CO2 conversion through the synthesis of CaCO3 nanoparticles

CO_2 conversion through the synthesis of $CaCO_3$ nanoparticles

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Summary

This PhD dissertation is focused on CO_2 conversion due to the high global emissions of the last decades. Mineral carbonation was considered and studied, as it makes it possible to obtain high conversion yields of CO_2 into stable carbonates as $CaCO_3$ that can store CO_2 for decades. Besides, these carbonates have a wide field of applications in the paper, plastic, and cement industries. Thus, the objective of this PhD dissertation is the optimization of $CaCO_3$ synthesis from CO_2.

This research was developed in the framework of an EU project. The aim is the CO_2 recovery and conversion from the cement industry. There is potential for it to be employed in the cement industry as $CaCO_3$ nanoparticles are widely used as cement filler because it increases the cementitious materials' mechanical properties. Thus, the proposal consists of implementing a circular economy process of CO_2 within the cement industry.

CaO and $CaCl_2$ were proposed as calcium sources, as they can be obtained from wastes of other processes, like steelmaking and Solvay processes, respectively. When $CaCl_2$ was used, NH_4OH was considered as an alkalinity source to favor the carbonation process, which can also be obtained from the anaerobic digestion of urban waste. Two carbonation pathways were studied, i) from CaO slurry and ii) from $CaCl_2/NH_4OH$ solution.

The preliminary lab-scale tests in a Continuous Stirred Bubbling Reactor (CSBR) showed that the first pathway led to obtaining calcite crystals. The second pathway made it possible to control the content of rhombohedral calcite and spherical vaterite crystals. By varying the operating parameters, it was possible to determine a proper work zone of operation to favor the synthesis of small $CaCO_3$ particles, improving their performance as cement filler, according to the literature.

This zone was characterized by low initial calcium concentrations and high pH values.

An intensification of the process was carried out in a Packed Bed Reactor (PBR) to enhance both the absorption and precipitation processes was conducted under semi-batch conditions. Gas and liquid came into contact in the PBR in co-current up-flow, where the CO_2 was absorbed, and the $CaCO_3$ particles precipitated. This system yielded smaller particles compared to the use of the CSBR: even nanosized crystals were synthesized. The gas and liquid flow rates were determinant in the characteristics of the precipitated $CaCO_3$. The literature suggests that the performance of the $CaCO_3$ particles as filler is highly linked to their morphology; therefore, potentially, the crystal shape and size control in the PBR could enhance the performance of the products in different applications. Further intensification process studies were carried out in microchannel reactor systems, making it possible to reduce the crystal size and control the crystal shape.

Results obtained in both systems were explained through a study of kinetics, which confirmed that the NH_4^+ ions reduced the nucleation and growth rates and favored vaterite formation. Moreover, it was found that the operating conditions - gas and liquid flow rates in the PBR - influenced the crystallization kinetics. It is, therefore, clear that $CaCO_3$ size can be controlled.

The synthesized product was employed in cement and polymers as fillers, and it was seen the crystal size and morphology influenced that performance. The performance of the synthesized $CaCO_3$ was good and at times higher than some commercial $CaCO_3$ in both applications.

Furthermore, the process was evaluated in terms of a Life Cycle Assessment and techno-economic analysis: results suggested that the cement industry's emission could be reduced by 69% if $CaCO_3$ is recirculated within the industry and employed as a filler in addition to notably increase the economic profits. This approach is also attractive because the so-synthesized $CaCO_3$ particles do not present any toxicity towards humans and the environment according to toxicity studies performed in this PhD dissertation framework.

Therefore, the carbonation route for the synthesis of $CaCO_3$ represents an alternative to converting CO_2 into stable $CaCO_3$. The carbonation process allows control of these crystals' properties, making them a versatile material that can be used in several applications without risks to the environment or human health because of the complete biosafety of $CaCO_3$ nanoparticles derived from CO_2.