbonizer reactor from the cylinder, its consumption was measured with a flow meter. The experiment was carried out at different temperatures in the range from 79 to 85 ºC. Gas consumption varied from 1 to 6 dm³/min per 1 dm³ of absorbent.

Experiments under different modes were carried out randomly, and in each mode, there were at least 3 of them. The average results of parallel experiments were taken into account.

During the experiment, samples of the solution were periodically selected in which the total alkalinity and concentration of sodium carbonate were determined. For control, the total concentration of carbonates in terms of CO₂ was determined. Based on these data, molar concentrations of bicarbonate equivalents, sodium carbonate in absorbent, the amount of solid NaHCO₃ formed, and the amount of absorbed carbon dioxide were calculated. Tests and calculations were carried out in accordance with the technological regulations for the production of sodium bicarbonate.

An indicator of the quality of sodium bicarbonate crystals, as is customary in the production of this product, was considered its granulometric composition. More precisely, the share of the fraction exceeding 100 µm. To evaluate this indicator in factory and laboratory experiments, the resulting suspension was filtered out on the funnel, sodium bicarbonate crystals were washed with ethyl alcohol, and dried. The granulometric composition of the obtained crystalline sodium bicarbonate was determined by sieve analysis.

Based on the results of chemical tests of the samples, the following indicators were additionally calculated:

- degree of carbonization of the solution, as the ratio of the sum of the equivalents of carbonate-ions to the number of sodium equivalents in percent;
- CO₂ absorption rate – the ratio of the difference between absorbed CO₂ in two samples to the time interval between them (in some cases, the graphical mirror method);
- the rate of formation of sodium bicarbonate – the ratio of the difference in the amount of solid sodium bicarbonate formed in two samples to the time interval between them.

### 5. The results of studying the effect of gas velocity and temperature on the result of the technological process of carbonization

#### 5.1. Investigating the effect of absorbent temperature on the degree of carbonate conversion into sodium bicarbonate

Fig. 2 shows the results of experiments on investigating the effect of the solution temperature on the degree of its carbonization.

The purpose of the experiments was to determine the rational temperature of absorbent at which, under conditions of a fairly high degree of transformation of carbonate into sodium bicarbonate, the maximum quality of the product crystals would be achieved. The share of the fraction with a size exceeding 100 µm is usually considered an indicator of quality.

The mathematical processing of our experimental results (Fig. 2) showed that the data obtained are satisfactorily described by linear dependence in the form of the following equation (determination coefficient 0.944):

\[
R = 129.0571 - 0.8214τ, \tag{1}
\]

where \(R\) is the degree of carbonization, %; \(τ\) – time, min.

The plot shown in Fig. 2 demonstrates that the degree of saturation of the absorbent with carbon dioxide significantly decreases with increasing temperature, which is due to an increase in equilibrium CO₂ pressure and gas humidity and a corresponding decrease in the driving force of the absorption. At the same time, rising temperatures contribute to an increase in the quality of NaHCO₃ crystals, as shown by Fig. 3.

Since the large fraction of crystals more than 100 µm provides not only high-quality separation of the suspension on the centrifuge but also a lower humidity of the crystals and a corresponding reduction in the cost of their drying. That is
why the most rational temperature of carbonization can be considered 80–82 °C.

When building equation (2), only terms of the third-power polynomial were left, for which the p-level of the coefficient was below 0.05. The equation rms error is 1.54 kg/m³ of absorbent, the coefficient of determination is 0.981.

In the initial period, when there is no solid phase in the absorbent, the absorption of carbon dioxide proceeds under the conditions of continuous growth of the supersaturation of the solution in terms of NaHCO₃. The absorption rate decreases first gradually, and then, as the solution approaches the maximum supersaturation – more sharply. In the second period, characterized by the visually defined beginning of the formation of sodium bicarbonate crystals, the absorption process proceeds under the conditions of NaHCO₃ supersaturation removal. In this case, the absorption rate increases and reaches the maximum value. Subsequently, as the absorbent approaches the saturation in terms of NaHCO₃, there is a gradual decrease in the absorption rate to the complete termination of the process.

Fig. 4 also demonstrates that the absorption rate of carbon dioxide increases with an increase in gas consumption, and, therefore, the speed of gas. The link between the absorption rate and gas consumption is more pronounced in Fig. 5, which shows the dependence of the CO₂ absorption rate on time at different gas consumption. To build this plot, data were used that were calculated for the time interval between two consecutive samples (Fig. 4) and fitted to the middle of this interval. Although such a plot is exclusively illustrative due to the curvature-dependent plot error, it makes it possible to more accurately establish the time of the largest solution supersaturation and the difference between the actual absorption speeds on the time intervals where the latter was stable enough.

It is usually considered, as already discussed in the literature review, that a positive correlation between the absorption rate and gas is evidence of limiting the dissolution of gas by diffuse resistance. Increasing gas consumption leads, in a bubbling absorber, first, to an increase in the number of bubbles in the volume of the apparatus and the development of the interphase surface, and, second, to the turbulence of the liquid and the reduction of the thickness of diffusion layers [13]. At the same time, a significant part of researchers [4, 6, 7, 13] believes that the kinetics of carbonization is determined by the rate of the chemical reaction of CO₂ binding in the liquid.
The contradiction between these views on the examined process can be removed if we take into consideration that the high temperature at which the experiments were conducted increased the reaction rate to a value comparable to the rate of diffusion. However, the greatest attention should be paid to the fact that the carbonization process takes place in a three-phase system: gas – Na₂CO₃ and NaHCO₃ solution – crystalline NaHCO₃. Therefore, the crystallization process, as purely diffusion, can play a significant role in determining the kinetics of carbonization in general. To elucidate this, one can use Fig. 6, which depicts the dependence of absorbent supersaturation with sodium bicarbonate on time.

Fig. 6. NaHCO₃ supersaturation dependence on process duration at different specific gas consumption

Fig. 7 shows experimental data characterizing the effect of gas velocity on the process of crystallization of sodium bicarbonate, from which a positive correlation between these parameters becomes apparent. Moreover, the dependence of the amount of settled NaHCO₃ on time is close to linear.

Table 1 gives data that characterize the impact of the conditions of the carbonization process on the quality of crystals. The latter was evaluated by the value of the average size of the crystals, which was determined by the results of sieve analysis and the specific surface.

Experimental data, given in Table 1, show that a decrease in temperature or an increase in specific gas consumption leads to a decrease in average size and an increase in the specific surface of sodium bicarbonate crystals. These data correlate with the corresponding change in maximum oversaturation depending on the temperature and specific gas consumption.

Table 1

| Temperature, °C | Gas specific consumption l/min. l solution | Crystal mean size, µm | Specific surface, m²/g |
|----------------|--------------------------------------------|----------------------|------------------------|
| 79             | 1                                          | 305.7                | 0.0088                 |
| 79             | 2                                          | 286.6                | 0.0121                 |
| 79             | 3                                          | 264.4                | 0.0135                 |
| 79             | 6                                          | 242.6                | 0.0157                 |
| 80             | 1                                          | 204.4                | 0.0164                 |
| 80             | 2                                          | 201.7                | 0.0176                 |
| 80             | 3                                          | 199.2                | 0.0196                 |
| 80             | 6                                          | 197.0                | 0.0214                 |
| 82             | 1                                          | 195.8                | 0.0216                 |
| 82             | 2                                          | 194.9                | 0.0218                 |
| 82             | 3                                          | 191.1                | 0.0221                 |
| 82             | 6                                          | 185.4                | 0.0232                 |
6. Discussion of results of studying the carbonization kinetics of the sodium carbonate-bicarbonate solution

As a result of our experimental studies, the fundamental possibility of intensification of existing carbonization columns by increasing gas consumption was confirmed. This is evidenced by the established positive correlation between the absorption kinetics of carbon dioxide and gas consumption, and, therefore, its speed in the carbonization column (Fig. 4, 5). This result coincides with the conclusions in works [9–11] and could allow us to believe that the stage that limits the process is CO₂ diffusion into a liquid phase, that is, mass exchange in the reactor. Indeed, with an increase in gas consumption, the number of bubbles increases, and, therefore, the surface of mass exchange. In addition, the turbulence of the absorbent leads to intensification of the renewal of the phase contact surface. These factors may be the reason for the increase in the speed and degree of CO₂ absorption with an increase in specific gas consumption. However, this conclusion contradicts the result by a number of researchers [4, 6, 7, 13] who found a chemical reaction in the liquid to be a stage that limits the kinetics of absorption. An explanation can be found if we take into consideration that the study was carried out at high temperatures. Increasing the reaction rate under this condition can make it comparable to the diffusion rate. However, the most likely cause of dependence of the absorption kinetics on gas consumption is inhibition of absorption by the diffusion crystallization process. This is confirmed by the dependence of the absorption rate on the supersaturation of the absorbent in terms of NaHCO₃ (Fig. 6). This explanation to some extent removes the contradiction noted in the literature review in the conclusions of various authors regarding the stages limiting the kinetics of absorption in the examined process.

It was found that lowering the temperature or increasing the specific consumption of gas leads to a decrease in the average size of sodium bicarbonate crystals, as can be seen in Fig. 2 and Table 1. Decisive effect on the reduction of supersaturation and the corresponding acceleration of absorption and quality of crystals can be exerted by the introduction of seed crystals of sodium bicarbonate into the binding zone of carbonization columns.

Our results make it possible to expect that when the carbonization process is intensified by increasing gas consumption in the column, the quality of the crystals would deteriorate and cause the contact elements to clog. Therefore, of practical interest is the further research into the ways to preserve the quality of crystals under factory conditions.

Intensification of existing carbonization columns by increasing gas consumption could help reduce carbon dioxide emissions into the atmosphere by increasing the degree of absorption. This direction of improvement of the processes of sodium bicarbonate production, in contrast to the increase in the dimensions of the equipment in the build-up of production, is promising for the ecologization of production in general.

Limiting the implementation of our results may be the requirement for an additional increase in CO₂ consumption for the technological process. In addition, it should be considered that when using laboratory equipment it is impossible to fully reproduce the features of the process that occurs under industrial conditions.

The prospects for further research are to check, under the industrial conditions, the established dependences, as well as to find other ways to intensify the process of carbonization of solutions in the production of purified sodium bicarbonate.

7. Conclusions

1. In order to increase the environmental safety of the production of purified sodium bicarbonate by reducing CO₂ emissions, we have studied the absorption of carbon dioxide (carbonization) with a sodium carbonate-bicarbonate solution, as well as the crystallization of sodium bicarbonate from this solution. It was found that the increase in the temperature of absorbent from 79 to 85 °C leads to a decrease in the maximum degree of carbonization of the solution, from 64 to 59 %. At the same time, the quality of the obtained sodium bicarbonate crystals, measured by the share of a fraction exceeding 100 µm, increases in the range from 79 to 82 °C, and, with a further increase, it stabilizes.

2. It has been shown that the rate of carbonization, as well as the quality of crystals, increase with an increase in the specific consumption of absorbent (carbon dioxide). The rate of absorption of carbon dioxide is characterized by a negative correlation with the value of absorbent supersaturation in terms of NaHCO₃, namely: it is significantly reduced with an increase in supersaturation, after which it increases to the maximum with its removal. A reasonable assumption has been accepted that the established dependence of the carbonization kinetics of Na₂CO₃ and NaHCO₃ solution on the gas velocity in the apparatus is explained by inhibition of CO₂ absorption, which is caused by diffuse resistance to the crystallization of sodium bicarbonate. To improve the quality of crystals and the productivity of carbonization by reducing the supersaturation in terms of NaHCO₃, it is recommended to introduce seed crystals into the zone of binding crystals in carbonization columns.

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