COMPARISON OF SEMICONTINUOUS AND BATCH PRECIPITATION OF CALCIUM CARBONATE

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A comparison of semicontinuous and batch precipitation of calcium carbonate is presented. In both processes, precipitated calcium carbonate (PCC) was synthesized by carbonation of slaked lime. The experiments in the batch process were performed by varying the initial mass concentration and temperature, and in the semicontinuous process by varying the supersaturation and temperature. It was found, that in the batch experiments the specific surface area and the average size of calcite particles decreased with increase of temperature. PCC nanoparticles can be produced at 25 °C, whereas the increase of the initial mass concentration of slaked lime enhances the degree of their aggregation. At higher temperatures (35 and 45 °C), scalenohedral micrometric calcite precipitates. By careful tuning of the semicontinuous process parameters, calcite in the form of rhombohedral, truncated prismatic, scalenohedral or nanosized particles can be produced. Specific surface area increases with increasing supersaturation and decreasing temperature. The excess of suspended Ca(OH)₂ has a decisive role in the formation of the calcite nanoparticles.

1. Introduction

Calcium carbonate has found a large application in various fields of industry, e.g. in paper, paints, plastics and rubber, mainly as filler and/or pigment. Its final application is determined by different physical and chemical properties. Calcite proves to be the most important polymorph because of its thermodynamic stability at standard conditions and its possibility to appear in various morphologies. From the technological point of view, two kinds of calcium carbonate products are distinguished: natural ground calcium carbonate (GCC) and precipitated (synthetic) calcium carbonate (PCC). Precipitation of calcium carbonate opens plenty of possibilities of yielding the product with predetermined properties. Batch carbonation of slaked lime is widely used method for industrial scale production of PCC [CHE97]. The main disadvantage of batch carbonation of slaked lime is the limited possibility of controlling the supersaturation of the system. Thus, by using a semicontinuous carbonation process, it is possible to adjust the driving force of this process, expressed as supersaturation. By adjusting the supersaturation, it is possible to control the morphology and size of the PCC [CAR03, GAR03, UKR07]. In this work, the physical-chemical properties of PCC, prepared by carbonation of slaked lime in the batch and semicontinuous processes, are compared.

2. Experimental Section

Batch process. Carbonation was performed in a double-walled glass reactor fitted with two vertical baffle plates to prevent vortex formation during stirring. Stirring $(n = 300 \text{ min}^{-1})$ was performed by a flat-bladed stirrer with two perpendicular blades, the

diameter being 1/3 of the reactor diameter. CO₂ gas was introduced through the nozzles placed at the bottom of these two baffles. Initial mass concentration of slaked lime (p. a., Merck) varied in the range 13.0 g dm⁻³ < γ (Ca(OH)₂) < 28.6 g dm⁻³. Gaseous CO₂ was introduced at a constant flow rate, Q = 820 cm³ min⁻¹. The temperature was kept constant during each experiment and was varied in the range 25 °C < θ < 45 °C. The propagation of the reaction was followed by measuring the electrical conductivity, κ_{25} , of the reaction mixture.

Semicontinuous process. Carbonation was performed in a thermostated glass reactor. The electrical conductivity was controlled and kept constant at the predetermined value within the range 0.5 mS cm⁻¹ < κ_{25} < 5.0 mS cm⁻¹. Peristaltic pump was used as actuator, which dosed the thermostated Ca(OH)₂ suspension (p. a., Merck, γ (Ca(OH)₂) = 100 g cm⁻³) into the reactor (Q_{max} (Ca(OH)₂) = 280 cm³ min⁻¹). A gas mixture was introduced at a constant flow rate, Q = 7.5 dm³ min⁻¹ into the vessel through the nozzles placed at the bottom of the two baffles. The gas mixture with approximately 20 % CO₂/80 % N₂ (Messer) was used, simulating the flue gases that are commonly used in the PCC industry during the carbonation process. Stirring (n = 400 min⁻¹) was performed by a flat-bladed stirrer with the diameter being 1/3 of the reactor diameter. The flow of the Ca(OH)₂ suspension was stopped 10 min after starting the experiment, while the gas flow was kept constant until the endpoint of the carbonation reaction, which was indicated by a drop of conductivity. The temperature was varied in the range 25 °C < θ < 45 °C and was kept constant during each experiment.

Characterization. At the end of each experiment, the final suspension was treated in a centrifuge for 10 min, $n_c = 4000 \text{ min}^{-1}$, the precipitate was separated and dried at 105 °C for three hours. The composition of the solid phase was determined by FT-IR spectroscopy (Mattson, Genesis Series). Each sample was dispersed in 0.1 mol dm⁻³ NaCl solution and the dispersion was exposed to ultrasound for 2 min before characterization of its particle size distribution, which was analyzed by an electronic device, Coulter Multisizer II. The specific surface area was determined by the multiple BET method (Micromeritics, Gemini) using nitrogen gas as the adsorbate. Samples were also analyzed by means of scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

3. Results and Discussion

Figure 1a shows changes of supersaturation in the precipitation system during the batch carbonation process, measured as electrical conductivity of the Ca(OH)₂ suspension. The initial, ascending, part of the κ_{25} vs. time curves corresponds to the dissolution of Ca(OH)₂, previously injected in the system. After reaching its maximum, κ_{25} value slowly decreases (approximately horizontal part of the curves) and then an abrupt drop is evident from the moment of disappearance of the suspended Ca(OH)₂ from the reaction mixture. The minimum value of κ_{25} indicates the end of the calcium carbonate formation. A subsequent increase of κ_{25} is a consequence of PCC dissolution in the excess of carbonic acid. The maximum value of conductivity and the carbonation time decrease with decreasing the initial mass concentration of Ca(OH)₂ added to the system (see Fig. 1a). Thus for instance, at 25 °C the maximum conductivities were $\kappa_{25} = 6.60$ mS cm⁻¹ and $\kappa_{25} = 7.80$ mS cm⁻¹ which roughly correspond to the concentrations of total soluble calcium: c = 0.0165 mol dm⁻³ and c = 0.0196 mol dm⁻³, respectively. The maximum conductivities obtained at 35 °C and 45 °C are lower than that obtained at 25 °C, due to the lower solubility of Ca(OH)₂ at higher temperatures.



Fig. 1. a) Changes of κ_{25} during the batch carbonation process performed at different temperatures and initial mass concentrations of Ca(OH)₂: (–) 13.0; (-–) 20.0, and (.....) 28.6 g dm⁻³; b) Progress curves of κ_{25} during the semicontinuous carbonation process performed at different temperatures and conductivities.

As it is well known, supersaturation is the most important factor that determines physicalchemical properties of a precipitate obtained from aqueous solutions [BRE00]. Thus, conducting a process under constant supersaturation enables better definition of the final product properties. So, the apparently constant supersaturation was maintained in each experiment of the semicontinuous process. For this purpose, the conductivity was kept at a predetermined value by controlling the feeding flow rate of the Ca(OH)₂ suspension. Figure 1b shows progress curves (κ_{25} vs. time) obtained during carbonation of slaked lime in the semicontinuous process performed at different temperatures (θ = 25 °C, 35 °C and 45 °C) and conductivities ($\kappa_{25} = 0.5 \text{ mS cm}^{-1}$, 1.0 mS cm⁻¹, 1.5 mS cm⁻¹, 3.0 mS cm⁻¹ and 5.0 mS cm⁻¹). The initial increase of conductivity corresponds to the Ca(OH)₂ dissolution during its introduction to the system. After the predetermined working value of κ_{25} was reached, the conductivity of the system was kept constant (conductivity plateau) by regulating the flow rate of the Ca(OH)₂ suspension. The addition of the Ca(OH)₂ suspension was stopped after 10 min when the carbonation process came to the end, but the flow of the gas mixture went on until precipitation of the excess Ca(OH)₂ was completed. This part of the process is denoted by a decrease of κ_{25} , and its minimum value indicates the end of the calcium carbonate formation. A subsequent increase of κ_{25} is a consequence of PCC dissolution in the excess of carbonic acid. The shape of the κ_{25} vs. time curve obtained in the experiment carried out at θ = 25 °C and κ_{25} > 1.5 mS cm⁻¹, differs somewhat from the other experiments, since the conductivity increases shortly after a period of constancy. Such a behaviour of the conductivity during the process of PCC formation is explained by being a consequence of nucleation and growth of a certain calcium carbonate precursor phase, probably an amorphous calcium carbonate, on the surface of suspended Ca(OH)₂ particles (so-called "surface mechanism of precipitation") [GAR03, GAR04]. Since the precursor is extremely unstable [BRE89], it rapidly dissolves in the process of transformation into thermodynamically stable calcite, thus liberating the surface of the $Ca(OH)_2$ particles and causing the uncontrolled increase in conductivity.

However, here we managed to control the conductivity and confirm the decisive role of the excess of suspended Ca(OH)₂. Under the same experimental conditions ($\theta = 25$ °C, $\kappa_{25} > 1.0$ mS cm⁻¹, γ (Ca(OH)₂) = 100 g dm⁻³), but applying a slow addition of Ca(OH)₂ suspension (Q_{max} (Ca(OH)₂ = 40 cm³ min⁻¹) during the set-point adjustments at the beginning of the process, the progress curves remain constant. Moreover, we observed the same effect if using the suspension of Ca(OH)₂ with considerably lower mass concentration of γ (Ca(OH)₂) = 20 g cm⁻¹. The non-existence of any accumulated solid Ca(OH)₂ in the system during carbonation, allowed the progress curve to remain constant at predetermined conductivity. Namely, owing to the slow initial addition of Ca(OH)₂ slurry, the dissolution of Ca(OH)₂ particles is much faster than the formation of PCC.



Fig. 2. Values of the specific surface area (*s*) of PCC obtained by the batch process at different temperatures (θ) and initial mass concentration of Ca(OH)₂ (γ).

The results of mineralogical analyses of the final products show that calcite was the only CaCO₃ polymorph obtained at the end of batch and semicontinuous carbonation experiments. In the batch experiments the specific surface area of calcite decreased with the increase of temperature (Fig. 2). By comparison of experiments performed at different temperatures, it is evident that the measured specific surface area of PCC decreases with increasing temperature, which is principally due to the lower solubility of Ca(OH)₂ and CO₂ at higher temperatures and with this connected change of the prevailing mechanism of nucleation. At $\theta = 25$ °C specific surface area considerably increases with the increase of the initial mass concentration of slaked lime. PCC with the highest specific surface area of s = 25.7 m² g⁻¹ was obtained at $\theta = 25$ °C and γ (Ca(OH)₂) = 28.6 g dm⁻³ with the mean particle diameter of the primary particles $d_m \approx 50$ nm, estimated by SEM (Fig. 3).



Fig. 3. SEM image of PCC sample obtained by batch process at θ = 25 °C and γ (Ca(OH)₂) = 28.6 g dm⁻³.

The mean particle diameter (expressed as the maximum value of particle diameter distribution) of PCC samples at γ (Ca(OH)₂)= 13.0, 20.0 and 28.6 g dm⁻³ were 5.3, 6.3 and 10.7 μ m, respectively. Thus, the increase of the initial supersaturation enhanced the degree of precipitate aggregation. At $\theta > 25$ °C scalenohedral calcite precipitates, with the mean particle diameter, $d_m \approx 1 \mu$ m. This is the most common morphology of PCC prepared by batch carbonation of slaked lime [CAR03].



Fig. 4. Values of the specific surface area (*s*) of PCC obtained by the semicontinuous process at different temperatures (θ) and conductivities (κ_{25}).

On the other hand, specific surface area of PCC obtained in semicontinuous process increases with increasing supersaturation and decreasing temperature (Fig. 4). PCC with the highest specific surface area of $s = 23.8 \text{ m}^2 \text{ g}^{-1}$ was obtained at $\theta = 25 \text{ °C}$ and $\kappa_{25} = 5.0 \text{ mS cm}^{-1}$. Typical PCC morphologies and their particles sizes obtained under

different experimental conditions in the semicontinuous process are shown in Fig. 5. In the experiments conducted at 25 °C and $\kappa_{25} = 5.0 \text{ mS cm}^{-1}$, PCC appeared in a form of nanosized calcite particles, with the mean particle diameter $d_m \approx 30 \text{ nm}$, estimated by TEM (Fig. 6a). At the same temperature and at $\kappa_{25} = 3.0 \text{ mS cm}^{-1}$, as well as in the process where the conductivity was fully controlled and kept at the predetermined value of $\kappa_{25} = 5.0 \text{ mS cm}^{-1}$ ($Q_{max}(Ca(OH)_2 = 40 \text{ cm}^3 \text{ min}^{-1}$ during the set-point adjustment), scalenohedral calcite precipitates (Fig. 6b). At high conductivities ($\kappa_{25} = 3.0 \text{ and } 5.0 \text{ mS cm}^{-1}$) and temperatures of $\theta = 35 \text{ °C}$ and 45 °C truncated prismatic calcite crystals are produced, with the mean particle diameter $d_m \approx 0.7 \text{ }\mu\text{m}$ (Fig. 6c). Such morphology was also observed in our previous study [UKR07]. Lower conductivities ($\kappa_{25} = 0.5 \text{ mS cm}^{-1}$, 1.0 mS cm⁻¹ 1.5 mS cm⁻¹) at all investigated temperatures ($\theta = 25 \text{ °C}$, 35 °C and 45 °C) gave rise to the formation of rhombohedral crystals of calcite (Fig. 6d). The morphological change from scalenohedral to rhombohedral was explained in terms of the increase of both the supersaturation and the calcium to carbonate ratio in solution [JUN00, GAR03].



Fig. 5. Characteristic TEM images of PCC obtained by semicontinuous process: (a) nanosized, (b) scalenohedral, (c) truncated prismatic and (d) rhombohedral particles.

4. Conclusions

In the batch experiments the specific surface area of calcite particles decreased with the increase of temperature. PCC nanoparticles can be produced at 25 °C, but the increase of the initial mass concentration of slaked lime enhances the degree of their aggregation. At higher temperatures (35 and 45 °C) scalenohedral micrometric calcite precipitates. Supersaturation is the main factor affecting the physical-chemical properties of a precipitate. Thus, conducting the process at predetermined and constant supersaturation enables better

definition of the product properties. By careful tuning of the semicontinuous process parameters, calcite in the form of rhombohedral, truncated prismatic, scalenohedral or nanosized particles can be produced. The excess of suspended $Ca(OH)_2$ has a decisive role in the formation of the calcite nanoparticles.

5. References

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