The Influence of Experimental Factors on Calcium Carbonate Morphology Prepared by Carbonation

MARIA HARJA 1, IGOR CRETESCU 1, LACRAMIOARA RUSU 2, RAMONA CARLA CIOCINTA* 1
1 “Gh. Asachi” Technical University of Iași, Faculty of Chemical Engineering, 71 Mangeron Blvd., 700500, Iasi, Romania
2 University of Bacău, Faculty of Engineering, 157 Mărășești Blvd., 600115, Bacău, Romania

The study of the precipitated calcium carbonate (PCC) has received much attention owing to the wide applications. Calcium carbonate has three kinds of crystal polymorphs: calcite, aragonite and vaterite. The control of crystal shape, size and morphology is fundamental from the viewpoint of technical application. The work has as main aim establishing the influence of the initial concentration of solution, temperature and stirring speed in the obtaining process of the precipitated calcite carbonate having imposed properties by carbonating Ca(OH)₂ suspensions. It was studied the influence of conditions over the shape and size of particles. Solid obtained was analyzed from the view point of its chemistry (IR spectra), granulometric distribution and morphology by SEM. The carbonation process was monitored by pH and conductivity adjustment. The necessary carbonation time varies linearly with the suspension concentration. Increasing the gas flow rate causes a decreasing of carbonation time. Increasing the stirring speed leads to a decreasing of the particle size. The most significant influence on the particle morphology and size is represented by the initial concentration of suspension.

Keywords: calcium carbonate, calcium hydroxide, carbonation time, morphology, distribution size

The precipitated calcium carbonate (PCC) has received much attention owing to its application in such industrial fields as paper, rubber, plastics, paint food and horticulture [1-4]. The application of calcium carbonate particles is determined by the great number of strictly defined parameters, such as morphology, structure, size, specific surface area, brightness, chemical purity, printing characteristic, oil adsorption, and so on. One of the most important is particle morphology [5]. Therefore, the control of crystal shape and size is fundamental from the viewpoint of technical application. Calcium carbonate has tree kinds of crystal polymorphs, which is generally classified as rhombic calcite, needle-like aragonite and spherical vaterite [1]. Among the different polymorphs of calcium carbonate, calcite is of great interest because of its wide use as a pigment or as filler in paper [6-11]. As filler or a reinforcing material, the plate like particles may confer high smoothness and excellent gloss to the composite materials. They may also confer high electric resistance and elasticity modulus to the composite [12, 13].

The PCC particles with specific properties are usually synthesized via liquid – liquid precipitation (double exchange) or gas – liquid carbonation methods [14]. In the carbonation method, the calcium hydroxide slurry usually reacts with carbon dioxide, but under carefully controlled conditions [5]. In case of residual solutions generated from the industry of caustic soda, the double exchange method is more recommended due to some advantages. However, the carbonation method of calcium hydroxide slurry that reacts with carbon dioxide under controlled conditions remains the main synthesis method of PCC [5]. Using the carbonation method the calcium carbonate is obtained via multi-step carbonation process or in the presence of additives such as organ phosphorus or boron compounds [5].

A considerable amount of attention and effort has been devoted to investigate the preparation of PCC from carbonation, to elucidate the relationship between the precipitation and the particle morphology [1, 15-17]. In previous papers the morphology was attributed to: the supersaturating level, pH of solution, ionic ratio of [Ca²⁺]/[CO₃²⁻] in solution, excess species of the reactants [18-21]. In spite of numerous investigations on the precipitation of calcium carbonate, the relationship between precipitation conditions and obtained properties of product is still cloudy and disputed.

The main objective of this paper is to point out the influence of precipitation conditions on PCC properties, i.e. chemical and morphological characteristics and the granulometric distribution.

Experimental part

The experimental installation used to investigate the obtaining process of calcium carbonate precipitate from calcium hydroxide suspensions is presented in Fig.1. The experimental installation is composed of a magnetic-stirred batch reactor, thermostat, systems of debit and gas pressure measuring, gas exhaustion system, EW 53614-20 pH-meter; temperature controller and OAKTON CON11 conductometer.

In order to carry out the experimental investigations, it was selected the variation range of the parameter whose influence is about to be studied, while the other parameters were kept at a constant throughout the determinations.

The study of the carbonation was performed by using reagents such as liquid carbon dioxide of alimentary quality and Bicaz lime that was previously analyzed. In order to carry out the determinations, 1 kg of technical CaO (limestone dissociation product) was weighed and dashed. A 10 g sample was drawn and weighed using an analytical balance and then analyzed. In the investigations, the lime was used without prior hydration by introducing in the reactor of various pre-established quantities (1, 1.5 and 3 g), weighted with an analytical balance. The lime was

* email.: mivanciu@ch.tuiasi.ro

1258 http://www.revistadechimie.ro

REV. CHIM. (București) • 60 • Nr. 12 • 2009
added into contact with 150 ml bidistilled water in reactor, the stirring being performed until a complete hydration. This is controlled by the means of the conduct meter (for 5 min, the conductivity should remain constant).

Results and discussions
The lime was characterized in relation to its chemical composition and technological properties [22]. Thus, it was obtained a lime chemical composition as it follows 97.2% CaO out of which 96.8% active CaO; 0.7% MgO; 0.5% Al₂O₃ + Fe₂O₃; 0.3% SiO₂, CO₂ – 1.3%. The study of solid nature was achieved by IR spectrophotometry. This analysis was performed using a DIGILAB FTS 2000 spectrophotometer. The recorded IR spectrum obtained is shown in figure 2. In figure 2 it can be noted the calcium oxide, the main component of the lime, but it could also be noticed the occurrence of two more picks correspondent to the impurities in the carbonaceous raw material, respectively the silicon dioxide and the non-dissociated calcium carbonate.

Influence of the suspension concentration
The initial concentration of the suspension was expressed as mass percentages between the total quantity of lime and suspension quantity (lime and deionization water). The experiences were carried out at 3 initial concentrations: 1, 1.5 and 3 g lime at 150 mL water, respectively: 0.66%, 1%, 2% quick lime. The volumetric flow rate of carbon dioxide (CO₂ - 99.9%) was varied between 1.99 10⁻⁴ m³ s⁻¹

The pH variation is presented in figure 3. Concerning the pH variation of the 0.66% suspension this decreases sharply from 12.3 to 7 in about 8 minutes. In case of 1% and 2% suspension, the pH value remains at 12.4 for 6 and 10 minutes respectively after which decreases slightly to 7. The fact that the pH remains relatively constant at higher initial concentrations of the suspension is attributed to the solution properties. In the carbonation process the solid is in the first phase dissolved at Ca²⁺ and HO⁻, while the CO₂ is absorbed in the form of carbonic acid and then converted into hidronium ions, bicarbonate and carbonate. Then Ca²⁺ reacts with CO₃²⁻ forming PCC and H⁺, with HO⁻ forming H₂O. At lower concentrations of suspension the solid is more easily dissolved, this stage being of short duration.

The experimental data regarding the conductivity are presented in figure 4. The conductivity decreasing is attributed to diminishing of the concentration of Ca²⁺ ions and HO⁻ due to the chemical reaction. After all of the hydroxide quantity reacted, the further of dioxide bubbling leads to a slight increasing of conductivity, the suspension being saturated with CO₂. Theoretically, carbonation is considered complete when the electrical conductivity reached a minimum value, which is stable more than 15 min. Then, the bubbling of carbon dioxide was maintained for minimum 10 min.

This time was considered from the moment of starting the gas bubbling until the conductivity of solution becomes constant (followed by a slight increase). The carbonation time (t) is linear with the concentration of suspension, as shown in figure 5.
An average diameter of 0.475 mm. Average particle diameter decreases reaching the value of 0.103 μm for suspensions of 1%, respectively 0.066 μm for suspensions of 2%. The decrease of average diameter can be explained by the increased number of crystallization germs due to an increase of the suspension concentration. It must be specified that because the particles have different shapes the results might be affected by the calculation strategy for the particle diameter (this are considered of spherical shape).

To determine the particle shape for the obtained PCC samples, SEM electron microscopy analysis was employed. Determinations were performed on a Vega Tescan SEM of 30 kV, the samples were covered with a layer of Ag. SEM images are shown in figure 9.

In case of the carbonation 0.66% calcium hydroxide suspension, not very clearly outlined, spherical-shaped particles are obtained, as can be seen in figure 9. In the solid obtained, rectangular particles can be also found. When pointed out that at low concentrations, rectangular particles are achieved, and by increasing concentration above 0.4%, particles become spherical. It is to be noticed, the completely different shape of PCC particles obtained by carbonating suspensions of 1% and 2% respectively.

The data from figure 5, are well fitted by a linear equation 
\[ t = 6.903 C + 3.0827 \]
which denote that the precipitation reaction of carbonate is of pseudo – first order.

The experimental data point out that the increasing gas flow rate determines the decreasing of carbonation time, (fig. 6).

Precipitated calcium carbonate (PCC) obtained was chemically characterized by IR analysis, grain size distribution analysis and SEM.

The IR spectra of 0.66%, 1 and 2% concentrations are shown in figure 7.

The IR spectra in figure 7, obtained for the solid formed by the chemical reaction between carbon dioxide and calcium hydroxide suspension indicates that the solid was in all cases calcium carbonate, while the characteristic peak (band) is reported at 1425 cm⁻¹. In the spectra occur also two absorption peaks at 711 cm⁻¹ and respectively at 875 cm⁻¹, corresponding to the impurities in lime (fig. 2).

The granulometric distribution is influenced by the initial suspension concentration. The granulometric distribution was performed with a particle size analysator type SALD-7001 laser diffractometer. This equipment is able to measure the particle size in the range between 15 nm (0.015 mm) and 500 mm. The samples were prepared in advance in order to avoid the particle agglomeration. The results are shown in figure 8.

Analyzing the data from figure 8 it was noted that in case of 0.66% suspension carbonation the particles have an average diameter of 0.475 mm. Average particle diameter decreases reaching the value of 0.103 μm for suspensions of 1%, respectively 0.066 μm for suspensions of 2%. The decrease of average diameter can be explained by the increased number of crystallization germs due to an increase of the suspension concentration. It must be specified that because the particles have different shapes the results might be affected by the calculation strategy for the particle diameter (this are considered of spherical shape).

To determine the particle shape for the obtained PCC samples, SEM electron microscopy analysis was employed. Determinations were performed on a Vega Tescan SEM of 30 kV, the samples were covered with a layer of Ag. SEM images are shown in figure 9.

In case of the carbonation 0.66% calcium hydroxide suspension, not very clearly outlined, spherical-shaped particles are obtained, as can be seen in figure 9. In the solid obtained, rectangular particles can be also found. When pointed out that at low concentrations, rectangular particles are achieved, and by increasing concentration above 0.4%, particles become spherical. It is to be noticed, the completely different shape of PCC particles obtained by carbonating suspensions of 1% and 2% respectively.

The IR spectra of 0.66%, 1 and 2% concentrations are shown in figure 7.
In case of 1% suspension, as can be seen in figures 9 and 10, were obtained mostly rectangular particles with rare acicular particles. If the suspension concentration increased from 2% in the system only aciculate particles.

**Influence of temperature on PCC morphology**

Establishing the influence of temperature on PCC morphology was achieved by using suspensions of constant

---

**Fig. 8.** Particle size distributions, 1- 0.66%, 2 – 1% and 3 – 2%

**Fig. 9.** SEM for PCC synthesized SEM images corresponding to 2 μm resolution are shown in figure 10.
concentration (1.5 g/150 g water), ensuring carbon dioxide supplied to a flow of 10 L / h and a pressure of 10 mm water column. Investigations were carried out at two temperatures: 293 and 313 K. Calcium carbonate obtained was analyzed and it was found that at low temperatures rectangular particles are obtained, while at a temperature of 313 K aciculate particles predominate, as shown in figure 11. These results indicate that temperature plays an important role in the polymorphism of the crystallization process by the occurring thermal vibrations. Following the studies, ambient temperature (293-298 K) is proposed as the working temperature, thus, besides a carbonate having an optimal particle shape, obtaining important savings due to elimination of heating.

**Study of influence of stirring speed on PCC polymorphism**

The investigations were carried out at stirring speeds between 200 and 500 rpm. Experimental data shown that the stirring speed did not influence the particle shape, but only the particle size.

At low stirring speeds fine particles agglomerated and formed dense particles, while at higher stirring speeds were achieved PCC particles with lower diameters. Results are determined by the influence of hydrodynamic conditions on the growth process of germs.

**Conclusions**

Analyzing the obtained results, the following conclusions could be summarized:

- carbonation of calcium hydroxide suspensions is an obtaining method of PCC with imposed properties;
- the performed experiments on carbonation of calcium hydroxide suspensions show that the pH and conductivity values decrease with time, being influenced by the initial concentration of suspension;
- carbonation time, regarded as the time from the beginning of gas bubbling until conductivity becomes constant, is linear with the concentration of the suspension;
- experimental data shown that increasing the gas flow rate causes a decreasing of the carbonation time;
- initial concentration of the suspension influences the mean particle diameter and PCC polymorphism. In case of diluted suspensions (under 0.4%) rectangular particles are obtained; for suspension in the range 0.5-1% are obtained mainly spherical particles, and in case of more concentrated suspensions acicular particles are formed;
- temperature influences the particles shape, the rectangular particles being achieved at low temperatures and diluted suspensions;
- stirring speed didn’t influence the particle shape, but only the mean diameter of particles, the increasing of the stirring speed reducing the mean diameter.
References
2. SZEP, Al., HARIA, M., Rev. Chim.(Bucuresti), 58, no.10, 2007, p. 870
3. SZEP, Al., BARBU, C. H., BURLACU, A., MIHĂILĂ, Gh., Rev. Chim.(Bucuresti), 51, no 1, 2000, p. 60
4. SZEP, Al., MIHĂILĂ, Gh., Rev. Chim.(Bucuresti), 56, no. 8, 2005, p. 768
13. OTA, Y., GOTÔ, N., MOTOYAMA, I., IWASHITA, T., NOMURA, K., USA Pat. 4857291, 1989

Manuscript received: 15.06.2009