Synthesis of highly dispersed calcium carbonate at excessive pressure of carbon dioxide

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Abstract. The purpose of the paper was to find out how the conditions for the synthesis of calcium carbonate, having the patent of the Russian Federation No. 2489355, affect the average particle size and their size distribution. The process was carried out in a transparent 1 liter plastic reactor; the excess pressure of carbon monoxide (IV) was quickly created and sharply dropped in no longer than 90 seconds at a temperature of 25°C and in no longer than 6 minutes at 6°C. The obtained highly dispersed carbonate was studied microscopically, and a histogram of the particle size distribution was constructed. The optimum process time at room temperature is 60 seconds. The resulting product is characterized by a narrow particle size distribution with a maximum of about 2.5 µm. The particle size reduction occurs when either the reaction time or the temperature decreases. Aggregate stability of the suspension depends on the molar ratios of calcium hydroxide and carbon monoxide (IV). The activation energy of the reaction is 59 kJ / mol.

1. Introduction

The sections of heterogeneous chemical reactions in solutions and synthesis of highly dispersed particles of the laboratory work in the course of chemistry for students majoring in technical subjects can be supplemented with the study of the process of obtaining highly dispersed calcium carbonate. This work will involve some scientific research and will help to revise physics, physical chemistry and chemistry of heterogeneous processes. The interdisciplinary approach will enable the work both in the basic version and the in-depth version using the case-method, which combines different types of practical activities and is practice-oriented, since the synthesis of highly dispersed materials is widely used in modern technological processes. This work is advisable after learning theoretical material and doing the corresponding homework which is based on object-oriented training materials. The choice of calcium carbonate as an object of students’ laboratory work is dictated by its safety, and makes it possible to work on the laboratory workbench. Calcium hydroxide and carbon dioxide are affordable and inexpensive reagents, whose properties are well known to students from the school course of chemistry. Highly dispersed and ultrafine calcium carbonate is widely used as a filler, thickener [1], depot for indicators [2] and medicines [3].

In the formation of chemical competencies, there are three components: cognitive, activity-practical and personality-motivational. The competence approach focuses on the development and evaluation of the level of severity of each component. The cognitive component is based on a set of knowledge about the materials used. In this case, they are well known to students from the high school...
chemistry course. The activity-practical component is built on the subject skills to implement heterogeneous reactions, filtrate and weigh the product. In addition, students develop a new skill of microscopic examination with the preparation of a histogram of particle size distribution and analysis. The personality-motivational component is based on the undoubted benefits of the method, supported by the extensive use of the product for various purposes, a simple and obvious way to control the quality of the resulting high-grade calcium carbonate. All stages of the experiment are clear, safe and aimed at the formation of the necessary professional skills in modern production. For microscopic examination of the obtained particles, a standard technique is used, the development of which will help in a number of other works. Along with it, [4] is offered for laboratory practice in the course of chemistry for students not majoring in chemistry. The purpose of the study was to optimize the parameters of the synthesis process of highly dispersed calcium carbonate in the interaction of a solution of calcium saccharate and carbon dioxide in the presence of surfactants at high pressure, and test the method for controlling the size of the resulting particles in a students’ laboratory work in chemistry.

2. Materials and methods of research

The synthesis of highly dispersed CaCO₃ was performed in accordance with RF patent No. 2489355 [5] both at atmospheric and at elevated carbon dioxide pressure. When carrying out the work, the same installations were used, one for three students, the installations consisting of a high-strength transparent plastic container with a volume of 1 l and a dosing device with a safety valve and an overpressure relief button. 1 liter of sucrose solution (100 g/l), at room temperature or pre-cooled, was placed in the container, then the required amount of calcium hydroxide (from 5 to 10 g/l) was added, and also a surfactant solution from 0.01% to 0.5%, counting on the weight of the initial calcium hydroxide. A pre-weighted standard container with food carbon dioxide was inserted into the dosing device. Simultaneously with the start of the reference time, carbon dioxide was dosed into the reaction solution near the bottom of the reaction vessel through a plastic tube with a scattering nozzle. The reaction time at room temperature did not exceed 60 sec. If a pre-chilled to 6°C solution was used, the reaction time did not exceed 6 minutes. After that, the excess pressure of carbon dioxide was discharged to atmospheric pressure. As an option, the synthesis was carried out at atmospheric pressure, bubbling carbon dioxide with an open overpressure relief valve for at least 3 minutes. Then the installation was disassembled, the reaction solution was filtered on a paper filter under vacuum, the resulting product was washed on the filter with distilled water, then with acetone and dried. The empty cartridge from the carbon dioxide was weighed by the techno-chemical balance and the mass of consumed carbon oxide (IV) was calculated. Highly dispersed calcium carbonate was weighed and the yield of the product was calculated.

For microscopic examination, a suspension of CaCO₃ was prepared; water was used as a dispersion medium. The sample of the synthesized carbonate was ground in a pounder with a small amount of water, then the mixture was transferred to the cylinder and diluted with water to obtain ~0.5% (mass.) of the suspension; after that a few drops of sodium diphosphate solution were added for preventing aggregation of particles. One or two drops of suspension were applied to the slide, covered with a cover glass and the size of the particles of the obtained highly dispersed calcium carbonate was determined microscopically on the micromed-2 device with the DCM-510 5.0 m camera. The result of the study was the microphotography of the sample. Then the dispersion composition was studied together with determination of the size, number and shape of the particles by micrographs. The processing of the photomicrographs was performed in a freely distributable program Image Tool 3.00. The results of the microscopic dispersed analysis were designed graphically as histograms of the distribution of particle size. For control, the particle sizes on separate fields of view were further specified with the help of a ruler on a frosted glass or a micrograph scale, for determining the maximum chord of the particles and counting the number of particles by fractions at least six times in different places of the specimen.
3. Results and discussion
Sucrose in an alkaline medium is able to dissociate with the formation of soluble calcium saccharates of various structures. After adding a sucrose solution of calcium hydroxide, the dissociation is dominated by the monovalent cation CaOH$^+$ and products of its interaction with sucrose, and divalent cations of calcium are virtually absent. At relatively high concentrations of hydroxide, Ca(OH)$_2$ particles with chemisorbed sucrose may also be present [5]. To avoid the formation of complicated complexes, the ratio of sucrose / calcium in all experiments did not exceed 1. An exchange reaction begins after dosing of carbon dioxide and leads to the release of calcium in the form of carbonate. This process is much slower than the direct interaction of calcium hydroxide with carbon dioxide, which allows us to control the completion of the process visually. At room temperature, when carbon dioxide is bubbled under atmospheric pressure, the process is completed in approximately 1.5 minutes (Figure 1); if dosing of carbon dioxide takes place at a pressure of 800 kPa, the process lasts about 60 seconds and ends with the formation of carbonate particles with a size of about 2.5 microns (Figure 2 left).

$$\text{Ca(OH)}_2 + C_{12}H_{22}O_{11} = C_{12}H_{20}O_{11}Ca + 2 \text{ H}_2\text{O}$$

$$C_{12}H_{20}O_{11}Ca + CO_2 + \text{H}_2\text{O} = \text{CaCO}_3 \downarrow + C_{12}H_{22}O_{11}$$

![Image](image1.png)

Figure 1. Micrograph (microscope "Biomed 5" with Levenhuk camera) and histogram of distribution of CaCO$_3$ particles obtained in accordance with RF patent No. 2489355 by bubbling CO$_2$ at atmospheric pressure.

![Image](image2.png)

Figure 2. Histograms of the size distribution of CaCO$_3$ particles obtained in accordance with RF patent No. 2489355 by dosing CO$_2$ at overpressure.

This neutralization reaction is relatively slow probably due to the presence of sucrose, but it has an important advantage: it is possible to smoothly adjust the particle size of the product in proportion to the reaction time, which is sufficient to guarantee the production of particles of the required size, and
yet is very small. The surface charge of the obtained calcium carbonate particles depends on the pH of the medium. Thus, at a pH value of 9.8, the formed sediment of CaCO	extsubscript{3} has a weak positive charge and, accordingly, a low adsorption capacity [5], and at pH 9.5 and below, soluble calcium bicarbonate is accumulated in the solution and the surface positive charge of calcium carbonate particles increases. This effect affects the aggregate stability of the calcium carbonate suspension and can be used to accelerate particle sedimentation. Further, the clarified solution is separated by decantation. This significantly reduces the solution volume for filtration solution and accelerates the experimental part of the work.

Figure 2 shows the results of studying the samples obtained under the same conditions, with the exception of temperature. It is seen that the position of the maximum particle size distribution does not change. At the same time, at a lower temperature, the particle size distribution becomes flatter.

A small number of particles larger than 3 μm appear. Violation of the symmetry of the particle size distribution at 22°C in the range of values from 1 to 1.5 microns is probably caused by the formation of an additional number of calcium carbonate particles of this size as a result of the decomposition of calcium bicarbonate after a sharp release of excess pressure of carbon monoxide (IV). A similar effect for the histogram obtained at 6°C is absent, since the solubility of carbon dioxide with a decrease in temperature from 22 to 6°C increases almost twice.

It is possible to estimate the value of the process of activation energy by using the data of the process time at these two different temperatures. To do this, a marker should be applied to the reverse side of the transparent reactor with the closely spaced strokes. The process is carried out until the turbidity of the reaction mixture, so that the strokes become indistinguishable, first, at one temperature value and then, at another one. The activation energy should be approximately 59 kJ / mol.

To obtain a target product with a particle size of less than 1 μm, the reaction time can be reduced. It is more convenient to do this at a reduced temperature to 6°C. The reaction time under these conditions is about 6 minutes and the particle size increases more slowly. This improves the reproducibility of particle size distribution and the most probable size from experience to experience.

Figure 3 shows the histogram of particle size distribution for commercially available highly dispersed calcium carbonate obtained by exchange reaction in solution between calcium chloride and sodium carbonate. The process in this case is much faster and is not complicated by the interaction with sucrose. It influences the shape of the distribution that has a more pronounced maximum than in Figure 1 or 2.

![Figure 3](image_url)

**Figure 3.** Histograms of the size distribution of CaCO	extsubscript{3} particles in the sample of highly dispersed calcium carbonate obtained by exchange reaction in solution.

4. Conclusion
Highly dispersed calcium carbonate was obtained and tested according to the patent of Russian Federation №2489355 for studying the main regularities of the synthesis of fine particles in the laboratory course of chemistry for students. The work can be carried out in two versions. The standard procedure involves the production of highly dispersed calcium carbonate with a particle size of 2.5 ± 1.0 µm at room temperature. The time until the end of the synthesis is about 60 seconds and is determined visually by the turbidity of the solution, in which the mark applied to the opposite side of the reactor is not visible. In the second variant, two additional experiments are carried out at a reduced temperature to a similar turbidity of the solution, investigating the dependence of the duration of the process on the temperature. Also, the ratio of calcium hydroxide and carbon monoxide (IV) is changed by studying the effect of the excess of the corresponding reagent on the aggregate stability of the suspension. The effect of the duration of synthesis on the size of calcium carbonate particles at low temperature is studied by examining three samples. For example, at 6°C, the samples are taken after 2 and 4 minutes, and the synthesis is completed at maximum turbidity of the reaction mixture after 6 minutes. In the first sample, the maximum distribution should be near 0.9 µm; in the second about 1.3 µm, in the third – 1.7 µm.

Available and inexpensive reagents are used in the work: calcium hydroxide and food carbon dioxide, packaged in standard cans for siphons. Calcium hydroxide belongs to low-hazard substances and is used as a pre-prepared low-concentration solution containing sucrose for better dissolution of hydroxide (RF patent No. 2489355). Food carbon dioxide and sucrose are absolutely harmless to health. Washing the product on a vacuum filter is produced with distilled water and only at the final stage to accelerate the drying of calcium carbonate, about 2 ml of acetone is used. This allows all students of the group to work simultaneously on the laboratory tables in the chemical laboratory.

Due to the simplicity of hardware design, the work is available in a mass chemical workshop. Mastering the work forms the ability and develops the skills of the technological process of synthesis of highly dispersed materials. Students learn to use microscopic studies to control the parameters of the process and assess the quality of products in the synthesis of highly dispersed materials; create histograms in Excel and analyze the type of particle size distribution; use theoretical knowledge to optimize the basic parameters of heterogeneous processes.

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