
# Utilization of the cement industry $CO_2$ in the production of calcium carbonate nanoparticles through precipitation process intensification on a packed bed reactor

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CREST
Catalytic Reaction Engineering for Sustainable Technologies

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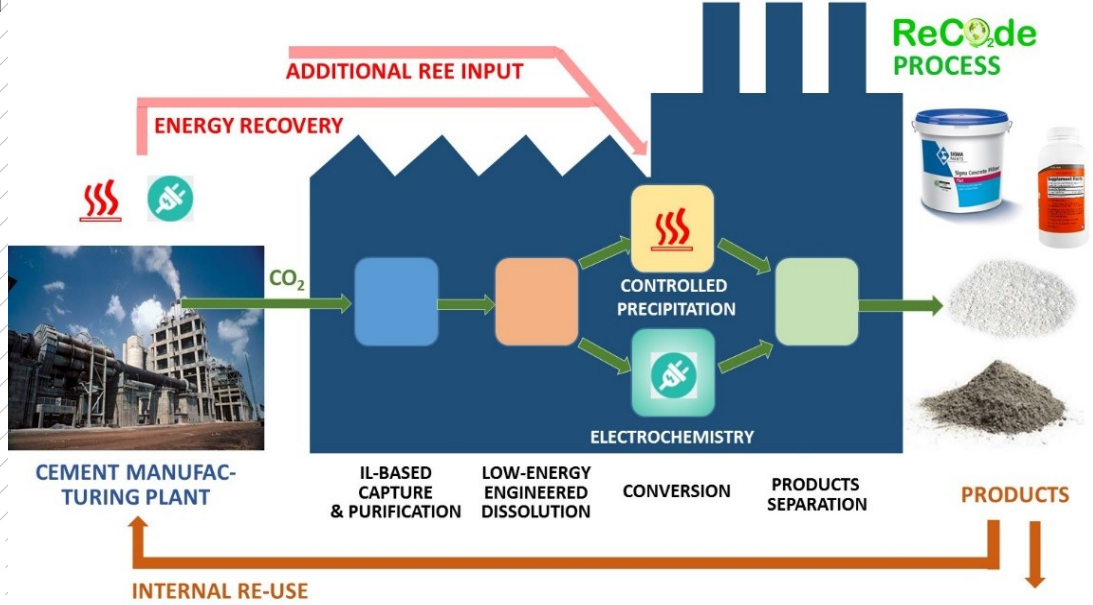
# ReCode: Concept overview



- Recycling Carbon dioxide in the cement industry to produce added-value additives
- Development of a demo plant to showcase $CO_2$ circular economy
- 13 European partners

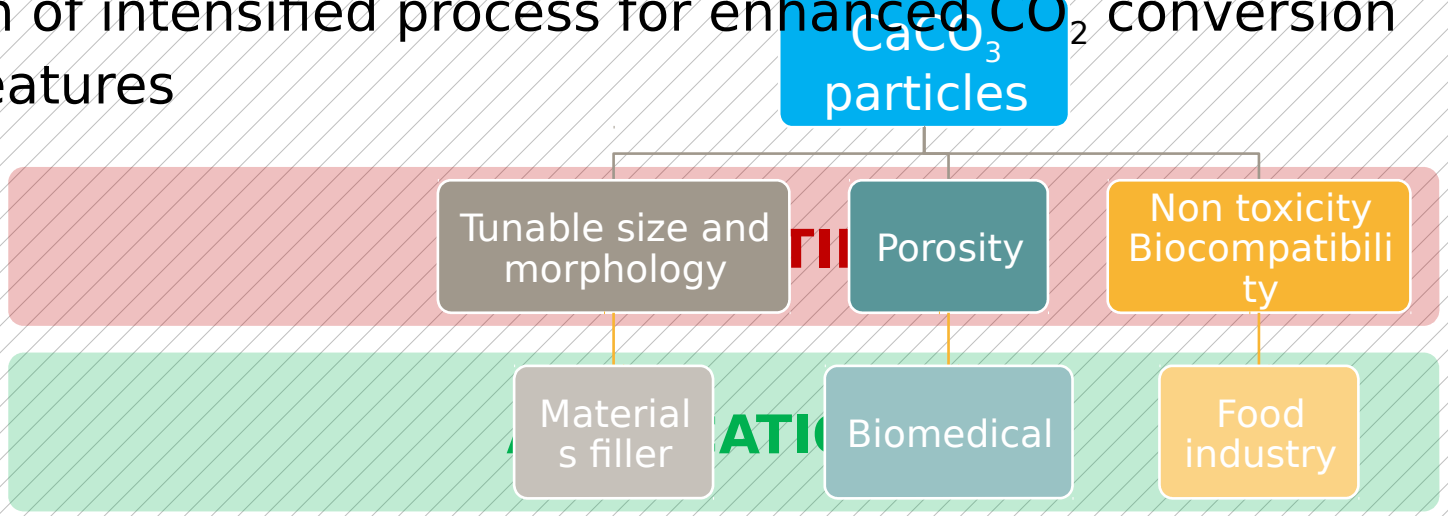



www.recodeh2020.eu

# Introduction



- ***Aim of the work:*** recovery of $CO_2$ from cement flue gases through carbonation route for obtaining Calcium Carbonate Nanoparticles (CCNPs)
- Optimization of intensified process for enhanced $CO_2$ conversion and CCNP features



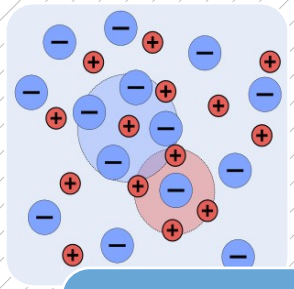

*Boyjoo, Yash and K. Pareek, Vishnu and Liu, Jian, 2014. Synthesis of micro and nano-sized calcium carbonate particles and their applications J. Mater. Chem. A*

# $CaCO_3$ formation

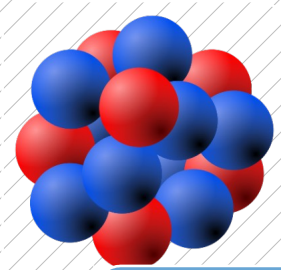


**Precipitation method** $Ca^{2+} + CO_3^{2-} \rightarrow CaCO_{3\,(s)}$ $K_{ps} = 8.7 * 10^{-9}$

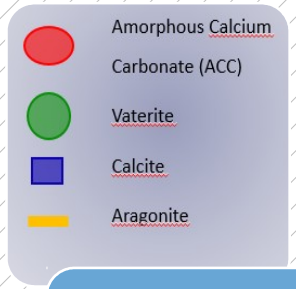
## Classical $CaCO_3$ precipitation mechanism



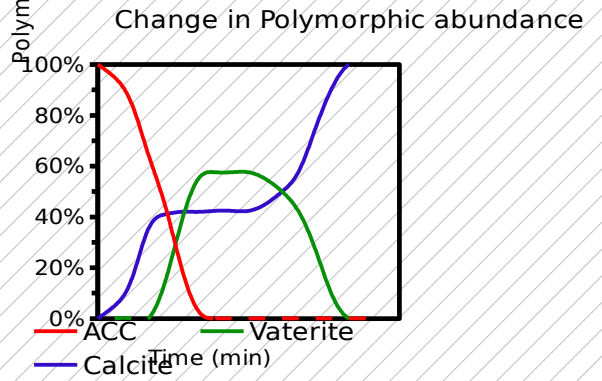
Pre nucleation
- Calcium and carbonate ions in solution
- Metastabile clusters



Nucleation
- Homogeneous nucleation
- Heterogeneous nucleation
- Clusters of critical size



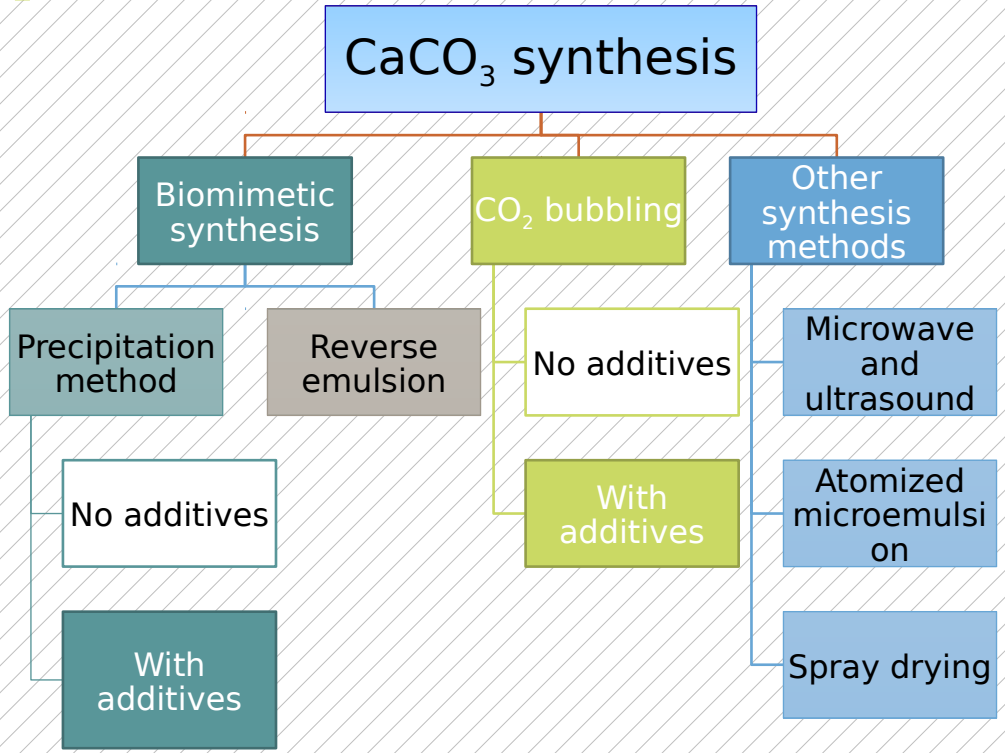

Post Nucleation
- Growth
- Aggregation and agglomeration

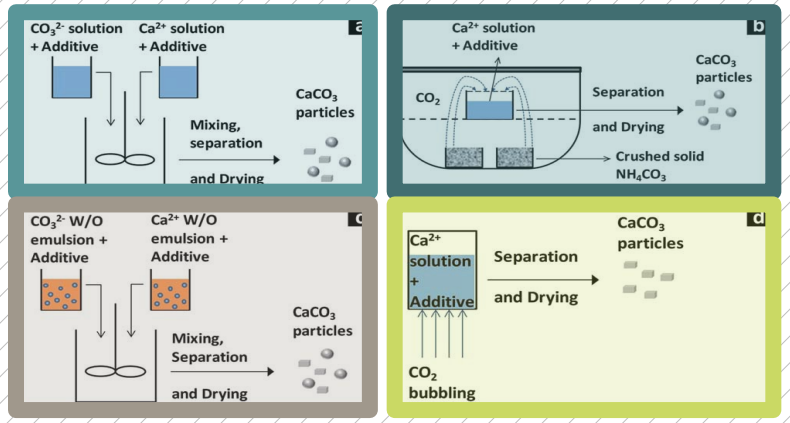



*Pure & Appl. Chem., Vol. 69, No. 5, pp 921-928, 1997.*

# Main synthesis methods






(a) the spontaneous precipitation method, (b) the slow carbonation method, (c) the reverse (W/O) emulsion method and (d) the CO2 bubbling method. The biomimetic method is represented by (a), (b) and (c).

*Boyjoo, Yash and K. Pareek, Vishnu and Liu, Jian, 2014. Synthesis of micro and nano-sized calcium carbonate particles and their applications J. Mater. Chem. A*

# Experimental procedure



$CaCO_3$ precipitation by carbonation process

$CaCO_3$ particles separation

- Vacuum Filtration with Membrane Filter (Pore diameter 0.45 µm)

Drying overnight at 90 °C

Particles characterization

- Particle size distribution
- Polymorphism
- Morphology

**Solution Equilibria**

Byproduct of other processes

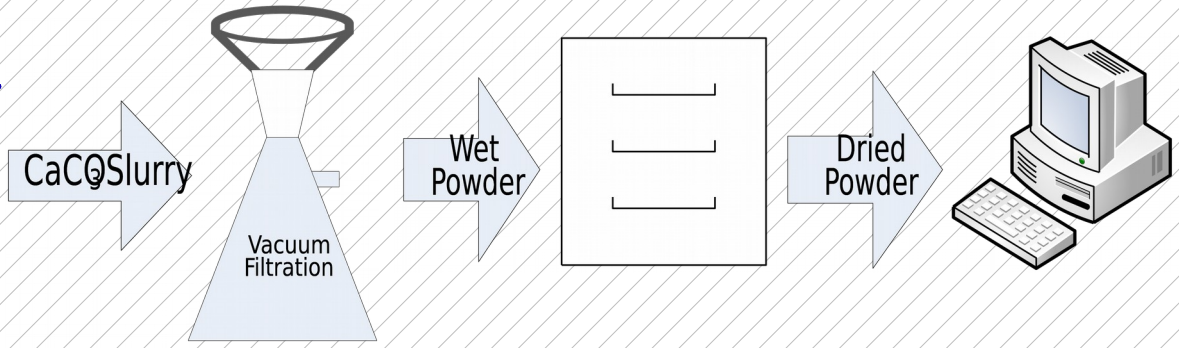
$$CaO + H_2O \rightarrow Ca(OH)_2$$

$$Ca(OH)_2 \rightarrow Ca^{2+} + OH^-$$

$$CO_2 + 2OH^-_{(aq)} \rightarrow CO_3^{2-} + H_2O$$

$$CO_3^{2-} + Ca^{2+}_{(aq)} \rightarrow CaCO_{3\,(s)}$$

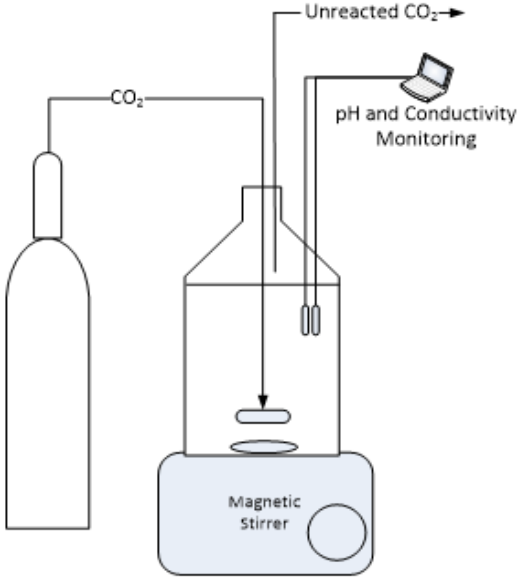
$$CaO + CO_2 + H_2O \rightarrow CaCO_3 + H_2O$$



# Bubbling reactor experimental setup



Bubbling Reactor (BR)

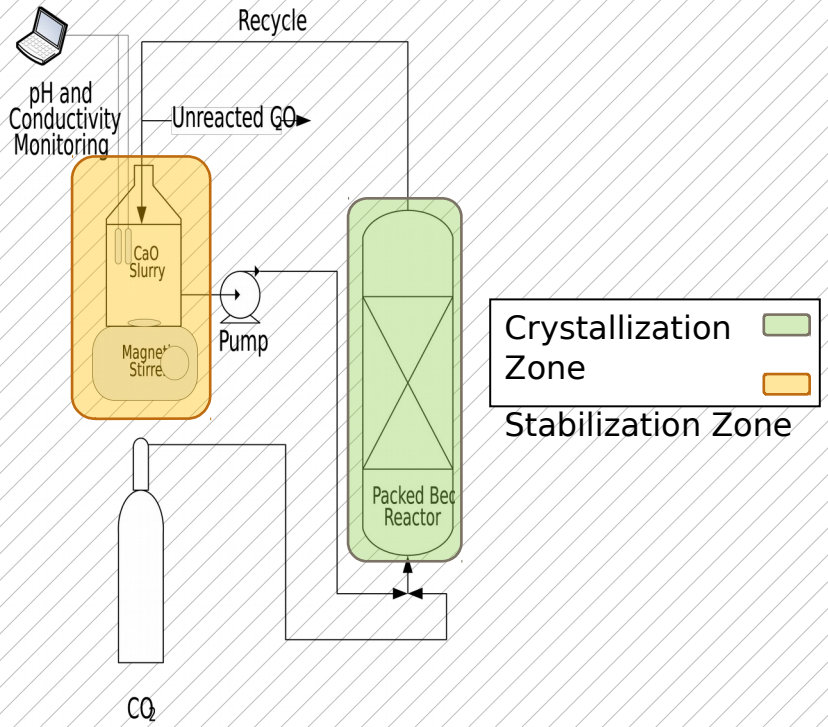



| Bubbling reactor parameters | |
|---|---|
| Length [mm] | 200 |
| Diameter [mm] | 100 |
| Sparger level [mm] | 30 |
| Stirrer length [mm] | 30 |

*Both experimental setup were tested varying the operating conditions, such as flowrates and initial concentrations, in order to obtain as small as possible particles.*

# Packed bed reactor experimental setup






| Packed bed reactor parameters | |
|---|---|
| Length [mm] | 370 |
| Inner Diameter [mm] | 10 |
| Packing Surface Area [$m^2/m^3$] | 2500 |
| ε [$m^3/m^3$] | 0.62 |

# $CaCO_3$ particles characterization



+ isopropanol

Ultrasound bath (15 min)

Particle size distribution analysis

Malvern zetasizer

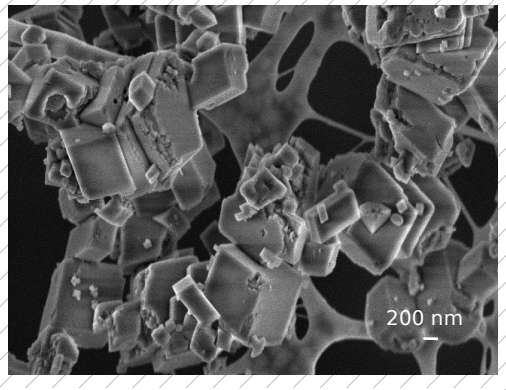

Zeiss Merlin FE-SEM for morphologic analysis

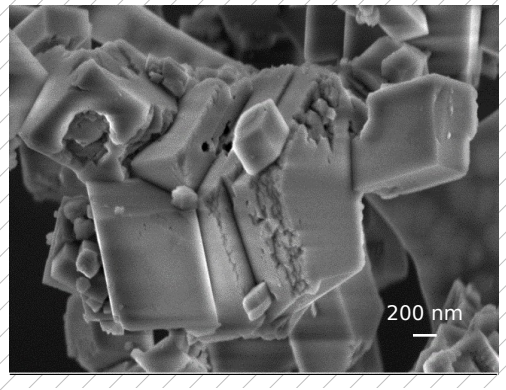
Xpert PRO (PANalytical) for XRD analysis

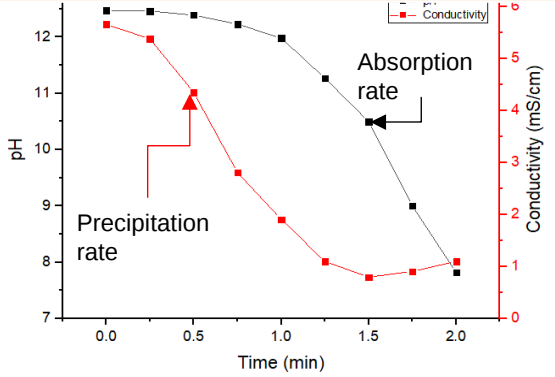
# Bubbling reactor performance

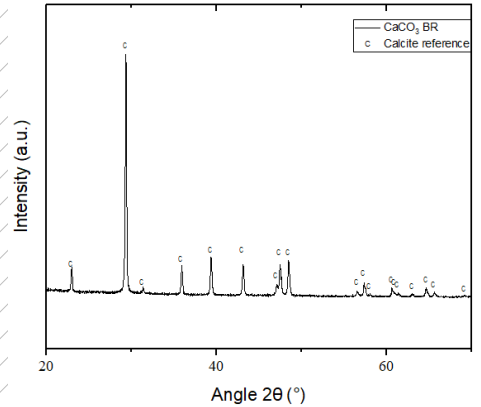


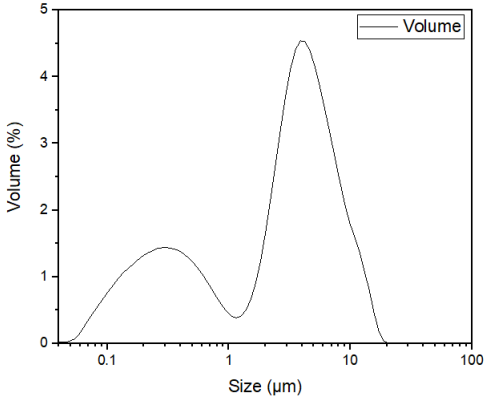
| Optimal operating conditions (BR) | |
|---|---|
| Gas flowrate (mL/min) | 250 |
| Liquid flowrate (mL/min) | -- |
| Initial CaO concentration (mol/L) | 0.015 |
| Initial pH | 12.45 |
| Synthesis time (min) | 1.5 |
| Calcium conversion | 83% |
| $CO_2$ conversion | 40% |



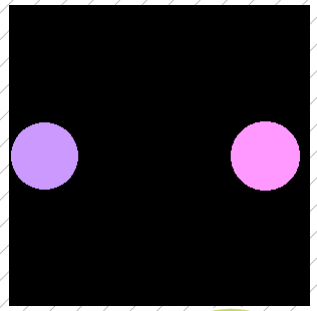



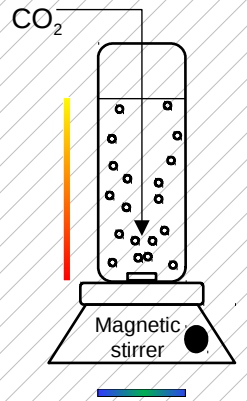



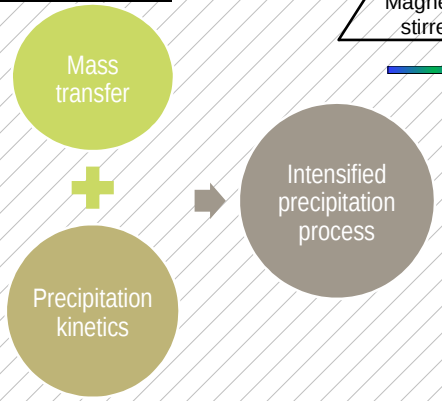
# Process intensification



- *Maximize the effectiveness of intra- and intermolecular events*
- *Give each molecule the same processing experience which results in products with uniform properties*
- *Optimize the driving forces at every scale and maximize the specific surface area*
- *Maximize the synergetic effects from partial processes which enable multitasking*





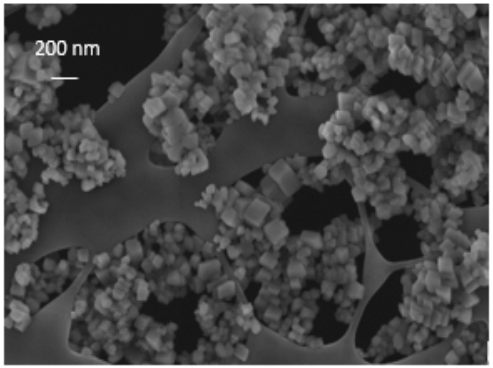

*Tian Y, Demirel SE, Hasan MMF, Pistikopoulos EN, Chemical Engineering and Processing - Process Intensification (2018)*

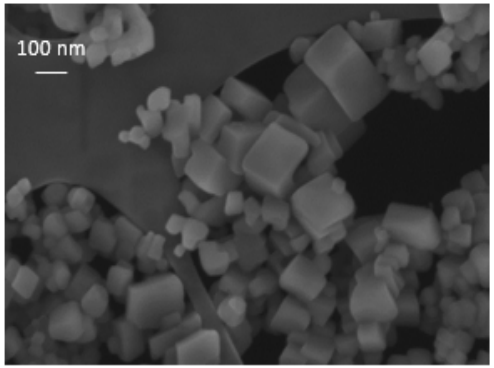
*Bao-Chang Sun, Xue-Mei Wang, Jian-Ming Chen, Guang-Wen Chu, Jian-Feng Chen, Lei Shao 2011, Chemical Engineering Journal, p. 731–736.*

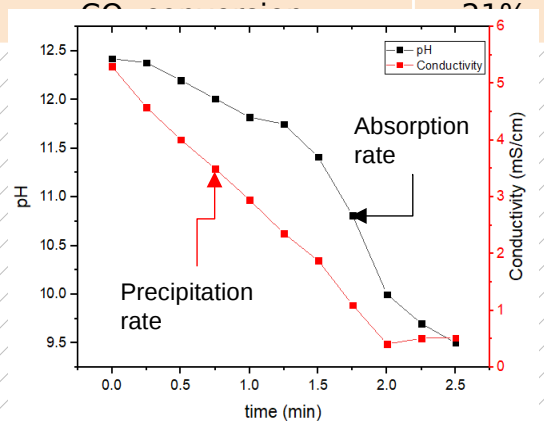
# Packed bed reactor performance

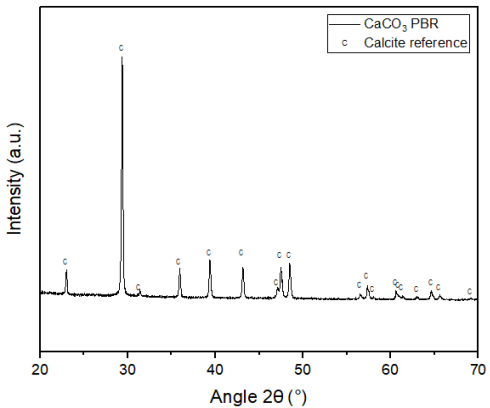


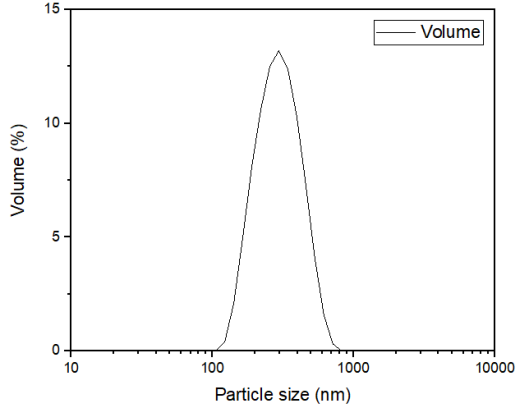
| Optimal operating conditions (BR) | |
|---|---|
| Gas flowrate (mL/min) | 571 |
| Liquid flowrate (mL/min) | 108 |
| Initial CaO concentration (mol/L) | 0.015 |
| Initial pH | 12.45 |
| Synthesis time (min) | 2 |
| Calcium conversion | 95% |
| CO₂ conversion | 21% |



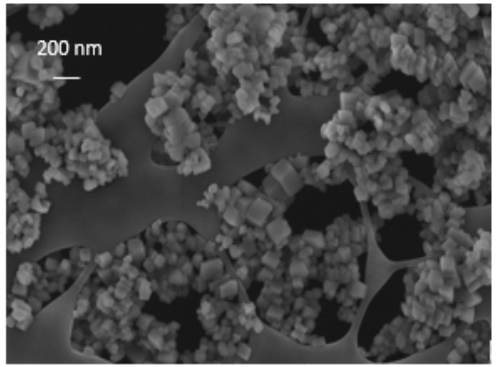



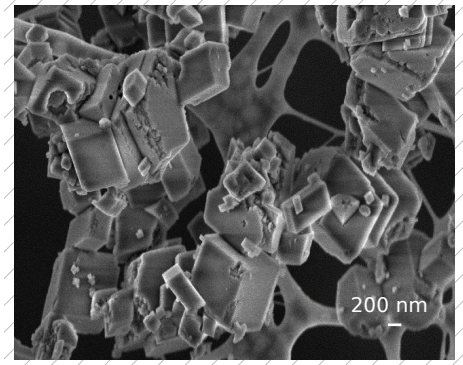



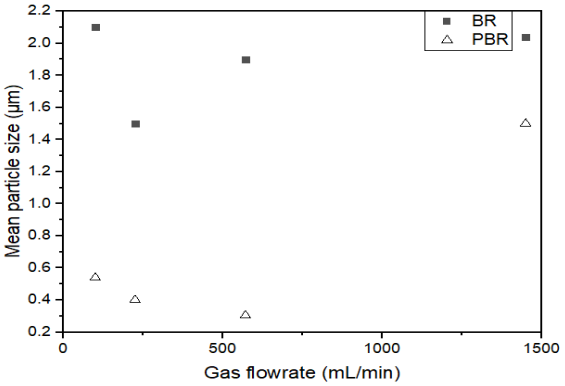



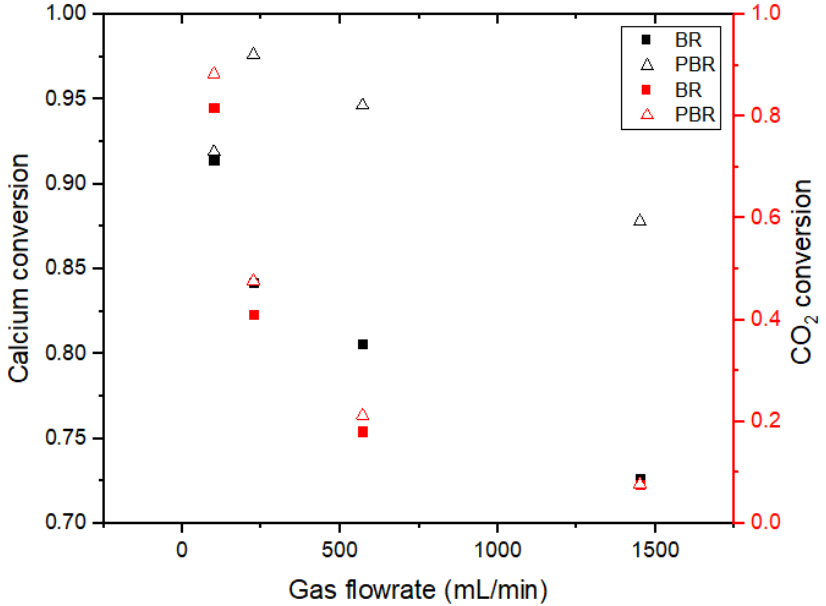
# Reactors comparison





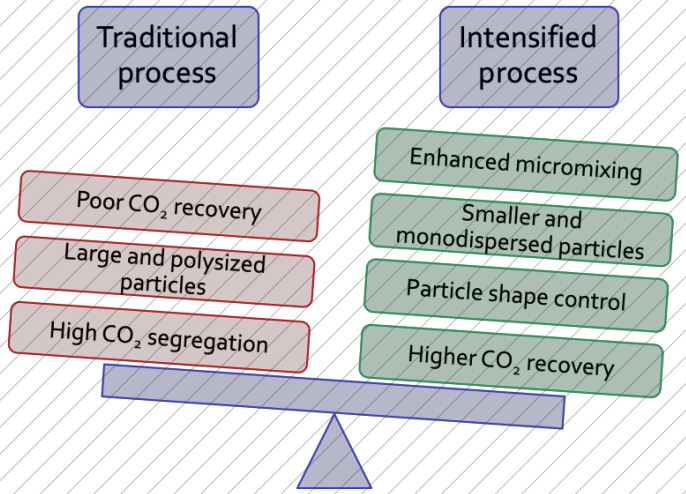



# Conclusions



- **$CO_2$ was successfully recovered into Calcium Carbonate Nanoparticles by a carbonation route**
- The process was intensified by employing a Packed Bed Reactor
- The intensification allowed to
  - maximize the effectiveness of **intra- and intermolecular events**
  - give each molecule **the same processing experience**
  - *optimize the driving forces at every scale*
- By this way, *growth and agglomeration were controlled* and **nanosized calcite $CaCO_3$ particles with narrow PSD** were produced, with *increased calcium and $CO_2$ conversion*



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**Thank you for your kind attention!**