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The overview of reactors used for the production of precipitated calcium carbonate via carbonation route

NATALIA CZAPLICKA, DONATA KONOPACKA-ŁYSKAWA
POLITECHNIKA GDAŃSKA, WYDZIAŁ CHEMICZNY, KATEDRA INŻYNIERII PROCESOWEJ I TECHNOLOGII CHEMICZNEJ

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ABSTRACT:

Carbonation is one of the methods for the production of precipitated calcium carbonate (PCC) on the industrial scale. A gaseous CO_2 is used as a reagent in this process. The hydrodynamic conditions generated in the reactor affect the course of the process and the characteristics of the precipitated calcium carbonate particles. This paper discusses the construction of standard reactors and new proposed construction used for the synthesis of calcium carbonate and presents the effect of precipitation conditions in selected reactors on the characteristics of PCC particles.

Przegląd reaktorów wykorzystywanych do wytwarzania strącanego węglanu wapnia w procesie karbonatyzacji

Słowa kluczowe: węglan wapnia, precypitacja, karbonatyzacja, reaktory

STRESZCZENIE:

Jednym ze sposobów produkcji na skalę przemysłową strącanego węglanu wapnia (PCC) jest karbonatyzacja, czyli proces wykorzystujący do reakcji gazowy dwutlenek węgla. Warunki hydrodynamiczne wytwarzane w reaktorze, w którym jest prowadzona precypitacja, wpływają na przebieg procesu oraz na charakterystykę wytrącanych cząstek węglanu wapnia. W niniejszej pracy omówiono konstrukcje standardowych reaktorów i nowe propozycje rozwiązań konstrukcyjnych stosowanych do syntezy węglanu wapnia oraz przedstawiono wpływ warunków precypitacji w wybranych reaktorach na charakterystykę cząstek PCC.

1. INTRODUCTION

Precipitated calcium carbonate (PCC) is an important additive used in production of papers, plastics, rubber, paints as well as food and pharmaceuticals. Diverse PCC applications require the use of well-defined calcium carbonate particles which are characterized by a polymorph composition, a particle morphology and a particle size distribution. Therefore the formation of PCC is intensively studied to indicate factors affecting the final product. PCC is produced by two main methods on the industrial scale: in the gas-slurry system, when gaseous carbon dioxide reacts with calcium hydroxide suspended in water phase or in the liquid-liquid system by mixing of aqueous solutions of soluble calcium salt (e.g. $CaCl_2$) and of carbonates (e.g. $NaCO_3$). Process parameters such as: the concentration of reagents, temperature, pH, duration of the reaction and the presence of various inorganic and organic additives affect the course of precipitation and product characteristics [1] β. Also, the selection of the reactor and hydrodynamic conditions, especially mixing of the reacting fluid and initial contact, are important factors affecting the course of the reaction due to their influence on supersaturation distribution in the reactor volume [1-4] β. In this paper, the overview of well-studied and a new constructions of reactors used to precipitation of calcium carbonate is presented.

2. CARBONATION PROCESS

The mechanism of precipitation of calcium carbonate in the gas-slurry system have been well understood. The overall carbonation reaction of calcium hydroxide can be written as:

$$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O \quad (1)$$

Kakaraniya and Mehra [3] proposed a model describing the precipitation of calcium carbonate in the stirred contactor. According to this model the gaseous carbon dioxide is bubbled through the $Ca(OH)_2$ suspension and get into the liquid phase through the gas-liquid interface. First, absorption of gaseous carbon dioxide to the interfacial liquid takes place. Bicarbonate ions are created rapidly by the direct reaction between carbon dioxide and hydroxyl ions, and then they are transformed to carbonate ions. Compare with these reactions, the mass transfer rate of carbon dioxide from the gas phase to the liquid phase is relatively slow [5]. Therefore, the supersaturation is mostly affected by the mass transfer of carbon dioxide from the gas phase into the liquid phase. The last stage is the reaction between Ca^{2+} and CO_3^{2-}, whereby calcium carbonate is precipitated. A general possible scheme of the mass transfer with almost instantaneous reaction near the interface in a suspension of calcium hydroxide is presented in Figure 1.

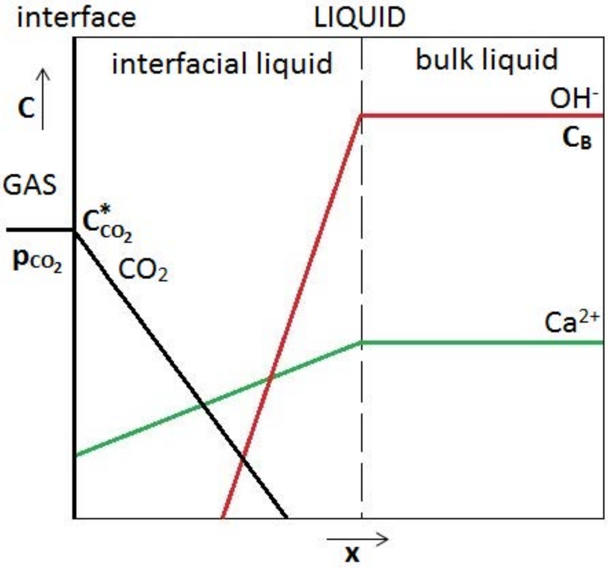

Figure 1 A general possible scheme of the case of mass transfer with almost instantaneous reaction in the interfacial and bulk liquids of suspension of calcium hydroxide: p_{CO2} – partial pressure of CO_2, x – distance from the interface, C – concentration of reagent, C^*_{CO2} – equilibrium concentration of CO_2, C_B – concentration of OH^-

Recently a carbonation of an aqueous calcium salt solution with addition of a carbon dioxide promoter is proposed to PCC synthesis [6, 7]. When ammonia is used as a CO_2 absorption promoter, the overall reaction is follows:

$$CaCl_2 + 2NH_3 + CO_2 + H_2O \longleftrightarrow CaCO_3 + 2NH_4Cl \quad (2)$$

During carbon dioxide absorption in the ammonia solution carbamic acid is formed. This unstable intermediate compound easily passes into ammonium carbamate, which is the dominant form at low CO_2 load and excess of ammonia. For higher CO_2 concentrations or for lower concentrations of free NH_3, the carbamate equilibrium is shifted, which promotes the formation of bicarbonate. During the carbamate production, H^+ ions are also formed, which lower the pH and promote the hydrolysis of ammonia. If complete hydrolysis of NH_3 occurs, then the pH is reduced and the formation of bicarbonate may stop due to a change in equilibrium [7].

3. REACTORS

In laboratory, a stirred tank reactor with gas distributor is the most commonly used. An example of the experimental set-up is shown in Figure 2.

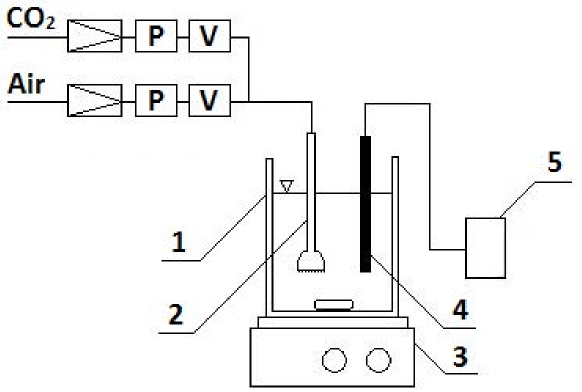

Figure 2 A simple laboratory set-up for carbonation in a gas-liquid or a gas-slurry system: 1 – glass reactor, 2 – sintered glass, 3 – magnetic stirrer, 4 – pH electrode, 5 – pH meter, P – manometer, V – rotameter

However, various types of reactors with more complex construction are also designed. The proposed equipment is both for batch and continuous processes, and allows to control a mass transfer. The course of the reaction can be carried out by an on-line monitoring of the main process variables. The next paragraphs present the main types of reactor used in the carbonation process for the production of precipitated calcium carbonate.

3.1 Stirred tank reactors (STR)

Stirred tank reactors can be operated in a batch or continuous mode. Batch reactors are used for the most of the reaction carried out in a laboratory, while continuous reactors are usually applied in an industry. Various types of mixers are tested in these contactors to create homogenous mixture of both calcium hydroxide suspension, PCC particles suspension and gas bubbles created in the reaction system. The selected stirrer types are in Table 1.

To prevent vortex formation, vertical baffles are placed in the tank. The gas phase can be fed to the reaction mixture by a surface contact [3, 5] nozzles in the bottom part of the vertical baffles [8] or sintered glass [12]. The temperature of reaction can be controlled by the use of a tank jacket in which the circulating water at a constant temperature is pumped [8]. In addition, particular constructions are proposed to prevent the accumulation of particles in the baffles junction, such as narrow gaps between baffles and the reactor wall that allow the slurry to flow freely [8]. A summary of a used stirrer, a gas distributor and additional equipment in tank reactors is presented in Table 1 and the selected precipitation processes carried out in stirred tank reactors are in Table 2.

Table 1 Stirrers, gas distributors and additional equipment in selected tank reactors

Stirrer type	**Gas distributor**	**Additional equipment**	**References**
Flat-blade turbine stirrer	Surface contactor	Rotameter	[3]
LSB agitator	Surface contactor	pH meter, temperature sensor	[5]
45° pitched-blade turbine stirrer	Nozzles at the bottom of the baffles	Thermostat, digital temperature sensors, conductivity meter, peristaltic pump, CO$_2$ analyzer, rotameter	[8]
Three-bladed pitched turbine	Pipe	Thermostat, pressure controller	[9]
Magnetic stirrer	Distribution tube Pyrex®, porosity grade 1	pH meter, thermostat, rotameter	[10]
Magnetic stirrer	Micropore-sized distributor	Thermostat, pH meter	[11]

Table 2 Precipitation conditions and characteristics of produced PCC in selected stirred tank reactors

Reactor type and studied system	Conditions	$CaCO_3$ characteristic	References
Tank contactor with flat-blade turbine stirrer and baffles: Gas – slurry $CO_2 – Ca(OH)_2 – H_2O$	T = 25°C p = 101325 Pa V_G = 0,00479 dm^3/h x_G = 1 n = 69,6 and 129,6 rpm	*d* = 4 µm	[3]
Surface-aerated tank reactor with LSB agitator: Gas – slurry $CO_2 – Ca(OH)_2 – H_2O$	T = 10-40°C p_{CO2} = 400 kPa $C_{Ca(OH)2}$ = 2-6% wt. y_G = 0,25-1,0 n = 175-425 rpm	*d* = 24-110 nm High-purity calcite crystals ↑ of rotating speed causes ↓ of *d* ↑ of initial concentration of $Ca(OH)_2$ and temperature causes ↑ of *d*	[5]
Tank reactor with turbine stirrer and baffles: Gas – slurry $CO_2 – Ca(OH)_2 – H_2O$	T = 20, 35 and 50°C $C_{Ca(OH)2}$ = 0,676, 1,351 i 2,027 mol/dm^3 V_G = 60, 180 and 300 dm^3/h x_G = 0,302-0,876 n = 800, 1100 and 1400 rpm	*d* = 0,02-2 µm The calcite particles in the rhombohedral, scalenohedral, spheroidal or truncated prismatic form No significant effect of the stirring rate on the *d* in the analyzed range	[8]
High-pressure tank reactor: Gas – liquid $CO_2 – Ca(Ac)_2 – H_2O$	T = 80°C p = 24 MPa p_{CO2} = $40 \cdot 10^5$ Pa x_G = 1 n = 500 rpm	*d* = 5-15 µm Needle-like aragonite organized into microsphere superstructure	[9]

T – temperature, p – pressure, C – initial concentration, V_G – CO_2 volumetric flow rate, x_G – CO_2 mass fraction, n – stirrer speed, *d* – particle diameter, ↑ – increase, ↓ – decrease

3.2 Bubble columns

Bubble columns (BC) are reactors used to create a gas-liquid contact and efficient mixing by a gas sparging in the liquid phase. These reactors can be operated both in semi-batch and continuous manner. The gas is fed into a column by a gas distributor placed at the bottom and rises in the liquid. During carbonation processes a CO_2 gas is supplied to the reactor as a pure gas or mixture with an inert gas and it is consumed in the reaction with calcium ions presented in the liquid phase. The some precipitation calcium carbonate processes carried out in bubble column reactors are presented in Table 3.

3.2.1 Internal loop airlift reactor

An internal loop airlift reactor consists of two coaxial columns. The gas is fed into the system through a gas distributor located just near the bottom edge of the inner column [2] or in the bottom of the reactor [16]. The stirrer can be mounted to intensify the mixing in the reactor. Figure 3 shows a schematic diagram of this reactor construction.

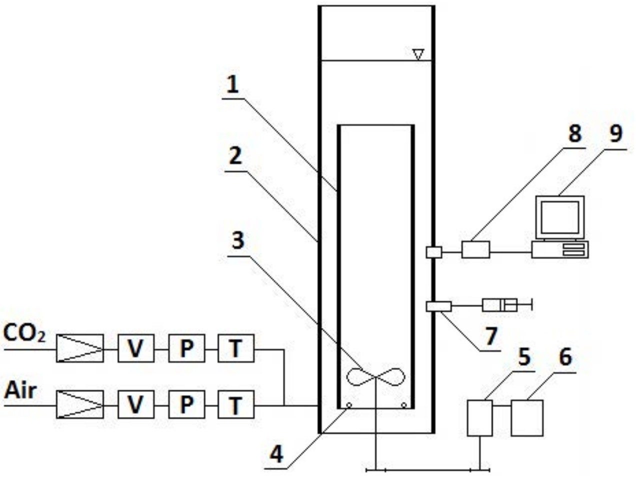

Figure 3 Schematic diagram of an internal loop airlift reactor: 1 – inner column, 2 – outer column, 3 – propeller stirrer, 4 – gas sparger, 5 – motor, 6 – tachometer, 7 – sampler, 8 – conductometer, 9 – computer, T – thermometer, P – manometer, V – rotameter

Table 3 Precipitation conditions and characteristics of produced PCC in selected bubble column reactors

Reactor type and studied system	Conditions	$CaCO_3$ characteristic	References
Internal loop airlift reactor: Gas – liquid $CO_2 – Ca(OH)_2 – H_2O$	$C_{Ca(OH)2}$ = 0,0077 mol/dm^3 V_G = 62-248 dm^3/h x_G = 0,2	*d* = 2,5 µm (without mechanical mixing) and *d* = 2 µm (with mechanical agitation) ↑ in reactive mixture circulation results in ↓ of *d*	[2]
BC with external circulation: Gas – liquid $CO_2 – CaCl_2 – H_2O$	C_{CaCl2} = 0,05 mol/dm^3 V_G = 3,8 dm^3/h x_G = 1 Additives: NH_3, amines	*d* = 1-10 µm Calcite and vaterite were obtained	[13]
BC with single bubble generator: Gas – slurry $CO_2 – Ca(OH)_2 – H_2O$	T = 20°C $C_{Ca(OH)2}$ = 0,0169 mol/dm^3 1 CO_2 bubble per 10 s x_G = 1	*d* = 2 µm Agglomerates formed from cubic/multi-walled and spindle units with size of 6 to 40 µm	[14]
Multistage column crystallizer: Gas – liquid $CO_2 – Ca(OH)_2 – H_2O$	T = 25°C $C_{Ca(OH)2}$ = 0,02-0,035 mol/dm^3 x_G = 0,526 n = 500 rpm	*d* = 4-15 µm *d* ↓ with ↑ of initial $Ca(OH)_2$ concentration *d* ↑ with ↑ of cross-sectional area of G-C contact between sections	[15]

T – temperature, C – initial concentration, V_G – CO_2 volumetric flow rate, x_G – CO_2 mass fraction, n – stirrer speed, *d* – particle diameter, ↑ – increase, ↓ – decrease.

3.2.2 Bubble column with external circulation

To provide a good mixing of a liquid-solid suspension formed during precipitation the external circulation of a liquid phase is applied [13]. The recirculation flow is kept constant by the liquid head in the recirculation vessel and by a membrane compressor operating at a constant suction gas flow rate by means of an additional air supply. The column is equipped with a glass microporous gas distributor and the gas flow is regulated by a rotameter. The gas flow intensity enables the formation of microbubbles that ensure a high gas-liquid contact surface.

3.2.3 Bubble column with a single bubble generator

A column with a generator of single gas bubbles consists of a two coaxial column. The gas inlet nozzle is flush-mounted on the wall. Single bubbles of carbon dioxide are injected into the system through a nozzle using a solenoid valve at time intervals. The size of bubbles is control by a regulation of the gas supply pressure from the gas cylinder. A device for taking up the suspension consists of a syringe, an air cylinder and a solenoid valve [14].

3.2.4 Multistage column crystallizer

A standard bubble column can be divided into several sections by perforated plates, i.e. for a three-stage column crystallizer two plates should be used [15]. The feed solution and mixed gas phase are fed co-currently to the bottom stage. The final liquid phase containing calcium carbonate particles is overflowed from the top of the column [15].

3.3 Other reactors

To obtain PCC particles with the required characteristics, precipitation requires a controlled gas-liquid mass exchange, which is associated primarily with the generation of interface. Also, during a reaction a control of mixing intensity is necessary to prevent local variations in supersaturation and agglomeration. Therefore, in addition to the modification of standard reactors, new designs are proposed. Precipitation conditions and characteristic of obtained calcium carbonate in selected new constructed reactors are presented in Table 4.

Table 4 Precipitation conditions and characteristics of produced PCC in selected reactors

Reactor type and studied system	Conditions	$CaCO_3$ characteristic	References
Couette-Taylor: Gas – slurry $CO_2 – Ca(OH)_2 – H_2O$	T = 20°C $C_{Ca(OH)2}$ = 0,008 and 0,016 mol/dm^3 V_G = 0,0124-0,00775 mol/(m^{3}s) x_G = 1 n = 400-1100 rpm	Particles in the form of agglomerates, multi-walled, spindle-shaped or needles *d* = 2-10 µm A bimodal particle size distribution ↑ of the rotating speed causes a ↓ of *d*	[17]
Spinning disc reactor: Gas – slurry $CO_2 – Ca(OH)_2 – H_2O$	T = 17°C $C_{Ca(OH)2}$ = 0,0187 mol/dm^3 V_G = 600 and 900 dm^3/h x_G = 1 n = 200-1000 rpm	No information about particles characteristic	[18]
Rotating disc reactor: Gas – slurry $CO_2 – Ca(OH)_2 – H_2O$	T = 18°C $C_{Ca(OH)2}$ = 0,027 mol/dm^3 V_G = 30, 60 and 120 dm^3/h x_G = 1 n = 30 to 180 rpm	*d* = 0,4-1,6 µm *d* ↓ with ↑ of discs rotation speed	[19]
Microbubble system: Gas – slurry $CO_2 – Ca(OH)_2 – H_2O$	$C_{Ca(OH)2}$ = 0,1, 0,3 and 0,5 mol/dm^3 V_G = 24, 48 and 60 dm^3/h x_G = 1 Additives: 0,1 mol/dm^3 NaCl	No information about *d*	[20]
Reactor with a microfiltration membrane: Gas – slurry $CO_2 – Ca(OH)_2 – H_2O$	T = 25-60°C V_G = 4,2-14,4 dm^3/h x_G = 0,298	*d* = 34,3-110 nm *d* ↑ with ↑ of flow rates of suspension and gas	[21]

T – temperature, C – initial concentration, V_G – CO_2 volumetric flow rate, x_G – CO_2 mass fraction, n – stirrer speed, *d* – particle diameter, ↑ – increase, ↓ – decrease

3.3.1 Couette-Taylor reactor

In the Couette-Taylor reactor, the radial fluid motion is generated by rotation of the inner cylinder, wherein the outer cylinder stays stationary [17]. At the moment when the rotating speed of the inner cylinder surpasses a certain critical value, the radial fluid motion creates toroidal Taylor vortices, which are a macroscopic flow patterns spaced periodically along the cylindrical axis. Taylor vortices characterize a unique mixing behavior of excellent radial mixing along with minimal longitudinal mixing. Each flow element includes counter-rotating vortices, while the axial length of each cell is approximately the same as the annular gap width. The liquid phase and the gas phase are fed co-currently in the inlet part of the reactor, and the post-reaction phase is drained in the opposite side of the reactor. In the Couette-Taylor system the chemical reaction runs very fast. All absorbed CO_2 is consumed within the thin fluid layer near the gas-liquid interface. Thus, a small amount of CO_2 occurs in the bulk liquid and can be negligible.

3.3.2 Spinning disc reactor (SDR)

In spinning disc reactors (SDRs), the formation of thin liquid film ensuring rapid heat and mass transfer occurs through the use of high centrifugal acceleration [18]. The liquid is pumped to the disc through a nozzle and the flow is controlled by a needle valve. The flow meter is mounted in the feed line and allows monitoring of the liquid flow rate. A gas phase is fed co-currently over the disc. The use of SDR reactors in several chemical processes very often results in an increase of the reaction and transport rates, as well as improved selectivity and yield. SDR application to $CaCO_3$ precipitation resulted in a generation of a wide range of particle sizes and morphology. The PCC characteristics is control by the disc rotational speed.

3.3.3 Rotating disc reactor (RDR)

The rotating disc reactor (RDR) is constructed of vertical discs placed in the chamber that is filled partially with a liquid phase and a gas reagent is supplied to the chamber as well [19]. The lower part of discs is immersed in a liquid reagent. The liquid film is formed on the rotating discs surface and it is contact with a gas phase. During rotation through the solution a constant renewal of the liquid layers and the reaction of reagent from liquid phase takes place. The pH and temperature are monitored during PCC precipitation. RDR can work in batch or continuous mode. This reactor allows to conduct reaction in gas-liquid-solid system and control reagent transfer from gaseous to liquid phase, and in reverse.

3.3.4 Microbubble system (MBS)

Microbubbles are a gas bubbles created in aqueous phases that are smaller than 50 µm. Larger bubbles more easily escape the aqueous phase due to buoyancy. In contrast, smaller bubbles may remain relatively longer in the fluid phase. The small size of gas bubbles and their long residence time cause the increase in the reaction efficiency compared to the systems having the conventional gas dispersion. To $CaCO_3$ precipitation process, a commercial microbubble generator designed for the treatment of polluted water can be used [20]. The synthesis of calcium carbonate using CO_2 microbubbles can be carried out in a gas-slurry [20] or a gas-liquid system [22]. The thermostat bath can be used to regulate temperature of reaction. Key parameters such as the pH, conductivity and temperature are monitored during the precipitation process.

3.3.5 Reactor with a microfiltration membrane

The reactor with a microfiltration membrane can be used to prepare nano-sized calcium carbonate particles [21]. Gas bubbles are generated by a strong shear of the continuous phase of calcium hydroxide slurry. Due to the high flow rate causing strong turbulence, effective mixing in the reactor is achieved. In this reactor, the $CaCO_3$ synthesis is carried out in a continuous mode. The size of PCC particles can be control by the regulation of temperature, pH, pressure, flow rate and supersaturation.

4. SUMMARY

$CaCO_3$ precipitation via carbonation route is still studied because the process variables are interrelated and difficult to control compared to reactions carried out in the liquid-liquid system. Synthesis of calcium carbonate with a defined characteristics requires to control many parameters and among them hydrodynamic conditions. Classical reactors such as stirred tank reactors and bubble columns having well described hydrodynamic parameters are used. Also modified constructions of well-studied reactors and new designs are proposed for this process.

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