**Morphology and size control of calcium carbonate particles through carbonation route in a packed bed reactor.**

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**Highlights**

* Size and shape of CaCO3 particles were controlled by varying operating conditions.
* Stable calcite particles were synthesized by employed a packed bed reactor.
* High pH values avoid the agglomeration and growth phenomena.

**1. Introduction**

Nowadays, there are serious environmental issues due to the Green House Gas emissions. The cement, iron and steel production can be included among the most polluting industries. Thus, there is an important need of recovering of CO2 from combustion gases of these industries, which in turn can be used to obtain added value products. Calcium Carbonate Nanoparticles (CCnP) are widely synthesized via carbonation route (1)and have a large gamma of applications, since their characteristics, such as size and morphology are easily tunable through the synthesis method. They are widely used as filler material and, because of their porosity, non toxicity and biocompatibility, they are also used in the biomedical and food industry (2). In this study, an alternative carbonation method to synthesize calcium carbonate particles and control their size and morphology by varying the operating conditions is reported.

**2. Methods**

CaCO3 particles were synthesized through carbonation (pure CO2) of a CaO slurry. A Packed Bed Reactor, with a monolith as structured packing, was employed for this study in a setup illustrated in Figure 1. The synthesis was carried out at constant gas and liquid flowrate and stirring. The CO2 flux was stopped once the pH was less than 10.5, value at which, according to the carbonate equilibria, the CO32- formation is not favoured, thus reducing the CCnP saturation. Two zones are individuated: *i*) the crystallization one in the PBR, whence the CO2 and the calcium solution get in contact and the precipitation takes place and *ii*) the stabilization one in the feed tank, where the pH is maintained high enough to provide a stable environment to the CCnP, since under alkaline conditions growth and agglomeration phenomena of the CCnP are not favoured (1). Then, once the process was finished, the synthesized particles were filtered by vacuum (pore size=0.45 μm) and repeatedly washed with deionized water to eliminate ion excess. By last, the CaCO3 powder was dried at 60 °C overnight and finally their size, morphology and crystal phase were characterized.



**Figure 1.** Packed bed reactor experimental setup.

**3. Results and discussion**

The operating conditions had an important effect on the properties of these particles. Cubic particles were obtained in the most of cases, in which the pH was maintained constant enough during the entire synthesis. The initial CaO concentration had an interesting effect on the particle size. Even if high CaO concentrations mean higher supersaturation levels, and then smaller particles would be obtained. At the beginning of the process, high saturation levels were present, but it led to higher synthesis times, and once the primary particles were formed, growth and agglomeration phenomena were prevalent, since they are favored by particle size and ion concentration respectively. Low liquid and CO2 flowrates also led to elevated synthesis times, hence larger particles were synthesized. The flow regime, instead, affected the CO2 absorption, controlling thus, the nucleation and growth rate. Higher liquid and gas flowrates led to smaller particles preparation, since they provide a more effective micromixing leading to a higher nucleation rate. In the cases where the CO2 flowrate was too high (higher than 550 mL/min) and the pH suffered a progressive change during the synthesis, agglomerates were although formed. Consequently, this had an effect on the morphology of these particles, since hollow and particles with a wide PSD were obtained. Therefore, particles with mean particle size less than 200 nm were synthesized at optimal operating conditions, starting from a CaO slurry 0.015 M and liquid and gas flowrates equal to 300 and 400 mL/min respectively.

**4. Conclusions**

The size and morphology of calcite particles have been controlled in a carbonation precipitation for the CO2 conversion. The shape of this particles reflects upon the operating conditions of the synthesis. The pH during the synthesis played a fundamental role, it controlled the agglomeration and growth phenomena. Hence, it had an important effect over the morphology and size. Higher pH values led to cubic calcite nanoparticles. Smaller particles were synthesized by employing higher liquid and gas flowrates, while low flowrates led to larger and agglomerated particles.

**References**

1. Nano-CaCO3synthesis by jet flow. Eda Ulkeryildiz, Sevgi Kilic, Ekrem Ozdemir. 2016, Colloids and Surfaces A: Physicochemical and Engineering Aspects, p. 34-40.
2. Formation of nanoparticles and nanostructures-an industrial perspective on CaCO3, cement, and polymers. Rieger, J., Kellermeier, M., Nicoleau, L. 2014, Angewandte Chemie - International Edition, p. 12380-12396.