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# Preparation of $CaCO_3$ nanoparticles in a surface-aerated tank stirred by a long-short blades agitator

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ABSTRACT

In this work, a novel long-short blades agitator was used to intensify the mass transfer process in the $Ca(OH)_2$-$H_2O$-$CO_2$ system for the preparation of $CaCO_3$ nanoparticles. $CO_2$ was entrained into the liquid through surface aeration in a 10 L stirred tank. Very uniform $CaCO_3$ nanoparticles with the mean size of 24–110 nm were obtained. The prepared particles are calcite crystals. The mass transfer of the precipitation process has also been analyzed. The gas-liquid interfacial area was measured by using the transport-reaction equations. The influences of the rotating speed of the agitator, the reaction temperature, the volume fraction of $CO_2$ in the gas phase, and the initial concentration of $Ca(OH)_2$, on the mean size, the particle size distribution, and the reaction time were discussed. Compared with other carbonation methods, this work provides an easy-operation and high-efficiency method for preparing uniform $CaCO_3$ nanoparticles with low risk of equipment blockage.



## 1. Introduction

Calcium carbonate ($CaCO_3$), in particular, at the nanoscale, has been used as a well pigment or functional filler in plastic, rubber, paper, paints, etc. [1,2]. In these fields, the morphology and size distribution of the particles are of great importance for practical application. Thus, a considerable amount of effort has been devoted to control these characteristics [3–7]. Moreover, it is one of the most popular materials for precipitation studies by heterogeneous carbonation reactions.

In the process of calcium carbonate precipitation by heterogeneous reactions of $CO_2$-$H_2O$-$Ca(OH)_2$, high supersaturation level is desirable for preparing nano-sized $CaCO_3$ particles at high nucleation rates [8–10], i.e. high concentrations of calcium ion and carbonate ion are required. In the slurry of the slaked lime, calcium hydroxide dissolves very fast and dissociates strongly in aqueous solution, so the concentration of calcium ion can be assumed to be sufficient [11]. Thus, increasing the concentration of carbonate ion is of crucial importance to prepare nano-sized calcium carbonate. It has been well understood that the carbonate ion is formed rapidly by the reaction of dissolved $CO_2$ with the hydroxyl ion, followed by the quick transformation of bicarbonate ion to carbonate ion. Compared with these ultrafast reactions, the mass transfer rate of carbon dioxide from the gas phase to the liquid phase is relatively slow [11]. Therefore, the supersaturation level in the carbonation route is directly determined by the gas-liquid mass transfer process.

In recent years, to enhance the mixing and mass transfer performance, many reactors such as high-gravity reactor [3,12], microstructure reactor [4], membrane reactor [5–7], etc. have been employed to prepare $CaCO_3$ nanoparticles. However, there still exists numerous margin for the improvement of the process. In addition, blockage of the equipment, e.g. the orifices on the gas-sparger of the stirred tanks, the micro-channel of the microreactors, still creates big obstacles to the practical applications. Thus, developing a low-cost carbonation process for easy operation control is still the demands of industry for the reduction of carbon emission.

Recently, our group has proposed and designed a new impeller, the long-short blades agitator [13]. The previous studies show that the gas can be entrained into the liquid and excellent gas-liquid mass transfer performance can be achieved when the LSB agitator is used for surface aeration [14]. The mechanisms of surface air entrainment [15] and the turbulent flow characteristics [16] in the vessel have been investigated experimentally and numerically. Compared with the conventional agitators, e.g. the classical Rushton turbine agitator, the LSB agitator can achieve high mixing performance and much better homogeneity in the distribution of the turbulent kinetic energy [14]. Therefore, the LSB impeller has potential applications in the preparation of $CaCO_3$ nanoparticles by carbonation method.

The objective of this work is to carry out an experimental study of carbon dioxide absorption into the slaked lime slurry for the preparation of $CaCO_3$ nanoparticles in the vessel equipped with the LSB agitator, as well as the theoretical discussion of the mass transfer process. The operating conditions, e.g. the rotating speed of the LSB agitator, the volume fraction of $CO_2$ in the gas phase, the reaction temperature,

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and the initial concentration of calcium hydroxide, are considered to study their effect on the performance of the prepared $CaCO_3$ nanoparticles, including the crystal form, the morphology, the mean particle size and the particle size distribution (PSD). The gas-liquid interfacial area is also predicted to evaluate why the carbonation process can be intensified by the LSB agitator.

## 2. Experimental

### 2.1. Materials

An analytical grade of calcium oxide (98% purity, Xilong Science Company), $CO_2$ gas (99.9% purity, Nanjing Shangyuan Industrial Gas Company), $N_2$ gas (99.9% purity, Nanjing Shangyuan industrial gas Company) and distilled water were used in the preparation of $CaCO_3$ nanoparticles. To prepare calcium hydroxide slurry, CaO was first slaked in distilled water for 4 h at 70 °C with continuous stirring, the slurry was then aged for another 24 h without stirring.

### 2.2. Apparatus and methods

The process flow diagram is shown in Fig. 1a. A cylindrical stirred tank with an elliptical bottom is used for the carbonation reactions. The inner diameter and the height of the tank are 210 mm and 245 mm, respectively. Constant-temperature circulating water is pumped through the jacket of the tank to control the reaction temperature. Four baffles of 19 mm in width and 200 mm in length are mounted at 90° intervals around the internal wall of the tank. The gas phase is entrained into the liquid through surface aeration by the LSB agitator, as shown in Fig. 1b, which consists of six short blades (SBs), two connection rings, three long blades (LBs) and one fixed bracket. Six SBs (width × height = 30 mm × 25 mm) are fixed in 60° under the connector rings. Three LBs are fixed on the outer connector ring of 10 mm in width and 100 mm in diameter in 120°. The characteristic size of LSB agitator, $D$, is defined as the diameter of the sweeping circle of the LBs and it is fixed at $D = 100$ mm. The pressure is regulated by a constant pressure valve.

Approximately 8 L calcium hydroxide slurry was initially poured into the stirred tank. When the temperature of the slurry reached a certain value, $N_2$ was firstly induced into the tank to reach a certain pressure. Then the valve of $N_2$ stream was closed and the valve of $CO_2$ stream was opened. The total pressure of the gas phase was fixed at 400 kPa by a constant pressure valve in this work. The $CO_2$ valve kept open during the whole process to supply $CO_2$ consumed by the reactions in the liquid. Thus, $CO_2$ partial pressure in the gas phase was a constant value. The pH values and the conductivity of the liquid were monitored during the whole reaction process. When the pH reached 7, the process was terminated. The suspension was then sampled for further filtration and drying.

### 2.3. Characterization of $CaCO_3$ nanoparticles

The crystal structure and the purity of the synthesized nanoparticles were measured by a multi-function levels X-ray powder diffraction (XRD, Ultima IV) using Cu K$\alpha$ radiation (40 kV, 40 mA). Transmission electron microscope (TEM, JEM-2100) was used to characterize the morphology and measure the particle size distribution (PSD) of the prepared $CaCO_3$ nanoparticles. Above 300 particles from >5 TEM pictures are counted to ensure the accuracy of the PSD results.

## 3. Theory

The mass transfer process of $CO_2$ absorption into $Ca(OH)_2$ slurry is illustrated in Fig. 2. From the view of two-film theory, firstly, carbon dioxide diffuses from the bulk of the gas phase to the gas-liquid interface. When the $Ca(OH)_2$ slurry is used, calcium hydroxide dissolves from the solid phase to the liquid quickly, and then dissociates strongly in aqueous solution. A broad consensus opinion is that the processes of dissolution and dissociation are fast enough that they are not the controlled steps [4], thus, the calcium and hydroxide ions can be assumed to be constant almost all the time. However, the mass transfer of $CO_2$ from the gas bulk to the liquid is a relatively slow process. Consequently, it is considered as the dominant step in the building up of the supersaturation.

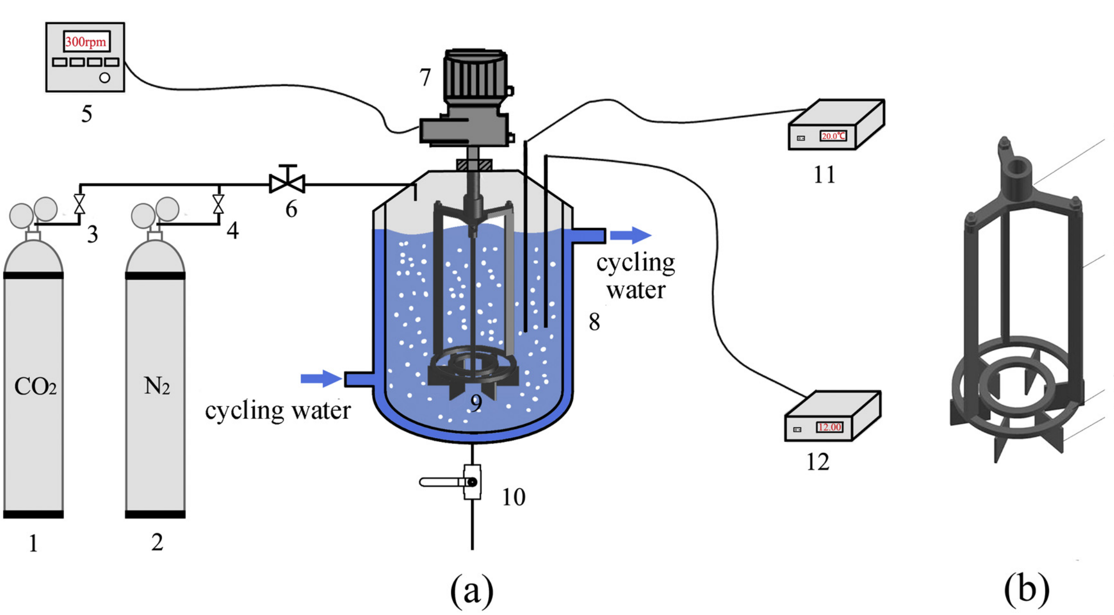


**Fig. 1.** (a) Experimental setup for the preparation of nano-$CaCO_3$. (1) $CO_2$ cylinder; (2) $N_2$ cylinder; (3, 4) valves; (5) rotating speed controller; (6) constant pressure valve; (7) electric motor; (8) stirred tank; (9) LSB impeller; (10) discharge control valve; (11) pH sensor; (12) temperature sensor. (b) Schematic diagram of the LSB agitator configuration. (13) Fixer; (14) Long blades; (15) Outer and inner connector rings; (16) Short blades.