Powder Technology 190 (2009) 319–323

Contents lists available at ScienceDirect

Powder Technology

journal homepage: www.elsevier.com/locate/powtec

Effect of liquid circulation in the draft-tube reactor on precipitation of calcium carbonate via carbonation

Donata Konopacka-Łyskawa *, Zbigniew Cisiak, Bożenna Kawalec-Pietrenko

Gdańsk University of Technology, Chemical Faculty, Department of Chemical and Process Engineering, Narutowicza 11/12 80-952 Gdańsk, Poland

ARTICLE INFO

Article history:
Received 8 June 2007
Received in revised form 28 January 2008
Accepted 5 August 2008
Available online 17 August 2008

Keywords:
Calcium carbonate
Precipitation
Carbonation process
Liquid circulation

ABSTRACT

Precipitation of calcium carbonate was carried out in a draft-tube reactor by mechanical agitation of calcium hydroxide solution with carbon dioxide. The circulation of a reactive mixture was created by gas flow and a stirrer. It was observed that a higher circulation decreased the precipitation time and improved CO_2 consumption. A higher circulation velocity of liquid contributed to smaller calcium carbonate particles at the end of precipitation.

1. Introduction

Precipitated calcium carbonate is a widely used compound in the paper, rubber, paint and pharmaceutical industries. Overall demand for precipitated calcium carbonate is forecasted to rise from 7.75 Mt in 2004 to 9.7 Mt by 2010 [1]. $CaCO_3$ is produced through a carbonation process that is a reaction of gaseous CO_2 with a calcium hydroxide solution, or as a by-product of some bulk chemical processes, e.g. caustic soda production.

The precipitated solid phase is characterized by its shape and size distribution. Operating parameters which influence the precipitate quality are of either a physicochemical or hydrodynamic nature. Such variables as temperature, concentration, pH, additives and reaction time play an important role during the precipitation of calcium carbonate [2–4]. Hydrodynamic conditions, especially initial contact and mixing of the reacting fluid, affect the control of precipitate quality due to their influence on supersaturation distribution in the reactor volume [5–9]. Moreover, the role of different scales of mixing, like macromixing, mesomixing and micromixing in precipitation processes, have been discussed in detail and investigated [5,8,10–11].

The influence of stirring rate or energy dissipation on the mean crystal size is not clear [10]. Some experimental results have proven that increasing agitation causes an increase in the precipitated particles size [10,12–13]. Nevertheless there is a group of experiments in which the opposite dependency has been observed [5,9,11,12]. Mean crystal size has been found to decrease with increasing feed rate [10]. It is obvious that changes in reactor geometry are the cause for the difference in hydrodynamic characteristics, and consequently they influence the quality of the precipitated particles [14–15].

The gas hold-up and the circulation of the reactive mixture are important parameters in the process of the gas–liquid reactive precipitation carried out in bubble reactors. The high gas hold-up allows a gaseous reactant like carbon dioxide to be better expended. The intensive circulation of the suspension in the reactor causes the concentrations of reacting substances to become homogeneous over the whole volume and keep suspended particles in a liquid phase. Furthermore, the circulation can affect the intensification of secondary nucleation as a result of crystal attrition [16].

Some efforts have been undertaken to propose models describing the gas–liquid precipitation [12,17–24]. Computational fluid dynamics (CFD) [20] has been adopted for the modeling of the precipitation of calcium carbonate in a batch reactor with a uniformly agitated gas–liquid interface. The CFD simulation has been compared to the film theory [12,21] and the penetration theory [17,22]. It has been noticed that the film theory demonstrates a nucleation dominated processes and a very small change in mean particle size, while the penetration theory predicts an overestimation of size for a given time that could be a consequence of growth dominated processes in the system. The CFD simulation results show only a portion of the bulk is used during the precipitation process, so that CFD predicts an intermediate behavior between that of the film and penetration theories. Recently, Kakaraniya and Mehra [23] have proposed a model based on Higbie's penetration theory combined with a population balance for the particles describing the precipitation of calcium carbonate in the stirred contactor. This model allows the prediction of the evolution of the particle size distribution, the mean particle size, and the average rate of absorption over the reaction time. Experimental results confirm that all the above examples concern a well defined, flat gas–liquid

---

* Corresponding author.
E-mail address: donata@chem.pg.gda.pl (D. Konopacka-Łyskawa).

0032-5910/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.powtec.2008.08.014

interface. However, Rigopoulos and Jones [24] have presented a dynamic model for $CaCO_3$ particle formation in a bubble column reactor. This model is limited to particle formation and growth in a dilute suspension, and the changing of pH and mean particle size during the precipitation process is in agreement with the experiment.

In this work calcium carbonate was obtained in the following reaction:

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3\downarrow + H_2O \tag{1}$$

The presence of CO_2 in the gas phase and $Ca(OH)_2$ in the liquid phase causes precipitation to take place in two regions: the gas–liquid interface and in the bulk. Each stage of crystal formation, i.e. nucleation, growth and agglomeration, depends on the local substrate concentration and is closely related to the mass transfer and to the chemical reaction. The reactions involved in the carbonation of calcium hydroxide are as follows:

$$CO_{2(g)} \rightarrow CO_{2(aq)} \tag{2}$$

$$CO_{2(aq)} + OH^- \rightarrow HCO_3^- \tag{3}$$

$$HCO_3^- + OH^- \rightarrow H_2O + CO_3^{2-} \tag{4}$$

$$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3\downarrow \tag{5}$$

Eq. (2) describes the CO_2 absorption and because the mass transfer process is the lower step of the global process, it is necessary to study carbon dioxide transport to the liquid phase [25]. The absorption rate of carbon dioxide *N*, in the case when a part of the chemical reaction between carbon dioxide and hydroxyl ions is carried out at the interface and the other part in the bulk, can be expressed as [25]:

$$N = [CO_2]^* a \sqrt{D_A k_3 [OH^-] + k_L^2} \tag{6}$$

where $[CO_2]^*$ and D_A are the solubility and diffusivity of carbon dioxide in the liquid phase, respectively, a is the interface area, k_3 is the rate constant for the reaction between carbon dioxide and hydroxyl ions (see Eq. (3)), $[OH^-]$ is the OH^- concentration in the aqueous phase bulk and k_L is the liquid side mass transfer coefficient.

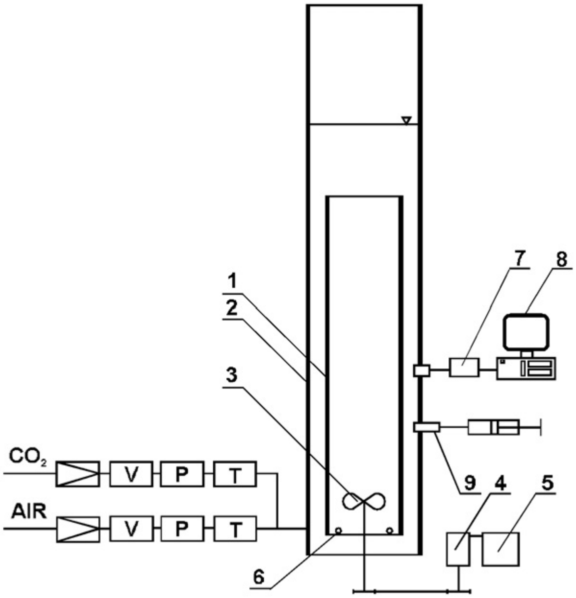

Fig. 1. Experimental set-up: 1—inner column, 2—outer column, 3—propeller stirrer, 4—motor, 5—tachometer, 6—gas sparger, 7—conductometer, 8—computer, 9—sampler, V—rotameter, P—manometer, T—thermometer.

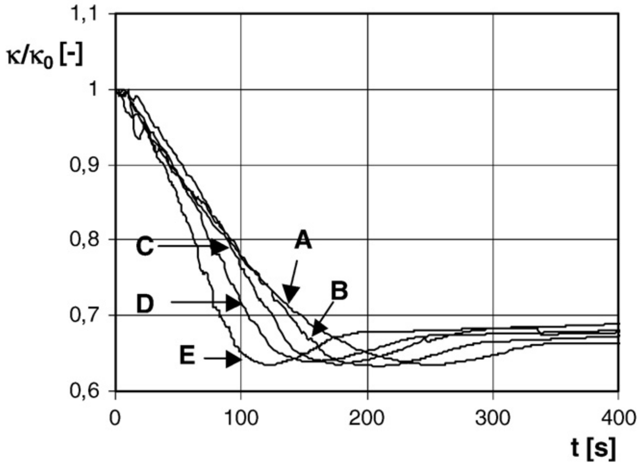

Fig. 2. Conductivity vs. time for pure CO_2; V_{CO2} [$m^3 \cdot s^{-1}$]: A—$3.4 \cdot 10^{-6}$, B—$4.5 \cdot 10^{-6}$, C—$5.6 \cdot 10^{-6}$, D—$6.8 \cdot 10^{-6}$, E—$10.1 \cdot 10^{-6}$.

The aim of this study was to contribute to the understanding of the effect of reactive mixture circulation on the precipitation of calcium carbonate carried out in a draft-tube reactor.

2. Experimental

Calcium carbonate was precipitated in an internal loop airlift reactor constructed from two coaxial columns. The outer column diameter was $D_o/D_i = 80/72$ mm and its height 550 mm. The draft-tube diameter was $d_o/d_i = 50/45$ mm and the height was 380 mm. The gas distributor was placed 40 mm above the bottom of the reactor, just near the lower edge of the inert column. The conductivity probe was located in the downcomer. Signals from the probe were saved by a computer with data acquisition software. The layout of the experimental set-up is shown in Fig. 1. The reading of the volumetric gas flow rate was corrected to the atmospheric conditions at the top of the reactor by pressure and temperature measured under the gas distributor. The corrected volume flow rate of the gas and the cross-sectional area of the riser were used to calculate gas velocity.

The experiments were carried out in a semibatch manner. The solution of $Ca(OH)_2$ was prepared with distilled water. The initial Ca^{2+} concentration was 7.7 mM in all experiments. Potassium hydroxide was added to increase the initial pH value to 12.4. The reactor was filled with a filtered calcium hydroxide solution up to a predetermined level, i.e. 70 mm above the top edge of the draft tube. CO_2 or a CO_2-air mixture was

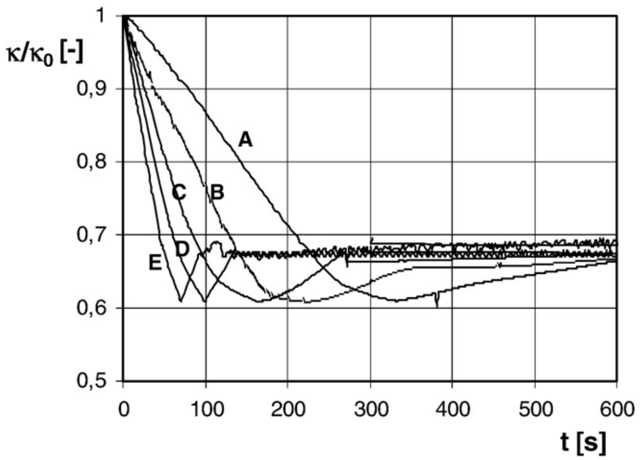

Fig. 3. Conductivity vs. time, CO_2–air mixture, $x_{VCO2} = 0.2$; $V_{CO2+AIR}$ [$m^3 \cdot s^{-1}$]: A—$17.3 \cdot 10^{-6}$, B—$28.7 \cdot 10^{-6}$, C—$34.6 \cdot 10^{-6}$, D—$51.8 \cdot 10^{-6}$, E—$69 \cdot 10^{-6}$ $m^3 \cdot s^{-1}$.