Chapter 5
Precipitation of Calcium Carbonate Using Sonochemical Reactor
In this work the possibility of continuous precipitation of calcium carbonate in sonochemical reactor has been investigated. The objectives of this work are to synthesize calcium carbonate in the presence of ultrasound and to compare the particle size and morphology of the calcium carbonate particles by ultrasound and conventional process. To study the effect of different operating parameters on particle size and morphology of calcium carbonate particles for both the methods.

5.1 Introduction

The precipitation of calcium carbonate is an important industrial operation which has been given a lot of consideration owing to its potential application as a starting material in the paint, plastic, adhesive, paper and rubber industries [1-2]. Such industrial applications require precipitated calcium carbonate (PCC) powders, with narrow particle size distribution, uniform shape, and crystallinity [3]. Pure calcium carbonate has three crystalline forms, calcite, aragonite and vaterite. The conventional morphologies of these crystalline forms are rhombohedral, needle-like and spheroidal, respectively [4]. Vaterite and aragonite are thermodynamically less stable than calcite and these two metastable phases eventually transform into calcite in an aqueous solution via a recrystallization mechanism [2]. The development of chemical routes leading to controlled crystallization is an important requirement in the synthesis of crystalline materials for various applications [5]. In the industrial scale production of precipitated calcium carbonate (PCC) adjusting the reactants concentration and/or using additives can be used for gaining control over the phase, morphology, and physical properties such as particle size, aspect ratio and specific surface area. The effect of carbonation conditions on industrially produced PCC have been thoroughly studied with the aim of tailoring yield, particle size and morphology, as well as degree of agglomeration [6].

The batch process which is regularly used for precipitated calcium carbonate production has number of limitations such as non-homogeneous mixing of three
different phases, diffusion of solute through highly concentrated slurry, secondary nucleation, variation in the particle size, shape and distribution. Therefore, it is preferable to use continuous process over the batch process. However the scale up of batch experimental setups increases mixing problems and homogeneity, therefore constituting a critical and often a very difficult step for chemical engineers interested in PCC synthesis [3].

At an industrial scale, it is necessary to produce large quantities of PCC and the production of uniform powders in a continuous mode is difficult. Preparation of calcium carbonate particles in continuous mode has been investigated in different types of reactors. Chakraborty et al. [7] carried out continuous precipitation of calcium carbonate in mixed suspension mixed product removal system (MSMPR). It was found that in a scaled reactor the nucleation was homogeneous and predominantly of vaterite which transformed to calcite within the reactor itself. Yagi et al. [8] used MSMPR crystallizer to study the nucleation and growth rates of calcium carbonate crystals. Crystal size distribution of crystals formed during the experiments was dependent on experimental conditions. The type and shape of the crystals changed with the concentration of Ca(OH)₂ slurry, but their mean size was marginally affected by the concentration of Ca(OH)₂ and the mean residence time of suspension. In a similar type of work Rodriguez-Clemente and Gomez-Morales [9] used a MSMPR reactor activated by microwave radiation and the results were compared with the batch process. In this work unusual morphologies of calcite were formed. In the batch experiments, monodisperse calcite crystals with ellipsoidal or peanut-like shapes were obtained, whereas in the continuous precipitation experiments, ellipsoidal shape calcite crystals were formed. Hostomsky and Jones [10] used a continuous-flow crystallizer for synthesizing calcium carbonate.

It was observed that the characteristics of the agglomerated PCC particles were controlled by the agglomeration of individual crystallites formed during the initial stage of synthesis.

The crystal form was seen to be dependent on the concentration of reagents, pH and residence time. Segmented flow tubular reactor was used to precipitate calcium carbonate. The basic objective of using this reactor was to avoid poor micromixing by using microvolume and to increase the homogeneity in reaction conditions as compared to larger volume to achieve improved powder characteristics [3]. The
morphology and size of calcium carbonate particles produced in a Couette–Taylor reactor was investigated by Jung et al. [11]. The change of particle morphology and size was caused by the excess species of reactants in the solution. Ultrasound has been used in crystallization for quite a long time and it modifies crystal properties of product and improves yield. Ultrasound assists for nucleation and inhibits crystal growth with better control over shape and size of crystals [12]. Ultrasound synthesis has advantages over other methods in terms of narrower size particle size distribution, smaller particle size, controlled morphology and rapid nucleation rate [13].

As reported in the literature review, ultrasound has been used for synthesis of calcium carbonate, but all those investigations are done with batch reactors [13-15]. This work presents systematic investigations on sonocrystallization of CaCO₃ particles in continuous mode in presence of ultrasound and by conventional method. A novel continuous flow sonocrystallization apparatus was used to prepare CaCO₃ particles using carbonation method. The effects of key operating variables such as calcium hydroxide slurry concentration, calcium hydroxide slurry flow rate and CO₂ flow rate on the particle size and morphology has also been studied.

5.2 Experimental Procedure

5.2.1 Experimental setup

The schematic of experimental set up used for the ultrasonically mediated continuous synthesis of CaCO₃ is shown in figure 5.1. This consists of a glass reactor with a sonication Probe (Dakshin make, 240 W, 22 kHz) along with a gas distributor, magnetic stirrer and CO₂ gas supply. The CO₂ gas distributor was placed at the bottom of the reactor. Small bubbles of around 1 mm diameter of CO₂ were produced through the gas distributor. The glass reactor was essentially a cylindrical container of 10 cm diameter. The diameter of ultrasound probe was 10 mm which was used for the generation of ultrasonic waves. The probe was immersed in the centre of reaction solution. The progress of the reaction was followed by continuous measurement of conductivity and pH of the reactor contents. As the solubility of CaCO₃ in water (∼0.0012 g/100g of water) is much lower than Ca(OH)₂, it precipitates out continuously [16]. Precipitation experiments were carried out in a continuous mode with and without ultrasound. For conventional synthesis ultrasound probe was removed and only stirring was used. All the experiments were carried out at constant
temperature by using the constant temperature bath, in which the CSTR assembly was immersed.

![Diagram of experimental setup](image)

**Figure 5.1:** Schematic of experimental setup for continuous production of CaCO₃ particles

### 5.2.2 Continuous precipitation of calcium carbonate

Initially the liquid reactant was prepared by dissolving Ca(OH)₂ (LR grade, High Purity Laboratory Chemicals, Mumbai) in water to get the desired concentration of Ca(OH)₂ slurry. This suspension was completely mixed using stirrer running at a constant speed of 500 rpm for 15 minute so as to get a homogenous mixture. The carbon dioxide gas was introduced at the bottom of the reactor through a sparger with 1mm diameter holes. The CO₂ gas and Ca(OH)₂ slurry was continuously fed to the reactor at a constant flow rate and the product was continuously withdrawn from the reactor. At the start of each run, the reactor was filled with calcium hydroxide slurry of desired concentration upto the overflow level. After that the flow of Ca(OH)₂ slurry, CO₂ gas and ultrasonic irradiation was started. For measuring the change in concentration of Ca(OH)₂ with time, the samples were collected from the reactor and titrated with 0.1 N HCl with phenolphthalein indicator to detect the end point of titration. Simultaneously the progress of the reaction was monitored by measurement of pH and conductivity of the reaction mixture as a function of time. The completion
of the carbonation reaction was indicated by drop in pH to a stable value of 7. Once
the pH of the reaction mixture remained constant at 7 it indicated the steady state of
the process. Then the samples from the reactor were collected for the characterization
purpose.

For acoustic cavitation the actual power supplied inside the vessel is lower than
provided by output controller. The total acoustic power injected into the sample was
calculated using calorimetric method. Calorimetric method is generally used to
determine the energy efficiency of the equipment [17]. Amount of energy dissipated
in the bulk of liquid was calculated by measuring the rise in temperature of a fixed
quantity of water for a given time. From the calorimetric studies the energy efficiency
of the probe was found to be around 4.55 %.

In case of conventional synthesis, ultrasound probe was removed and it was replaced
by simple stirrer. For both the synthesis methods temperature of the reaction mixture
was maintained constant at 30±2°C. All the experiments were carried out in a
continuous mode to study the effect of different operating parameters such as
Ca(OH)₂ slurry concentration, Ca(OH)₂ slurry flow rate and CO₂ flow rate on the
particle size and morphology of CaCO₃. To study the influence of Ca(OH)₂ slurry
concentration, CO₂ flow rate was maintained constant at 45 Liter per hour (LPH) and
Ca(OH)₂ slurry flow rate was 20 mL/min while the slurry concentration was varied
from 1.96 to 5.66 wt%. The effect of CO₂ flow rate was studied in the range 25-65
LPH for fixed volumetric flow rate of 20 mL/min for Ca(OH)₂ slurry and the
concentration of Ca(OH)₂ slurry was maintained at 3.85 wt%. Ca(OH)₂ slurry flow
rate was varied from 12 to 28 mL/min at fixed CO₂ flow rate of 45 LPH and Ca(OH)₂
slurry concentration of 3.85 wt%. The actual volume of the reaction mixture was 700
mL indicating that the residence time of reactants in the reactor would be 35 minutes
corresponding to 20 mL/min slurry flow rate. The collected precipitate was washed
two times with water and thrice with isopropanol in order to remove the impurities.
After each washing, the CaCO₃ particles were separated by centrifugation. Finally
CaCO₃ powder was dried at 80°C for 24 h before it was used for characterization.

The well known reaction mechanism for CaCO₃ synthesis consists of the following
steps [18]:

1. \[ \text{Ca(OH)}_2 + \text{CO}_2 \rightarrow \text{CaCO}_3 + \text{H}_2\text{O} \]
2. \[ \text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2 \]
3. \[ \text{CaO} + \text{H}_2\text{O} \rightarrow \text{Ca(OH)}_2 \]
Ca (OH)$_2$ (S) $\leftrightarrow$ Ca$^{2+}$ (aq) + 2OH$^-$ (aq) \hspace{1cm} (1)

CO$_2$ (g) $\leftrightarrow$ CO$_2$ (aq) \hspace{1cm} (2)

CO$_2$ (aq) + OH$^-$ (aq) $\rightarrow$ HCO$_3^-$ (aq) \hspace{1cm} (3)

HCO$_3^-$ (aq) + OH$^-$ (aq) $\rightarrow$ H$_2$O + CO$_3^{2-}$ (aq) \hspace{1cm} (4)

Ca$^{2+}$ (aq) + CO$_3^{2-}$ (aq) $\rightarrow$ CaCO$_3$ (s) \hspace{1cm} (5)

### 5.2.3 Structural characterization

In order to ensure any discrepancies in the sampling for characterization purpose, the samples from the reactor for characterization were collected only after the reactor has achieved a steady state condition (approximately after four to six residence times). Conductivity measurements were done by using a conductivity meter (SYSTRONICS conductivity meter 304). XRD patterns of CaCO$_3$ powders were recorded by means of powder X-ray diffractometer (Philips PW 1800) between 20° and 80° with a scan rate of 2°/min. The Cu Kα radiation (LFF tube 35 kV, 50mA) was selected for the XRD analysis. FTIR spectra were recorded on a FT-IR spectrometer (SHIMADZU 8400S) in the region of 4000–400 cm$^{-1}$ with samples pressed with KBr as pellet. The morphology of CaCO$_3$ particles was investigated by using Scanning Electron Microscopy (SEM) (JEOL JSM, 680LA 15 KV, magnification 10000X). For particle size, Dynamic light-scattering (DLS) measurement was performed on a Malvern Zetasizer Instrument (Malvern Instruments, Malvern, UK).

### 5.3 Results and Discussion

#### 5.3.1 Monitoring the carbonation process

The progress of the carbonation process can be followed by measuring the electrical conductivity of the aqueous suspension as the reduction in the concentration of ions takes place as the reaction progresses [19]. Similarly the hydroxyl ions which are released due to calcium hydroxide dissociation are consumed for the calcium carbonate production, permits the study of reactive process on the basis of the changing pH values [20]. Hence the conductivity and pH of the reaction mixture was continuously monitored as a function of carbonation time to monitor reaction progress as well as the phenomena of nucleation and crystal growth.
Figure 5.2 and 5.3 shows the comparison of variation of conductivity and pH during the carbonation reaction with respect to time for both methods of synthesis. The readings are shown for a representative experiment corresponding to the experimental conditions of 3.85 wt% Ca(OH)$_2$ slurry concentration, 45 LPH of CO$_2$ flow rate and 20 mL/min Ca(OH)$_2$ slurry flow rate for both methods of synthesis.

Figure 5.2 depicts the conductivity readings for conventional and ultrasound assisted synthesis methods. For both methods it is observed that the conductivity drastically dropped with time. This drop in conductivity indicates the start of nucleation where massive nuclei of calcium carbonate are just formed and these small nuclei are getting adsorbed on the surface of Ca(OH)$_2$ particles. This results in the formation of a viscous gel which offers the resistance to the transfer of Ca$^{2+}$ and OH$^-$ ions [13-14, 21]. Again the conductivity reverted quickly because of rapid deagglomeration of the gel. The deagglomeration of the gel took place due to the further dissolution of Ca(OH)$_2$ particles as K$_{sp}$Ca(OH)$_2$ > K$_{sp}$CaCO$_3$. Simultaneously there was substantial increase in the number of nuclei of calcium carbonate with continuous supply of CO$_2$ into the reactor. The value of conductivity reached to a minimum at the pH near 7, since the Ca(OH)$_2$ phase completely disappeared and the carbonation reaction was completed. Comparing the curves for two synthesis methods it is observed that for conventional method, delayed nucleation is there with lower magnitude drop in conductivity, indicating that the precipitation is accelerated in the presence of cavitation [22]. The large number of calcium carbonate nuclei are formed in the presence of ultrasonic irradiations compared to conventional stirring. During the ultrasound irradiation, bubbles are formed in the reaction mixture which grow to a certain size and then collapse violently. The extreme conditions of high temperature and pressure created due to collapse of bubbles produces intense local heating, as well as very high cooling rates. Rapid local cooling rates, in the range of $10^7 - 10^{10}$ K/s, dramatically reduce the solubility of Ca$^{2+}$ causing a supersaturation of Ca$^{2+}$ ions, leading to a rapid nucleation of calcium carbonate and improves the solute transfer as well. Further, localized pressure increase reduces the crystallization temperature and the cavitation events associated with this nucleation allow the excitation energy barriers to be surmounted [23].

Generally the size distribution of nanometer particles is determined by the rate of nucleation and the subsequent growth. The fast nucleation produces smaller particles
whereas if the growth rate is predominant, the crystallite usually is composed of larger particles [24]. The trend shown by conductivity readings provides a possibility of probable formation of smaller size particles with ultrasound. Pronounced effect of ultrasound was evident from these results.

Figure 5.3 reports the changes in pH of the reaction mixture as a function of time for carbonation reaction with and without ultrasonication. From figure 5.3 it can be seen that the similar trend in variation of pH is exhibited for carbonation reaction with and without ultrasonication. At the beginning stages of the reaction and for most of the carbonation time the pH remained constant at around 12 to 12.5. In the initial stages dissolution rate of Ca(OH)$_2$ is less compared to the rate of its addition to the reactor, hence the concentration of OH$^-$ ions and pH remains constant. This indicates that the pH is only dependent on OH ion concentration and not influenced by the transfer of ions [13-14, 21]. When the carbonation reaction is about to be completed, both conductivity and pH levels drop rapidly in a shorter span of time from the initial slow stage. This happens because of the steady decrease of Ca(OH)$_2$ which results into the formation of Ca$^{2+}$ and OH$^-$ ions and further gradual decrease of Ca$^{2+}$ and OH$^-$ contents in the solution [25].

At the pH value of around 7, all the Ca(OH)$_2$ has been totally carbonated and the carbonation reaction was completed resulting in the formation of CaCO$_3$. Similar trend of variation of conductivity and pH with time was observed for all other experiments.
Figure 5.2: Variation of electrical conductivity versus carbonation time (Ultrasound frequency = 22 kHz, Ultrasound power = 240 W, Probe diameter - 10 mm, Speed of agitator- 500 RPM)

Figure 5.3: Variation of pH versus carbonation time (Ultrasound frequency = 22 kHz, Ultrasound power = 240 W, Probe diameter- 10 mm, Speed of agitator- 500 RPM)
5.3.2 XRD analysis

The phase structure of prepared CaCO₃ particles was detected by using the wide angle X-ray diffraction pattern. Figure 5.4 shows the X-ray diffraction patterns of representative samples of CaCO₃ particles prepared by ultrasonic and conventional stirring method. Figure 5.4A depicts the XRD patterns of CaCO₃ for 3.85 wt% Ca(OH)₂ slurry concentration (CO₂ flow rate = 45 LPH, Ca(OH)₂ slurry flow rate = 20 mL/min), figure 5.4B shows XRD patterns for 55 LPH CO₂ flow rate (3.85 wt% Ca(OH)₂ slurry concentration and Ca(OH)₂ slurry flow rate = 20 mL/min), and figure 5.4C is for 16 mL/min slurry flow rate (3.85 wt% Ca(OH)₂ slurry concentration and CO₂ flow rate = 45 LPH) for both methods of synthesis.

For all the operating conditions of Ca(OH)₂ slurry concentration, CO₂ flow rate and Ca(OH)₂ slurry flow rate studied in this investigation, the XRD pattern shows the peaks at 2θ = 23.1, 29.4, 34.2, 36, 39.5, 43.2, 47.6, 48.6, 57.6, 60.9, and 64.9°. All these peaks reflect calcite phase of calcium carbonate [26-28] indicating that only the calcite phase was principally formed during carbonization process. These diffraction data are in good accordance with those of JCPDS PDF2 standard card (005-0586) (Mineral Powder Diffraction File Data Book ICDD No.5-586) [27]. Additionally it is also observed that the intensity of the peaks in XRD patterns in the case of ultrasound assisted method is significantly lower compared to that of conventional method. Further, broadening of XRD peaks is observed for ultrasound assisted method representing the smaller particle size of CaCO₃ particles with less crystallinity [29].
Figure 5.4: X-ray diffraction patterns of CaCO$_3$ particles (A) 3.85 wt% Ca(OH)$_2$ slurry concentration, (B) 55 LPH CO$_2$ flow rate and (C) 16 mL/min Ca(OH)$_2$ slurry flow rate.
5.3.3 FTIR analysis

FTIR spectroscopy is a useful tool in the molecular characterisation of inorganic species [30]. Figure 5.5 depicts the FTIR spectra of calcium carbonate particles prepared by ultrasonic and conventional stirring method and mixed sample of 90 wt% CaCO$_3$ and 10 wt% Ca(OH)$_2$.

As per the literature reports [21, 27-28, 31-33] the absorption bands in the region of 712-717 and 874-876 cm$^{-1}$ are assigned to characteristic v4 and v2 absorption of CO$_3^{2-}$ ions respectively and 1430-1460 cm$^{-1}$ are assigned to v3 absorption bands of calcite. In the present investigation, results of FTIR analysis shows main absorption peaks located in the regions of 715-717, 876-877 and 1430-1496 cm$^{-1}$. Therefore absorption bands in the region of 715-717 cm$^{-1}$ are assigned to characteristic v4 absorption of CO$_3^{2-}$ ions, while the bands in the region of 876-877 cm$^{-1}$ may be attributed to the characteristic v2 absorption of CO$_3^{2-}$ ions. The absorption bands in the region of 1430-1496 cm$^{-1}$ can be assigned to v3 absorption bands of calcite. Thus for both the synthesis methods formation of calcite phase of CaCO$_3$ particles was confirmed by the presence of absorption bands. These FTIR results are strongly supported by XRD results discussed earlier in section 3.2. The slight discrepancy between experimental and published IR values could be ascribed to the required grinding of a CaCO$_3$ sample with KBr to produce pellets [34].

As mentioned earlier the progress of the reaction was monitored by pH and conductivity measurements and the completion of the reaction was indicated by fall in pH and conductivity values. Additionally, in order to confirm the conversion of Ca(OH)$_2$ with both methods, the FTIR patterns of CaCO$_3$ prepared experimentally were compared to the FTIR pattern of synthetic mixture of 90 wt% CaCO$_3$ and 10 wt% Ca(OH)$_2$ as shown in figure 5.5. Gu et al. [33] has reported that the characteristic peak for Ca(OH)$_2$ is at 3654 cm$^{-1}$. In the present work, in case of the synthetic mixture of 90 wt% CaCO$_3$ and 10 wt% Ca(OH)$_2$, the sharp peak is observed at 3645 cm$^{-1}$ which can be attributed to the presence of Ca(OH)$_2$ in the sample. However, in the FTIR pattern of experimentally prepared CaCO$_3$ by ultrasound assisted and conventional stirring method, this peak is completely diminished indicating the complete conversion of Ca(OH)$_2$ during the carbonization reaction.
5.3.4 Comparative assessment of ultrasound against conventional carbonation method on particle size and morphology of CaCO₃

To study the effect of different operating parameters on the particle size and morphology of CaCO₃, the experiments were carried out under varying conditions of Ca(OH)₂ slurry concentration, CO₂ flow rate and Ca(OH)₂ slurry flow rate under ultrasonic environment and by conventional method. The results are discussed in subsequent sections.

5.3.4.1 Influence of Ca(OH)₂ slurry concentration

The influence of Ca(OH)₂ slurry concentration on the morphology and particle size of calcium carbonate was studied for different slurry concentrations ranging from 1.96 to 5.66 wt%. The volumetric flow rate of slurry was maintained at 20 mL/min and the CO₂ flow rate was kept at 45 LPH for both synthesis methods. SEM images of the CaCO₃ particles at different Ca(OH)₂ slurry concentrations for both the methods of synthesis are sown in figure 5.6. In all the figures it can be clearly seen that the cubical/rhombohedral CaCO₃ particles are formed with both methods of synthesis. For both synthesis methods the similar type of crystals are formed, however, there are mixed results reported in the literature related to the type of crystals formed in
presence and absence of ultrasound. Some authors have obtained similar crystals in the presence and absence of cavitation whereas others have reported considerable differences [23]. Nishida [35] has studied the precipitation of calcium carbonate by ultrasonic irradiation and he has reported that the morphology was not affected by the ultrasonic irradiation. Conversely in the work of Enomoto et al. [36] during the oxidation of iron hydroxide it was observed that the ultrasound promoted the goethite formation while magnetic stirring favoured the formation of magnetite. Moreover SEM images also indicate that in case of ultrasound particle size decreased with an increase in the Ca(OH)$_2$ slurry concentration from 2.92 to 4.76 wt % and for conventional method of synthesis, the particles size is found to be decreased with an increase in the Ca(OH)$_2$ slurry concentration from 2.92 to 3.85 wt % and again it is increased for 4.76 wt% Ca(OH)$_2$ slurry concentration.

The particle sizes for some of the representative samples were measured and reported in Table 5.1. For both synthesis methods it is seen that the particle size decreased with increasing Ca(OH)$_2$ slurry concentration, but this trend was observed to be followed to certain value of Ca(OH)$_2$ slurry concentration. In case of mechanical stirring the particle size decreased as the concentration increased from 1.96% to 3.85 wt%, whereas for ultrasound assisted method the particle size reduced till a slurry concentration 4.76 wt%, beyond which it started increasing. This trend can be attributed to the fact that as the concentration of Ca(OH)$_2$ increases excess of Ca$^{2+}$ ions are present in the solution. These excess Ca$^{2+}$ ions may be adsorbed on the preferred faces of the calcium carbonate particle and then the adsorbed ions inhibit the face growth of a particle leading to a reduction in the mean particle size [1, 11].

As compared to conventional method of synthesis the particle size of CaCO$_3$in the presence of ultrasound is smaller. In any crystallization operation the particle size is generally determined by the rate of nucleation and the subsequent growth. The ratio between the rates of these two processes determines the size and number of the particles. Accelerated nucleation and inhibited growth, therefore, are the key factors for the synthesis of nanometer particles in aqueous solutions [24]. In the presence of ultrasound it is possible to attain early nucleation at a faster rate leading to the formation of large number of nuclei and it limits the particle growth which can form the nanometer size particles. It is already explained in Section 3.1 that in case of ultrasound the nucleation started earlier as compared to conventional method.
Further the particle size is dependent on the distribution of supersaturation in a reaction system. The physical effects of ultrasound such as creation of turbulence can enhance the mixing and lead to fairly uniform distribution of supersaturation in the reaction medium ultimately resulting in the formation of nanometer sized CaCO$_3$ particles. However this is not the case with conventional synthesis of CaCO$_3$, hence comparatively larger sized particles are obtained. Thus the smaller particle size of CaCO$_3$ with ultrasound is attributed to the significantly improved micromixing, enhanced solute transfer rate, rapid nucleation and the formation of large number of nuclei due to the physical effects of the ultrasound. Additionally the fast kinetics of the ultrasound assisted reaction, does not provides enough time for the growth of CaCO$_3$ particle leading to an ultimate reduction in the particle size [32].

As discussed earlier, the particle size decreased with increasing Ca(OH)$_2$ concentration till a certain concentration and again it increased. For conventional stirring the increase in the particle size was observed when the concentration of the Ca(OH)$_2$ was increased to 4.76 wt% while in case of ultrasound method the particle size increased when the concentration reached 5.66 wt%. At higher concentration of Ca(OH)$_2$, large number of dissolved particles of Ca(OH)$_2$ are present which lead to formation of a continuous gel-like network in the solution due to coexistence of Ca(OH)$_2$ and CaCO$_3$ particles. The excess Ca(OH)$_2$ particles may interfere with the effect of ultrasonication and the formed gel-like network cannot be efficiently dispersed resulting in nonuniform nucleation. [14]. Similar reasons are also applicable in case of stirring as massive solid particles of Ca(OH)$_2$ and CaCO$_3$ coexist in the solution and agglomerate with each other, resulting in non homogeneous mixing. The effect of ultrasound was evident from these results also as higher solids concentration was efficiently dispersed by ultrasound as compared to conventional stirring.

The difference in the sizes determined by particle size analyzer and SEM images would be due to the coagulation or agglomeration of the particles during sample preparation for particle size measurements [37].
Figure 5.6: SEM images of CaCO$_3$ particles for different Ca(OH)$_2$ slurry concentrations (wt%) and preparation methods, (A) 2.92 wt% (Ultrasound), (B) 3.85 wt% (Ultrasound), (C) 4.76 wt% (Ultrasound), (D) 2.92 wt% (Stirring), (E) 3.85 wt% (Stirring), (F) 4.76 wt% (Stirring)

Table 5.1: Particle size of CaCO$_3$ particles - Effect of Ca(OH)$_2$ concentration

<table>
<thead>
<tr>
<th>Slurry Concentration (wt%)</th>
<th>Particle size, nm</th>
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<tr>
<td></td>
<td>Stirring</td>
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<tr>
<td>3.85</td>
<td>601</td>
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<tr>
<td>4.76</td>
<td>967</td>
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<td>5.66</td>
<td>1151</td>
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5.3.4.2 Influence of CO$_2$ flow rate

The influence of CO$_2$ flow rate on the particle size and morphology of calcium carbonate was investigated for different flow rates of CO$_2$ (25 to 65 LPH) at fixed
volumetric flow rate of 20 mL/min for Ca(OH)$_2$ slurry and 3.85 wt% slurry concentration.

SEM images of the CaCO$_3$ particles at 55 LPH CO$_2$ flow rate for both methods of synthesis are shown in figure 5.7. From figure 5.7A it is seen that with ultrasound assisted synthesis, rhombic and distorted cubes of CaCO$_3$ particles are formed whereas conventional method shows the formation of plate like particles (Figure 5.7B). In this case the change of morphology was observed with change in synthesis method. Rhombohedral calcite crystals were formed with ultrasound whereas stacked plates were formed with conventional method. This change in morphology of CaCO$_3$ may be attributed to the dissolving rate of CO$_2$ at different conditions. A favourable condition for the formation of plate-like particles may be created due to lower carbonation rate with conventional rate with conventional stirring method.

As reported by Wen et al. [38] a lower value of [$\text{Ca}^{2+}]/[\text{C}]_T$ is favourable for the formation of plate-like CaCO$_3$ particles, where $\text{Ca}^{2+}$ is the concentration of calcium ions in the reactor and $[\text{C}]_T$ is the total concentration of carbon-containing components in solution. In discussing the effects of ultrasound it is already explained that ultrasound can enhance the supersaturation of $\text{Ca}^{2+}$ which means that with ultrasound the ratio of [$\text{Ca}^{2+}]/[\text{C}]_T$ is higher. However in case of conventional stirring method the value of [$\text{Ca}^{2+}]/[\text{C}]_T$ would be lower which may be responsible for formation of plate-like particles.

SEM images also indicate that the particle size of CaCO$_3$ is smaller in case of ultrasound assisted synthesis. This observation is equally supported by the particle size analysis of the samples given in Table 5.2. The calcium carbonate precipitation process is controlled by the mass transfer at the gas liquid interface [16,18]. Thus the film resistance at gas-liquid interface plays an important role in the progress of the reaction. During the conventional synthesis the concentration of CO$_2$ might be less in the reaction zone due to higher film resistance at gas-liquid interface. On the other hand due to vigorous micromixing with ultrasound, reduction in the gas-liquid film thickness takes place and the reaction proceeds at a faster rate. On account of the rigorous mixing generated by ultrasound the dissolution of Ca(OH)$_2$ is improved in this three phase reaction. This rigorous mixing improves the transport of gas molecules to the solid surface ultimately leading to an increase in the mass transfer and therefore the overall reaction rate. Further the shock waves and microjets
generated due to cavitation effect of ultrasound can accelerate the motion of the liquid molecules and increase molecular impacts to speed up the reaction. The thickness of the stagnant film and the adsorption layer adjacent to the growing crystal surface depends on the relative solid-liquid velocity and both these things are decreased in the presence of ultrasound [39].

It is also observed that the particle size increased with an increasing CO$_2$ flow rate. This can be attributed to the solubility of CO$_2$ which is constant at any given conditions. The solubility of carbon dioxide is about 90 cm$^3$ of CO$_2$ per 100 ml of water at room temperature. When the flow rate of CO$_2$ is increased some amount of the interacted CO$_2$ gas cannot be absorbed by water but it runs out of the solution directly, as a result it is not efficiently utilized for the reaction [40]. On the other hand, at low CO$_2$ flow rate, the consumption rate of CO$_2$ gas by unit mass of Ca(OH)$_2$ for the reduction is very close to its absorption rate. Similar results of increase in particle size with CO$_2$ flow rate has been reported by Triveni et al. [41]. Conversely He et al. [14] have reported totally opposite results where particle size decreased with CO$_2$ flow rate. Considering the results of present investigation it can be concluded that the increase of CO$_2$ flow rate may not always result in smaller particle size [16].

One more important feature which is seen from the results is that, for both the methods at the CO$_2$ flow rate of 65 LPH the particle size has increased by almost more than twice the size at 55 LPH. During the calcium carbonate precipitation electrostatic forces of water molecules can polarize CO$_2$ molecules, increasing their ability to penetrate the water phase. Basic requirement for the formation of CaCO$_3$ is that, the CO$_2$ molecules must enter the phase containing the Ca$^{2+}$ ions and therefore mass transport resistance is a very important parameter. For the transfer of CO$_2$ into the water lot of resistance is there because the viscosity of CO$_2$ is less compared to the viscosity of water though compressed CO$_2$ is more viscous than atmospheric CO$_2$, but still considerably less viscous than water. Once CO$_2$ is absorbed in water it hydrates to yield bicarbonate ions (HCO$_3^-$) and carbonate ions (CO$_3^{2-}$) but these transformations are very fast and only about 1% of the absorbed CO$_2$ is transformed into carbonate ions.

Thus at high CO$_2$ flow rate there are two reasons for the lesser penetration of CO$_2$ molecules in water phase. Firstly it is the higher mobility of CO$_2$ molecules with respect to water and second is the large viscosity difference between water and
CO₂ which ultimately results into CO₂ bypassing the solution [41]. This results in the nucleation at limited locations and this continues to grow leading to formation of larger sized CaCO₃ particles.

**Figure 5.7:** SEM images of CaCO₃ particles for CO₂ flow rate of 55 LPH (A) Ultrasound, and (B) Stirring.

**Table 5.2:** Particle size of CaCO₃ particles - Effect of CO₂ flow rate

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<thead>
<tr>
<th>CO₂ flow rate (LPH)</th>
<th>Particle size, nm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Stirring</td>
</tr>
<tr>
<td>35</td>
<td>575</td>
</tr>
<tr>
<td>45</td>
<td>601</td>
</tr>
<tr>
<td>55</td>
<td>521</td>
</tr>
<tr>
<td>65</td>
<td>1144</td>
</tr>
</tbody>
</table>
### 5.3.4.3 Influence of Ca(OH)$_2$ slurry flow rate

To study the influence of Ca(OH)$_2$ slurry flow rate it was varied from 12 to 28 mL/min with increment of 4 mL/min. During these experiments Ca(OH)$_2$ slurry concentration was maintained at 3.85 wt% and CO$_2$ flow rate was maintained at 45 LPH. Figure 5.8 depicts the SEM images of the CaCO$_3$ particles at Ca(OH)$_2$ slurry flow rate of 16 mL/min for both the methods of synthesis. SEM images are showing two totally different morphologies of calcite phase for two methods. From figure 5.8A it can be seen that the use of ultrasound leads to a formation of rhombic CaCO$_3$ particles with sharp edges which are randomly stacked and densely distributed. With ultrasound same morphology has been observed during the study of various parameters. Whereas in the absence of ultrasound (conventional stirring method), scalenohedral CaCO$_3$ particle formation is predominant with larger particle size as well (Figure 5.8B). The possible reason for spindle like morphology of CaCO$_3$ may be that the spindle shape is formed by the aggregation of primary particles in a preferential direction and CaCO$_3$ primary particles have some sort of anisotropy [42]. For the present case at 16 mL/min Ca(OH)$_2$ slurry flow rate the residence time of the reaction mixture in the reactor is longer which may have promoted the adsorption of primary particles in a preferential direction.

The particle sizes corresponding to different slurry flow rates for the two synthesis methods are shown in Table 5.3. For both the methods increase in the slurry flow rate resulted in reduction in particle size. With increased slurry flow rate, the mean residence time of the reaction mixture in the reactor was decreased which results into smaller particle size. The smaller size of particles is achieved in the presence of ultrasound against conventional stirring for all the slurry flow rates studied in this work. The results can be attributed to the effects of ultrasound in accelerating the reaction and the smaller size of CO$_2$ bubbles formed during ultrasonic irradiations. The overall gas-liquid interfacial area is higher with the small size CO$_2$ bubbles as against the surface area of bigger bubbles [16]. Production of fine bubbles of CO$_2$ under the cavitation environment was found to be responsible for the dispersion and mass transfer of CO$_2$ which may have resulted in the intensification of the carbonation process and the formation of very fine CaCO$_3$ particles [25].
Figure 5.8: SEM images of CaCO$_3$ particles for 16 mL/min Ca(OH)$_2$ slurry flow rate (A) Ultrasound, (B) Stirring

Table 5.3: Particle size of CaCO$_3$ particles - Effect of Ca(OH)$_2$ slurry flow rate

<table>
<thead>
<tr>
<th>Slurry flow rate (mL/min)</th>
<th>Particle size, nm</th>
<th>Stirring</th>
<th>Ultrasound</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
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<tr>
<td>12</td>
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<tr>
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<td>24</td>
<td></td>
<td>577</td>
<td>244</td>
</tr>
</tbody>
</table>
5.4 Conclusion

Synthesis of calcium carbonate by precipitation method was carried out at ambient temperature in a continuous mode in a stirred reactor under ultrasonic environment and the results were compared with the conventional stirring method. The influence of key operating variables such as Ca(OH)$_2$ slurry concentration, CO$_2$ flow rate and Ca(OH)$_2$ slurry flow rate on the particle size and morphology of CaCO$_3$ was investigated for both the methods of preparation. Conductivity-time curves of the reaction mixture were used to indicate the onset of nucleation and crystal growth. The experimental analysis of the obtained data suggests that the Ca(OH)$_2$ slurry concentration, CO$_2$ flow rate and Ca(OH)$_2$ slurry flow rate significantly influence the particle size and the morphology to some extent. The use of ultrasound resulted in smaller size particles against conventional stirring. The particle size decreased with an increase in the concentrations of Ca(OH)$_2$ and increased with increasing CO$_2$ flow rate for both the synthesis methods. The slurry flow rate had a substantial influence on the particle size and the particle size reduced with increased slurry flow rate. Characterization techniques such as FTIR and XRD confirmed the formation of only calcite form of calcium carbonate. During most of the experiments formation of rhombohedral calcite particles was observed.

The production of calcium carbonate is mainly done in batch processes and large quantities of CaCO$_3$ are required in industries due its widespread usage. Developing the new processes for these types of systems with larger throughput will always be a topic of investigation. The continuous process suggested in this work may be feasible for industrial applications to produce larger quantities.

References

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