Calcium Carbonate Precipitation Using New Segmented Flow Tubular Reactor

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A new segmented flow tubular reactor for the continuous production of powders was used to synthesize calcium carbonate by precipitation. This new reactor uses a nonmiscible phase (air in most cases) to create individual microvolumes of the reacting mixture or suspension ensuring that a plug-flow regime is maintained. In a microvolume, poor micromixing can be avoided and the homogeneity in reaction conditions is increased better than in larger volumes, leading to a better control of powder characteristics. Calcium carbonate with controlled characteristics could be precipitated continuously using this new segmented flow tubular reactor. Pure calcite could be obtained in the tubular reactor by segmenting a Ca^{2+} solution with a reactive CO_2/NH_3 gas mixture. This synthesis process is very promising for industrial production since the scale-up should easily be achieved by multiplying the number of tubes working in parallel.

Introduction

In recent years, there has been much activity in the search for high-performance materials and the use of new materials for applications in paint, textile, plastic, adhesive, rubber, bioceramic, and paper industries. Precipitated calcium carbonate (PCC) has received much attention because of its numerous applications in these areas. Such industrial applications require well-defined PCC powders, which consist of particles with a narrow size distribution, uniform shape, and crystallinity. Marentette et al. (1997) have shown that these characteristics play a crucial role in product properties and their control has become necessary. Although there are several precipitation techniques in the literature which report the preparation of PCCs, the fine control of morphology and particle size is not as well exploited as in nature itself as reported by Mann (1988)—where control of size, shape, and architecture adapts the material to meet its environmental requirements. According to several authors (Xyla et al., 1991; Mann et al., 1988; De Groot and Duyvis, 1966; Dalas and Koutsoukas, 1988; Vucak et al., 1997; Dupont et al., 1997), the determination of the relationship between precipitation conditions and product morphology is still a major challenge for research scientists. At an industrial scale, it is necessary to produce large quantities of PCC and the production of uniform powders in a continuous mode is not simple. The scaling 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.

The continuous $CaCO_3$ precipitation from solution has been developed in a small continuous flow crystallizer by Budz et al. (1986) and Hostomsky and Jones (1991). The dominant growth mechanism was shown to be the agglomeration. The agglomeration of individual crystallites formed during the early stage of synthesis controlled the characteristics of these agglomerated PCCs, which were not regular or homogeneous and varied strongly with precipitation conditions. Chakraborty et al. (1994) have developed the continuous precipitation of PCC using a mixed suspension mixed product removal (MSMPR) batch process. It was found that in the scaled reactor the nucleation was homogeneous resulting in a predominantly vaterite phase, which transforms gradually into calcite even in the reactor itself. However, the morphology of as prepared PCCs were not very regular and the particle-size distributions were broad. Rodríguez-Clemente and Gómez-Morales (1996), under certain experimental conditions and

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using a MSMPR reactor activated by microwave radiation, have obtained calcite crystals with ellipsoidal or peanut-like shapes and with narrow particle-size distributions. The morphology and crystal phase have also been thoroughly investigated by Vucak et al. (1997) and show the very large variety of morphologies that can be produced in stirred-tank reactors under the various reaction conditions.

For such a complex system, the use of tubular reactors is very interesting because of the relative ease of using them to produce powders in a continuous mode. The transfer of PCC precipitation from laboratory to industrial production may then simply be achieved by multiplying the number of individual tubular reactors running in parallel—"scale out" rather than "scale up". The concept of a plug-flow reactor has been thoroughly investigated, since it can provide a narrow residence time distribution necessary to generate uniform particles of narrow size distributions. A new continuous tubular reactor, the segmented flow tubular reactor (SFTR), has recently been conceived by Lemaître et al. (1996), which deals with the plug-flow regime. This reactor uses two nonmiscible phases to create individual microvolumes of previously well-mixed reactants. This reactor has been successfully used in the case of forced precipitation where the mixing step is of major importance for the chemical and physical characteristics of the synthesized powders, and also for precipitation starting from a homogeneous solution where the precipitating ion is generated in the reacting mixture by means of the slow decomposition of one co-reactant (Vacassy et al., 1998). In the case of forced precipitation, a static micromixer is added upstream of the process as an individual part of the new segmented flow reactor. The micromixer ensures an efficient and reproducible mixing of the initial co-reactants before their introduction into the tubular reactor. Depending on the choice of the mixer adjustment and the reactor parameters, the nucleation and aggregation kinetics can vary and influence the precipitate properties.

$CaCO_3$ can be synthesized by various methods as reported in the abundant literature on the topic. The carbonation process is generally used in the industry, because of its low-cost and the availability of the raw materials as claimed by Jones et al. (1992) and Vucak et al. (1997). This process often includes the calcination of the limestone to produce quicklime and calcium oxide, which are then purified separately before recombining, and the $CaCO_3$ precipitation follows via a liquid-gas reaction. The purpose of the present study was to investigate alternative routes including the carbonation process to precipitate PCC at high supersaturation (relative supersaturation 10^6) in the SFTR starting from $CaCl_2$ or $Ca(OH)_2$.

The synthesis of calcium carbonate from forced precipitation at high supersaturation was first carried out in a simple batch reactor prior to transfer to the SFTR. The control of temperature and mixing conditions, including supersaturation and reactant concentrations and their influence on the nature and morphology of the precipitated phase, has been investigated. The use of a shear-thinning additive–Xanthan–has been studied, particularly its influence on the reactant mixing step. A systematic study has then been carried out to determine the synthesis conditions needed to prepare pure calcite. The carbonation process using gaseous CO_2 was investigated as an alternative method to prepare PCC.

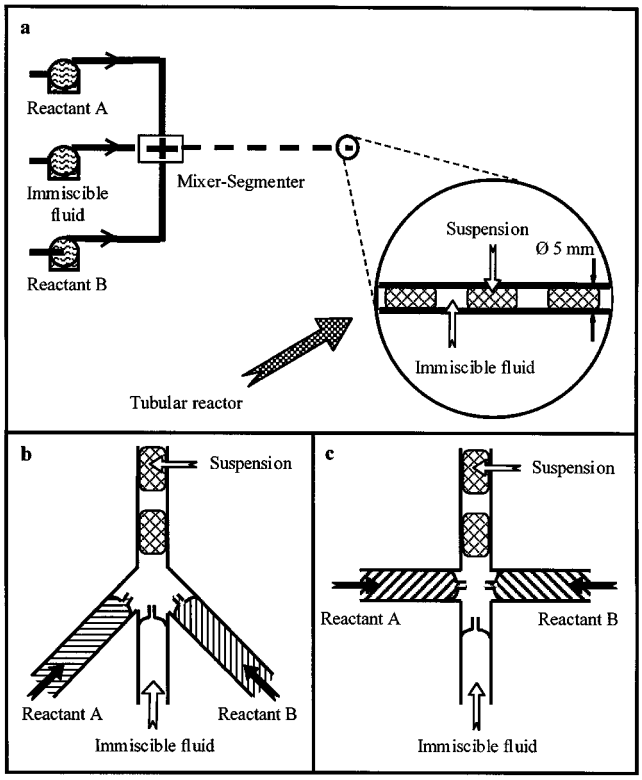

Figure 1. New segmented flow tubular reactor (a) with two mixer-segmenters: the segmented and restricted Y (b) and the cross-mixer (c).

Some preliminary investigations of other methods, involving the carbonation of a $Ca(OH)_2$ suspension or a $CaCl_2$ aqueous solution using gaseous CO_2 or a CO_2 (100%)/NH_3 (10% in N_2) mixture, were also investigated in the SFTR.

Experimental Studies

Segmented flow tubular reactor (SFTR)

The SFTR developed for the forced precipitation consists of two main independent parts: the first part is a mixer which also plays the role of a flow-cutter or "segmenter". The mixer is placed on the upstream side of the reactor setup (Figure 1a). The second part, which is always placed on the downstream side of the setup, is a tubular reactor (Figure 1a). The reactants and the nonmiscible phase needed for operating the reactor are fed into the setup by means of peristaltic pumps.

The functions of the mixer are both to mix thoroughly the reactants and to segment the liquid reaction mixture into small identical sections separated by an immiscible fluid (Figure 1a). This separating fluid ensures that individual volumes of the reacting mixture will progress with no backmixing in the tubular reactor situated on the downstream side of the setup. In the present study, the mixer is composed of plexiglas. The design of the mixer can be adjusted to the needs of the precipitation thermodynamics and kinetics. In the present study, two mixer configurations were investigated: the segmented and restricted Y (Figure 1b) and the cross-mixer (Figure 1c). Reactants are injected into a restricted volume in

opposite directions leading to a highly turbulent mixing. The dissipation of kinetic energy ensures a thorough mixing, especially in the cross-mixer where the two injectors are directly opposite one another. Mixing and segmentation take place simultaneously in the mixing chamber, out of which the reacting mixture is expelled as a segmented flow.

The second part of the SFTR is the tubular reactor itself (Figure 1a). This is the part where the reaction progresses to produce powder particles. The inner diameter of the tubular reactor may be chosen according to the desired flow rate and residence time. For the present study, where aqueous solutions are involved, PTFE tubes have been used because this material can sustain the reaction conditions without degradation and remains unaltered in contact with the reacting mixture. The inner diameter of the tube was 4 mm and the length of the tube was fixed at 10 m.

PCC synthesis

The precipitation of $CaCO_3$ was produced by mixing a solution containing CO_3^{2-} anions (pH 12) and a solution of Ca^{2+} cations. $(NH_4)CO_3$ (Fluka) was selected as the anion source and $CaCl_2$ was used as the cation source. The characteristics of all prepared reacting solutions are presented in Table 1. Small amounts of xanthan gum (shear-thinning additive, Scheller, food grade) was sometimes added to the different solutions to increase the viscosity.

Precipitated powders were separated, after the precipitation step, from the precipitating medium by centrifugation at 4,000 rpm. All precipitates were cleaned and washed twice with water and then three times with isopropanol. Between each cleaning step, the precipitate was separated from the washing solution by centrifugation. The cleaned powders were dried overnight at 50°C until complete evaporation of the solvent.

PCC precipitation was investigated more systematically by varying the temperature, the CO_3^{2-}/Ca^{2+} ratio and the content of shear-thinning additive (xanthan). Table 2 presents the selected parameters and their low and high levels. An experimental design was then prepared to further analyze statistically the results. The experimental array is summarized in Table 3.

Powder characterization

The powder structure and morphology were investigated by scanning electron microscopy (SEM, Philips XL 30). X-ray diffraction using a CuK_α line (Inel CPS-120) was investigated to determine the crystalline structure of as-prepared PCC powders. The calcite content in the powder was determined from X-ray diffractometry: this has been calculated with calcite/vaterite mixtures by measuring the intensity ratio between the most intense peaks of calcite (104, I_c) and vaterite (101, I_v).

For selected samples, surface area measurements and particle-size distribution were made. PCC powder surface areas were characterized by nitrogen adsorption at 77 K (BET, Micromeritics). The particle sizes of synthesized powders were determined using a particle-size analyzer (Horiba Capa 700), based on centrifugal sedimentation of powder suspensions in isopropanol using light adsorption to detect particle concentration. The data presented are averages of three repeated measurements.

Table 1. Characteristics of Reactant Solutions for PCC Synthesis

Solutions	1	2	3	4
$CaCl_2$ (mol/L)	0.200 $\pm 0.2\ 10^{-3}$	—	—	—
$(NH_4)_2CO_3$(mol/L)	—	0.300 $\pm 1\ 10^{-3}$	0.240 $\pm 1\ 10^{-3}$	0.160 $\pm 1\ 10^{-3}$
pH	5.15	12.2	12.1	12.1

Table 2. Definition of Selected Factors for the Systematic Study on PCC Synthesis in the SFTR

Factors	Definition	Levels			
A	CO_3^{2-}/Ca^{2+}	0.80	1.20		
B	Temperature (°C)	10	20		
R(C, D)	[Xanthan] (wt. %)	0.05	0.10	0.20	0.40

Results and Discussion

Batch experiment in the $Ca(Cl_2)/(NH_4)_2CO_3$ system

PCC was precipitated by mixing solution 1 and solution 2 that gave an excess of CO_3^{2-} concentration compared to Ca^{2+} concentration (ratio $CO_3^{2-}/Ca^{2+} = 1.5$). PCC was obtained by mixing these two solutions using a simple Y connector without segmentation. The precipitation was carried out in a batch reactor with an additional rate of each co-reactant of about 100 mL/h. The results of this forced precipitation reaction and the PCC characteristics are presented in Table 4.

Figure 2 shows SEM images of the as-prepared powder. A mixture of micrometer-sized spherical and brick-shaped particles was obtained in batch reactor using this simple Y connection as a mixer (PCC 1, Figure 2). These morphologies are related to vaterite and calcite phase, respectively. The X-ray diffractogram of PCC 1 is characteristic of a vaterite-calcite mixture. This suggests that the nature of the PCC

Table 3. Experiments Performed for the Systematic Study of PCC Synthesis in the SFTR

Treat. Code	Test No.	Test Order	PCC No.	Factors		
				CO_3^{2-}/Ca^{2+}	Temp. (°C)	[Xanthan] (wt. %)
'1'	1	2	7	0.80	10	0.05
a	2	3	8	1.20	10	0.05
b	3	15	9	0.80	20	0.05
ab	4	9	10	1.20	20	0.05
'2'	5	1	11	0.80	10	0.10
2a	6	5	12	1.20	10	0.10
2b	7	12	13	0.80	20	0.10
2ab	8	11	14	1.20	20	0.10
'3'	9	4	15	0.80	10	0.20
3a	10	6	16	1.20	10	0.20
3b	11	14	17	0.80	20	0.20
3ab	12	16	18	1.20	20	0.20
'4'	13	8	19	0.80	10	0.40
4a	14	7	20	1.20	10	0.40
4b	15	13	21	0.80	20	0.40
4ab	16	10	22	1.20	20	0.40

Table 4. Results of PCC Precipitation for Different Operating Conditions

	PCC 1	PCC 2	PCC 3	PCC 4
Reactor	Batch	SFTR	SFTR	SFTR
Mixer type	simple Y (4 mm)	segmented and restricted Y	segmented and restricted Y	cross-mixer
Feeding rate (mL/h)	100	100	100	700
Ca^{2+} (mol/L)	0.100 $\pm 0.1\ 10^{-3}$	0.100 $\pm 0.1\ 10^{-3}$	0.100 $\pm 0.1\ 10^{-3}$	0.100 $\pm 1.0\ 10^{-3}$
Additives	No	No	Xanthan (0.4 wt. %)	No
Temperature (°C)	20	30	30	30
PCC yield (%)	82.8	60.4	71.7	65.3
End pH	8.7	8.6	8.5	8.6
Morphology of PCC	Spherical and brick-shaped particles	Spherical particles	Spherical particles	Spherical particles
Crystalline phase	vaterite + calcite	Vaterite	Vaterite	Vaterite

crystalline phase is influenced by the way the reactants are mixed. The formation of calcite in PCC 1 may also be favored by the reaction temperature. The presence of NH_4^+ cations or Cl^- anions is also an important parameter which may influence the PCC phase precipitated. However, we shall only focus on the mixing problems in this study. The PCC synthesis gave interesting morphologies in this batch mode, and it is the aim of the present study to transfer it to the continuous SFTR.

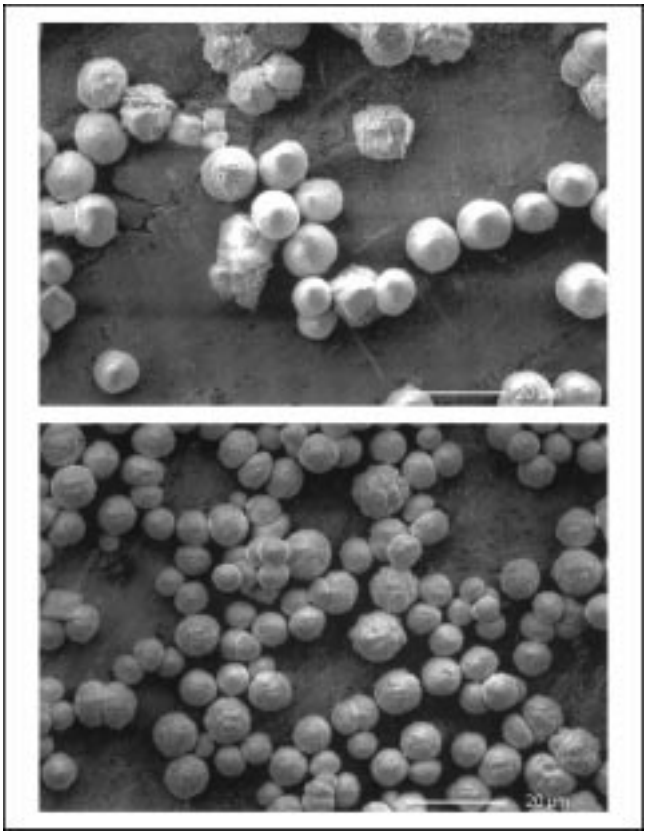

Figure 2. SEM micrographs of PCC 1 (a) and (b) precipitated in a batch reactor (simple Y).

PCC precipitation using the SFTR in the $Ca(Cl_2)/(NH_4)_2CO_3$ system

The influence of the SFTR on the PCC synthesis was then investigated. PCC was precipitated by mixing the co-reactants (solutions 1 and 2) at a rate of about 100 mL/h per reactant in the restricted Y with air segmentation. The influence of xanthan, a thickener commonly used in the food industry, was also investigated.

In the case of PCC 2 and PCC 3 synthesis, the segmentation by air during mixing was observed to act as a purge and prevented fouling in the capillary (restriction). The segmentation was reasonably regular in the tubular reactor resulting in spherical, homogeneous, and nonaggregated vaterite particles (PCC 2, Figure 3a). A deposition of $CaCO_3$ occurred on the plexiglas at the mixer exit and also at the beginning of the teflon tube. This adsorption affected the regularity of the segmentation during a short period ($\sim$ 1 min.), which became more regular after a layer of adsorbed PCC had formed. As shown in Figure 3b, the xanthan has an effect on the particle size, but at 0.4 wt. % in the reaction mixture, the viscosity was too high to ensure good working conditions and a fouling phenomenon occurred in the capillary every 15 min with a back flow in the air feed line. The segmentation by air during mixing was helpful in purging the mixer every time a fouling appeared in the restriction. As a result, the synthesized spherical particles (PCC 3) were not as homogeneous in size when compared to PCC 2 (Figure 3). Thus, the mixing conditions seem of primary importance regarding the size, homogeneity, and morphology of PCC.

X-ray diffractograms of PCC 2 and 3 were characteristic of the vaterite phase (JCPDS 24-30, Figure 4) with a trace of calcite (JCPDS 5-586). As estimated by the Scherrer method, these vaterite particles are composed of nanometer-sized primary particles. PCC 2 and PCC 3 shown in Figure 3 are simply agglomerates of smaller crystalline particles of 10–12 nm. Further experiments were conducted under the same conditions, but using only 0.1 wt. % xanthan. Although better and more regular working conditions were achieved (no fouling in the restriction) with this lower xanthan content, similar powders as PCC 3 were obtained, consisting of vaterite with a broad size distribution. This indicates that the fouling phenomenon encountered in the previous experiment was not

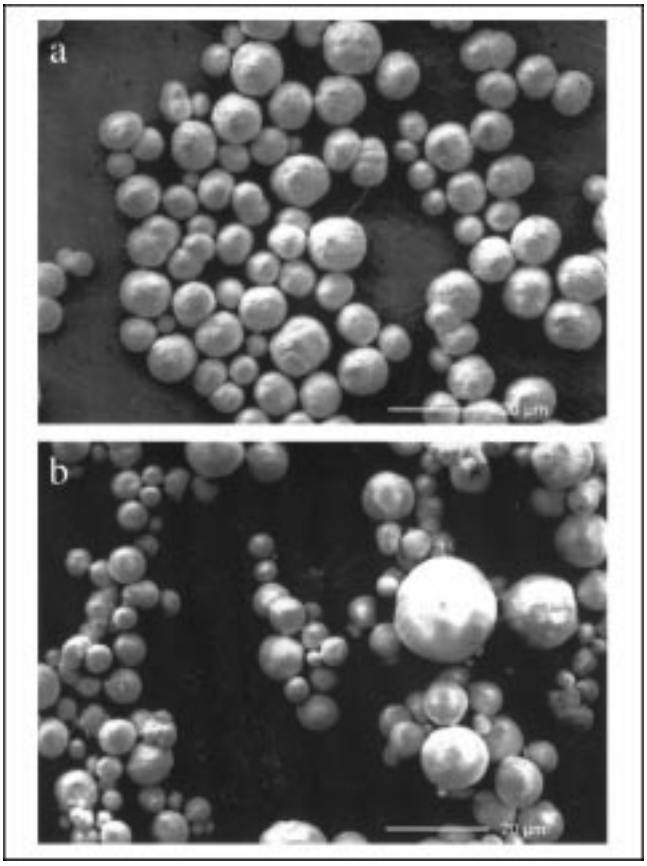

Figure 3. SEM micrographs of two PCCs precipitated in the SFTR using the segmented and restricted Y: PCC 2 (a) and PCC 3 (b) precipitated with xanthan added.

responsible of the resulting size inhomogeneity, suggesting that the mixing was not as efficient with these higher viscosities.

In previous studies (Marentette et al., 1997; Pach et al., 1996), it has been observed that calcite formation was obtained by roughly mixing the co-reactants in a simple batch system. Particularly, calcite is obtained, for a CO_3^{2-}/Ca^{2+} ratio lower than 1, when adding the CO_3^{2-} solution to the Ca^{2+} solution. This observation suggests that the mixing conditions, particularly the supersaturation and, consequently, reactant concentrations, are of primary importance for the precipitation of calcite. To determine the relative importance of mixing, other experiments were conducted separately in the SFTR to investigate the effects of temperature, nature of the ions, and mixing conditions. The cross-mixer (Figure 1c) was designed to investigate the effect of the latter parameter at a high addition rate of the co-reactants (700 mL/h) in order to reproduce the calcite formation conditions, as indicated in these previous studies. The results of our investigations showed that lowering the temperature to 20°C does not influence the calcite formation in the $CaCl_2/(NH_4)_2CO_3$ system and that the nature of the associated ions does not determine the PCC crystalline phase and morphology, particularly if NH_4^+ and Cl^- are replaced by Na^+ and NO_3^- ions. A rapid mixing of the co-reactants in the cross-mixer leads also to vaterite spherical particles without a detectable trace of calcite (PCC 4, Figure 5). Such mixing conditions are not appropriate for the precipitation of the calcite phase. However, the productivity of PCC synthesis is increased by a factor of 7 using the SFTR with the cross-mixer without affecting the nature and the morphology of calcium carbonate. Some typical measurements of the particle-size distribution using the Horiba Capa 700 (without light scattering correction) have shown that the particle size is slightly increased at the higher mixing rate (Figure 6). The PCC median diameter increases from 5.0 to 5.9 μm by increasing the addition rate of the reactants from 100 to 700 mL/h (PCC 2 and PCC 4). This results is interesting for industrial applications because the productivity of the process can be increased from 1.2 to 64. g/h per tube without greatly affecting the particle-size distribution or precipitated phase–indicating that the SFTR is relatively insensitive to this level of scale-up.

The formation of vaterite is likely due to synthesis conditions that favor the formation of nanometer-sized particles with a different surface free energy than that of calcite. At

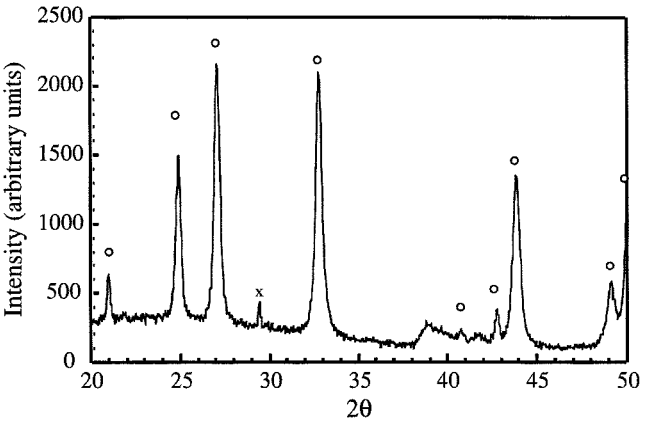

Figure 4. X-ray diffractogram of PCC 2.

Indexing corresponds to the vaterite phase (O, JCPDS 24-30) with a small amount of calcite (x, JCPDS 5-586).

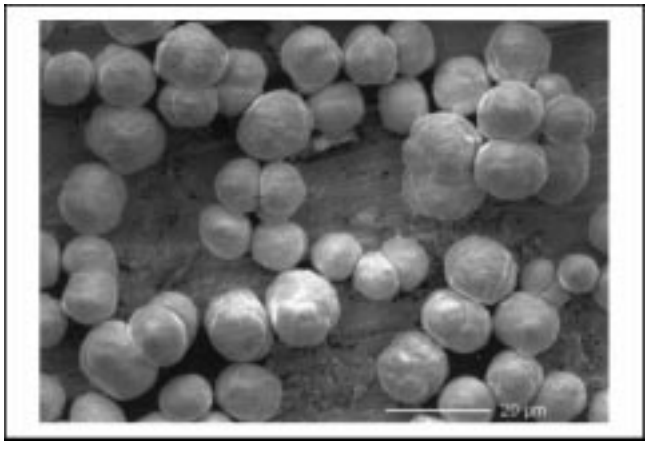

Figure 5. SEM micrographs of PCC 4 precipitated in the SFTR using the cross-mixer at high mixing rate (700 mL/h per coreactant).

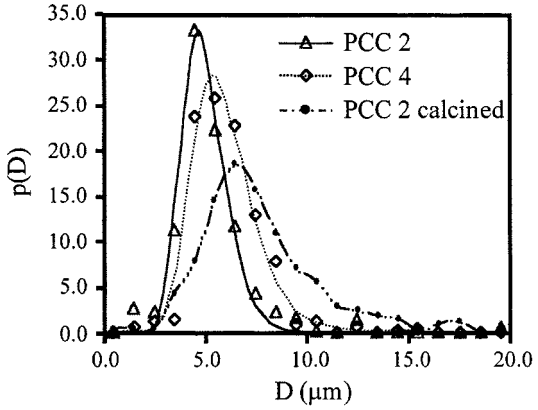

Figure 6. Particle-size distribution of two PCCs synthesized at different mixing rates, determined using the HORIBA Capa 700 (without light scattering correction).

Figure 8. SEM micrographs of PCC 2 calcined at 400°C (pure calcite).

such small sizes, the chemical behavior is dominated by the surface free energy resulting in the agglomeration of primary particles into spherical agglomerates. Vaterite is a metastable phase which gradually transforms into calcite when moist or when the powder is aged in its supersaturated reacting solution as observed by Brooks et al. (1950) and Wray and Daniels (1957). These are two ways that can be used to convert the vaterite phase into calcite. Since vaterite is a metastable phase, calcite can also be obtained by heating the powder up to the phase transformation temperature which is 365°C. PCC 2 was then calcined at 400°C in air with a heating rate of 5°C/min. and a 2 h/dwell time.

As shown in the XRD data in Figure 7, calcined PCC 2 is completely transformed into pure calcite. SEM observations reveal that the morphology of the heat-treated powder remains unchanged and consists of calcite spherical particles (Figure 8). Following this procedure, the PCC median diameter increases from 5.0 to 7.1 μm and this calcined powder shows a broader particle-size distribution as compared with PCC 2 (Figure 6). This indicates that a small particle growth occurs during calcination resulting in more agglomerated spherical calcite particles. According to the Scherrer calculations, the primary particle size of such particles was likely in the 100 nm range indicating that the calcite powder is still an agglomerate. The observed primary particle growth is responsible for the slight particle-size broadening. To our knowledge, the existence of spherical calcite particles has never been mentioned in the literature and the round morphology indicates that the entire particle is not a single continuous crystal.

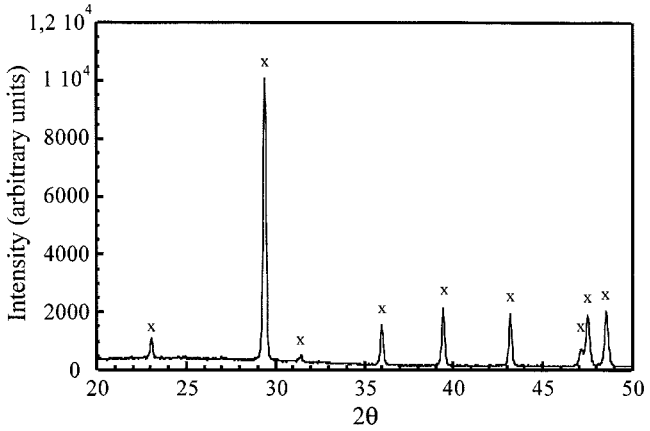

Figure 7. X-ray diffractogram of PCC 2 calcined at 400°C.

Indexing corresponds to the calcite phase (x, JCPDS 5-586).

Two other experiments were carried out under the same conditions as for the PCC 4 synthesis. The new concept used in these experiments came from previous observations, where it was found that calcite is obtained by adding the CO_3^{2-} solution to the Ca^{2+} solution. In order to increase the viscosity of the Ca^{2+} solution (solution 1), xanthan was introduced into the starting solution. Because of the higher viscosity of the Ca^{2+} solution, there should be a diffusion of CO_3^{2-} solution into the Ca^{2+} solution reproducing the mixing conditions by which CO_3^{2-} is added to Ca^{2+}. Table 5 summarizes conditions and results of these experiments.

Good working conditions were found when using the new cross-mixer and the xanthan containing Ca^{2+} solution (0.4 wt. % xanthan). By introducing the xanthan in only one of the co-reactants (Ca^{2+}) and using the new cross-mixer, the

Table 5. Results of PCC Precipitation at Different Operating Conditions

	PCC 5	PCC 6
$[Ca^{2+}]$ (mol/L)	0.1	0.1
Xanthan in $CaCl_2$ (wt. %)	0.1	0.4
Xanthan in NH_4CO_3 (wt. %)	No	No
Total xanthan (wt. %)	0.05	0.2
Temperature (°C)	30	30
Morphology	Spherical particles	Spherical (+brick-shaped) particles
Crystalline phase	Vaterite+(calcite)	Vaterite+calcite
Calcite content (%)	5	40
PCC yield (%)	71.9	81.9

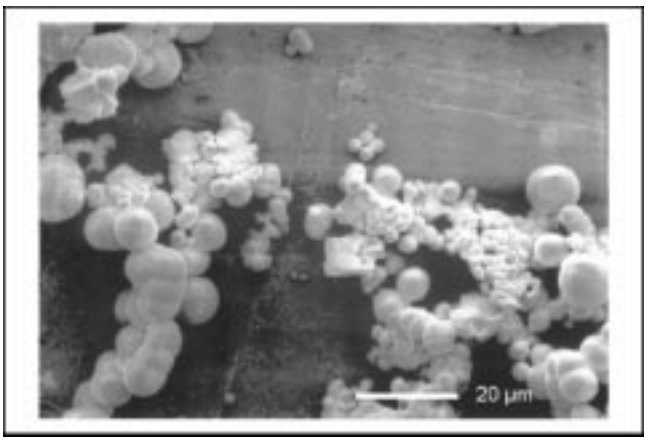

Figure 9. SEM micrograph of PCC 6 precipitated at 30°C in the SFTR using the cross-mixer.

0.4 wt. % xanthan was added in the Ca^{2+} solution.

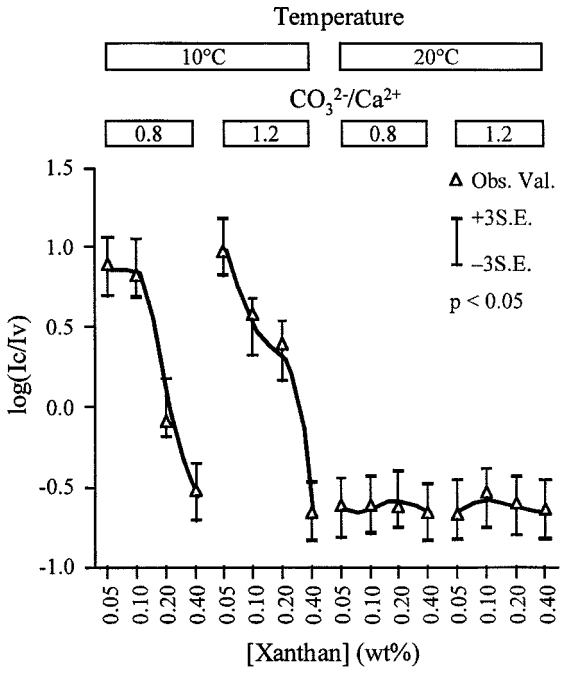

Figure 10. Statistical analysis of the results of systematic study: selectivity for calcite (log(Ic/Iv)) in PCC synthesis in the SFTR.

Ic and Iv: XRD line intensities for calcite and vaterite, respectively.

amount of calcite phase in the powder is increased, the higher the amount of xanthan, and the higher the calcite content (Table 5). As shown in Figure 9, the as-prepared powders consist of spheres of vaterite and cubes of calcite. Some smaller particles are obtained in the presence of xanthan, and the powder shows a broader particle-size distribution compared to PCC 4.

Results of the experimental design-systematic study

According to the literature (Xyla et al., 1991; Gómez-Morales et al., 1996), several parameters can influence the calcite phase formation, such as temperature and pH. Other key parameters are the concentrations and the reactant mixing hydrodynamics, which can lead either to calcite or vaterite during precipitation at high supersaturation as highlighted by the results in the previous section. Thus, the PCC precipitation was investigated more systematically by varying several parameters such as temperature, CO_3^{2-}/Ca^{2+} ratio, and xanthan content, which affects the viscosity of the Ca^{2+} solution and acts directly on the mixing hydrodynamics. Results of the experimental design are presented in Table 6, and the statistical analysis of the results are shown in Figures 10 and 11. As shown in Figure 10, calcite is favored at low temperature (10°C) in the $(NH_4)_2CO_3/CaCl_2$ system. No effect of the CO_3^{2-}/Ca^{2+} ratio on the selectivity was revealed in this experimental range. An effect of xanthan is visible at low temperature: the lower the concentration of xanthan, the higher the calcite content. Furthermore, at 10°C, the behavior of the curves indicates that there might be an optimal

Table 6. Results of the Experimental Design of PCC Synthesis in the SFTR

Test No.	PCC No.	log[x/(1−x)]*	log(Ic/Iv)**	[% Calcite]	PCC Yield y (%)†	log [y/(1−y)]
1	7	0.087	0.904	55.00	72.00	0.410
2	8	0.176	0.978	60.00	95.24	1.301
3	9	−2.299	−0.618	0.50	50.03	0.000
4	10	−3.000	−0.672	*0.10*	68.77	0.343
5	11	0.017	0.829	51.00	72.47	0.420
6	12	−0.194	0.583	39.00	96.07	1.388
7	13	−2.299	−0.619	0.50	41.36	−0.152
8	14	−1.996	−0.532	1.00	68.32	0.334
9	15	−0.908	−0.092	11.00	64.43	0.258
10	16	−0.389	0.405	29.00	95.25	1.302
11	17	−2.299	−0.631	0.50	42.07	−0.139
12	18	−2.299	−0.604	0.50	74.47	0.465
13	19	−1.996	−0.518	1.00	69.00	0.348
14	20	−3.000	−0.662	*0.10*	93.82	1.182
15	21	−3.000	−0.665	*0.10*	59.94	0.175
16	22	−0.308	0.472	33.00	81.90	0.656

*x = % calcite.
**log I_c/I_v = intensity of XRD reflections 104 for calcite (I_c) and 101 for vaterite (I_v).
†y = yield.

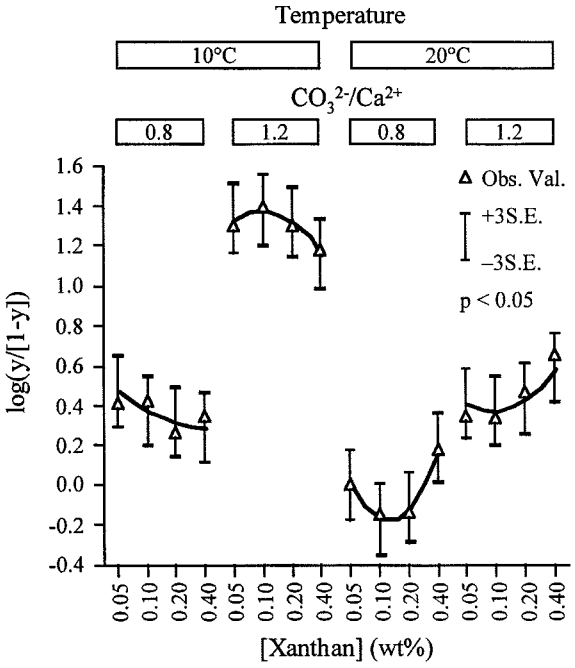

Figure 11. Statistical analysis of the results of systematic study: yield index (log(y/[1-y])) in PCC synthesis in the SFTR (y: PCC yield).

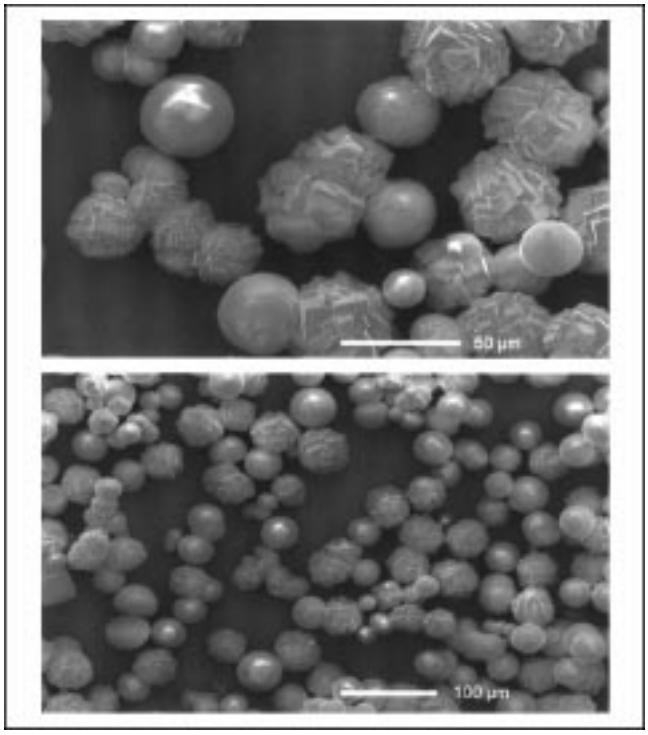

Figure 12. SEM micrographs of the PCC powder from experiment No. 5 (PCC 11, (a) and (b)) showing the two types of smooth and faceted spherical morphologies.

concentration of xanthan below 0.05 wt. % for calcite selectivity. Several interactions between these factors on the selectivity were detected by the statistical analysis, but their effects are very small.

Concerning the yield, general conclusions can be drawn from the statistical analysis in Figure 11. For a given temperature, the yield is significantly improved at the high level of the CO_3^{2-}/Ca^{2+} ratio (1.2). Only a very small effect of xanthan concentration is observed on the PCC yield. For a given CO_3^{2-}/Ca^{2+} ratio, the yield is higher at the lower temperature (10°C). Again, some interactions between these factors on the yield are clearly seen in Figure 11.

SEM observations show that most of the PCC powders contained both vaterite and calcite in the form of spherical particles and spherical agglomerates of cubes, respectively (Figure 12). These powders present a broad particle-size distribution. The PCC powders containing more than 95% of vaterite consists only of spherical particles. The BET surface area of vaterite spherical particles give values of about 11–13 m^2/g. Assuming that all particles are spherical and dense, and from: $d_{BET} = 6/(S \cdot \rho)$, where S is the surface area and ρ is the particle density (2.65 g/cm^3 for vaterite, and 2.71 g/cm^3 for calcite), a BET particle diameter d_{BET} of about 180 nm is found for these PCCs. This indicates that the particles are highly porous, and it denotes a growth by agglomeration of the primary particles in the case of vaterite. The calcite phase was identified in these powders as spherical aggregates of smaller cubic sub-units, as presented in Figure 13. To our knowledge, such a morphology has never been observed before for calcite. The formation of such spherical aggregates of cubes could be explained following three processes:

(1) There is a competitive nucleation of calcite and vaterite seeds, due to large differences in the precipitation kinetics of these two phases, followed by a different selective agglomeration/growth process for these two phases that forms pure vaterite and pure calcite particles as observed by Swinney et al. (1982). In the case of calcite, the particle growth results in a spherical aggregation of interpenetrated growing cubes;

(2) Vaterite is formed initially via a polynuclear mechanism and is then converted into the thermodynamically stable calcite, as claimed by Xyla et al. (1991).

(3) Vaterite is firstly formed through a homogeneous nucleation followed by a fast aggregation process and spherical particles are formed rapidly. Then, a heterogeneous nucleation of calcite occurs at the surface of the vaterite particles, the calcite growth results in the observed spherical agglomerates of cubes.

The latter mechanism could be in agreement with the competitive homogeneous and heterogeneous mechanism observed by Gómez-Morales et al. (1996) and Schierholz and Stevens (1975). Further work on the kinetics of this system should help elucidate the calcite growth mechanism.

Following this experimental design, more than 10 grams of PCC were produced continuously using the SFTR with the cross-mixer at a high addition rate. The overall synthesis was carried out in a period of 80 min by mixing 800 mL of solution 1, and 800 mL of solution 3 at 10°C (productivity of 8.75 g/h). The CO_3^{2-}/Ca^{2+} ratio was fixed at 1.2 and no xanthan was added. The resulting powder consisted of a mixture of

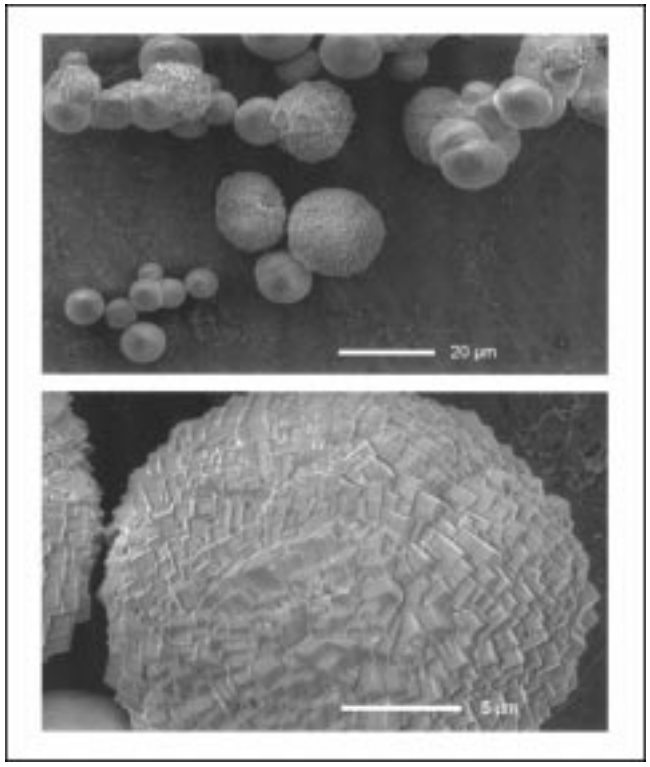

Figure 13. SEM micrographs of the powder from experiment No. 3 (PCC 9, (a) and (b)), showing the submicron crystals that make up the calcite particles.

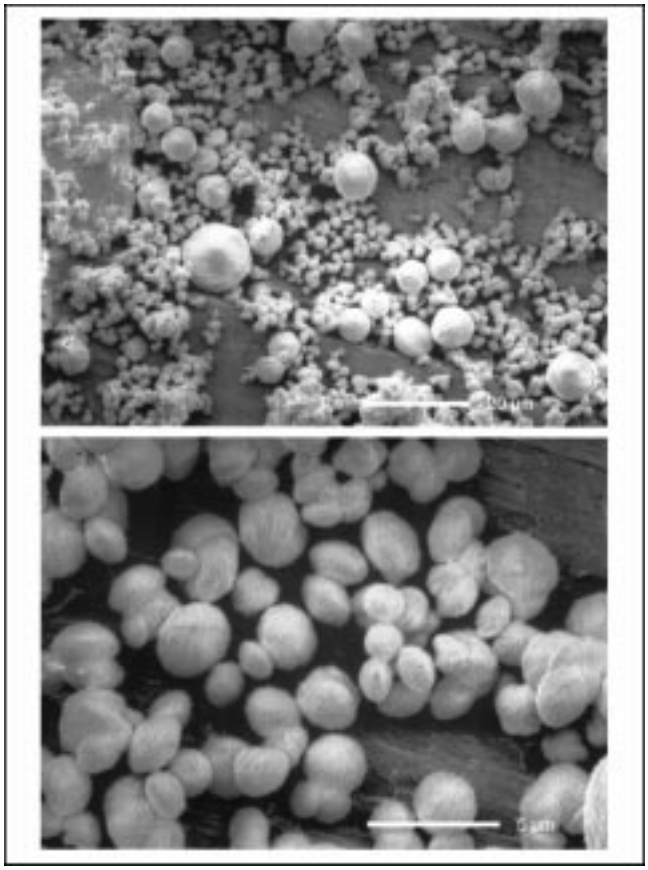

Figure 14. SEM micrographs of PCC 23 (a) and (b) precipitated in the SFTR from the mixed CO_2/NH_3 gas route at 30°C.

calcite and vaterite (~ 40% calcite determined from X-ray analysis), lower than the 60% in powder PCC 8 which was prepared under similar conditions, but with 0.05 wt. % xanthan. From the observed effect of xanthan, a maximum yield of calcite should be obtained for xanthan concentration below 0.05 wt. %. These results are interesting and suggest a way for obtaining pure calcite, that is with a xanthan content between 0 and 0.05% at 10°C.

Alternative methods using the SFTR

(a) PCC Precipitation Using a CO_2/NH_3 Gas Mixture as the Segmenting Fluid. PCC can also be precipitated using gaseous CO_2, and this was investigated in the SFTR by segmenting solution 1 with a CO_2/NH_3 gas mixture. This liquid-gas reaction depends strongly on the gas dissolution at the gas/calcium solution interface. The addition of NH_3 is necessary to increase the pH and to compensate for the counterions left in solution after precipitation. Three preliminary tests were carried out in the SFTR at various temperatures to investigate this route to PCC synthesis. The results are presented in Table 7.

By operating without xanthan, a PCC powder consisting of large spheres of vaterite and oval particles, which may be either calcite or vateriate, is obtained (Figure 14). The residence time was fixed at 15 min, but the precipitation was observed to start after about 5 min residence time. The as-prepared powder (PCC 23) shows a bimodal size distribution.

Table 7. Results of the PCC Synthesis with CO_2 Gas

	PCC 23	PCC 24	PCC 25	PCC 26
[Ca] (mol/L)	0.2	0.2	0.2	0.2
Temperature (°C)	30	20	10	30
Additives	—	Xanthan (0.025 wt. %)	Xanthan (0.025 wt. %)	—
Morphology	Spherical + elliptical particles	Brick-shaped particles	Spherical particles	Agglomerated brick-shaped and elliptical particles
Crystalline phase	Vaterite + calcite	Calcite	Vaterite	Vaterite + calcite
PCC yield (%)	62.6	82.4	29.4	41.4

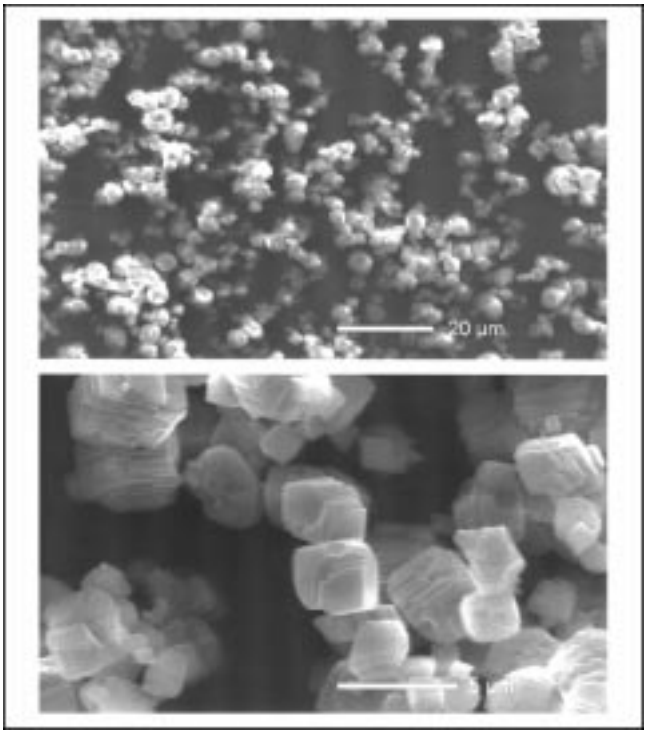

Figure 15. SEM micrographs of PCC 24 (a) and (b) precipitated in the SFTR from the mixed CO_2/NH_3 gas route at 20°C and using 0.025 wt. % xanthan.

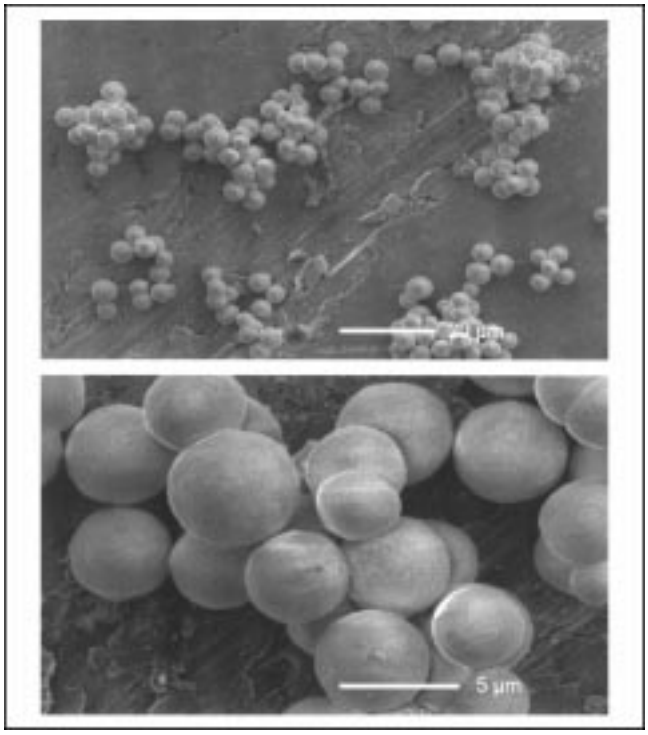

Figure 16. SEM micrographs of PCC 25 (a) and (b) precipitated in the SFTR from the mixed CO_2/NH_3 gas route at 10°C and using 0.025 wt. % xanthan.

To confirm our hypothesis concerning the role of xanthan, PCC 24 and 25 were synthesized in the presence of 0.025% xanthan at 20° and 10°C, respectively. The solution became slightly cloudy after about 5 min residence time which was fixed at 15 min. With a low xanthan content, more than 95% (according to the x-ray diffraction) of the product is calcite when the synthesis is carried out at 20°C (Figure 15). The BET surface area of this powder was determined as 3–5 m^2/g with an estimated d_{BET} of about 550 nm. On the other hand, at a temperature of 10°C, only spherical vaterite particles are synthesized (Figure 16). This indicates that the precipitation mechanism of calcite is completely different than the one of vaterite (12.7 m^2/g, d_{BET} of 178 for PCC 25), and further kinetic experiments are needed for a better understanding of these mechanisms. It is also interesting to note that the yield of this synthesis route is strongly affected by temperature: the lower the temperature, the lower the yield. Surprisingly, calcite is obtained at 20°C, whereas vaterite precipitates at 10°C. In this system, the temperature dependence of the proportion of calcite precipitated is reversed compared to the forced precipitation in the xanthan/$(NH_4)_2CO_3$/$CaCl_2$ system.

(b) Dissolution in a $(NH_4)_2NO_3$ Solution and PCC Precipitation Using Gaseous CO_2

To test the versatility of the SFTR, PCC was precipitated by reacting a calcium hydroxide solution with gaseous CO_2. As mentioned in the U.S. patent No. 3 920 800 (Harris, 1975), the dissolution of $Ca(OH)_2$ can be carried out directly in a NH_4Cl or NH_4NO_3 solution which can be purified by filtration. PCC can then be precipitated by segmenting the dissolved lime solution with CO_2 gas and separated from the mother solution by centrifugation or filtration. The advantage of this process is in the recycling of the mother solution to further redissolve $Ca(OH)_2$, provided no CO_3^{2-} ions are left in the supernatant liquid after PCC precipitation.

This system was investigated using a NH_4NO_3 solution at 2 mol/L prepared to dissolve the commercial $Ca(OH)_2$. The pH of the NH_4NO_3 solution reached a value of 4.8, which is acidic enough for $Ca(OH)_2$ dissolution. A solution of calcium hydroxide at 0.2 M was prepared and stirred overnight. The pH of the suspension stabilized at 8.77. Insoluble impurities were filtered using a 0.2 μm membrane. PCC was then precipitated in the SFTR (30 min residence time) by segmenting this lime solution with pure CO_2 (Figure 17, PCC 26). The solution became slightly cloudy after 15 min residence time. A mixture of vaterite and calcite (41.4 % yield) was obtained with a calcite content of about 35% according to x-ray diffraction analysis. This result is very interesting, because PCC can be produced easily following this procedure and the mother solution may be recycled after filtration in the process.

Conclusions

This study has demonstrated that PCC can be synthesized continuously using a new segmented flow tubular reactor (SFTR). Several precipitation methods were tested successfully in the new reactor (liquid-liquid forced precipitation and gas-liquid precipitation). Very similar particle-size distribu-

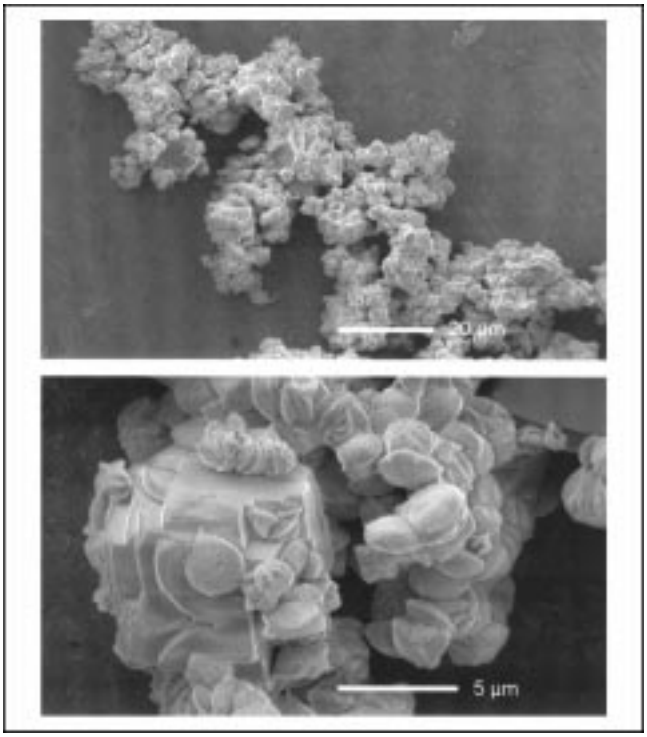

Figure 17. SEM micrographs of PCC 26 (a) and (b) precipitated in the SFTR by reacting pure CO_2 and $Ca(OH)_2$ dissolved in a NH_4NO_3 solution at 30°C.

tions (vaterite) were recorded for flow rates of 100 and 700 mL/h in the same tube diameter indicating the segmentation is playing its expected role and keeping the precipitation conditions homogeneous in the tubular reactor. Spherical nonagglomerated particles consisting of vaterite were most frequently observed in the PCCs. A good productivity has been achieved by mixing the reactants in a cross-mixer at high addition rates with the SFTR. The precipitated crystalline phases, vaterite or calcite, were strongly influenced by supersaturation, the way the reactants are mixed, the operating temperature, and the synthesis route (gas-liquid or liquid-liquid). Pure calcite is easily obtained by heat-treating a pure vaterite PCC at 400°C. The spherical morphology remains after calcination, but a slight particle growth occurred resulting in more agglomerated spherical calcite particles.

PCC could be prepared by various methods in the SFTR including the carbonation of a $Ca(OH)_2$ solution using a CO_2/NH_3 gas mixture as the segmenting fluid showing the versatility of the new reactor. $Ca(OH)_2$ could be directly dissolved in a NH_4NO_3 solution and the carbonation carried out using CO_2 as the segmenting fluid. The advantage of this later is the possibility to recycle the mother solution and reuse it to redissolve again the calcium hydroxide.

A statistically designed series of experiments has shown that the formation of calcite and vaterite phases, which have nearly the same solubilities, is strongly influenced by very small changes of the precipitation conditions. The direct effects of several factors, such as temperature, pH, reactant nature and concentration, use of an additive and reactants mixing mode, have been observed, but this system also presents several interactions between these factors that render the PCC precipitation very challenging and interesting. The competitive phase precipitation involved in this system is very complex and experimental domains in which a pure phase can be synthesized are very narrow. This was highlighted in the reversal of the effect of temperature on the preparation of calcite formed when using CO_2 or NH_4CO_3 as the carbonate source, both in the presence of xanthan. However, different ways to precipitate pure calcite and pure vaterite have been found during this study. In general, calcite consists of crystalline agglomerates of varied morphologies, whereas vaterite is composed of spherical particles. More detailed studies on the mechanisms and kinetics of the formation of the PCC phases should lead to a better control of the morphologies and sizes, allied to the good selectivity demonstrated in this study.

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