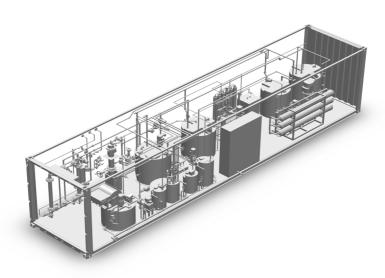


Conversion of CO₂ into nanoCaCO₃

a step towards a CO₂ circular economy





Background

The application of packed-bed reactor (PBR) and/or membrane-based precipitator (MBP) technologies for converting $\mathrm{CO_2}$ from energy-intensive industry flue gases into carbonates, in a single-step multiphase process, is a key enabler of the circular economy for the cement industry, a major contributor to global industrial $\mathrm{CO_2}$ emissions. Nano $\mathrm{CaCO_3}$ particles obtained through the carbonation reaction can be directed back into the cement production as fillers for partially substituting cement in high-performance concrete. High $\mathrm{CO_2}$ conversion efficiency and a high product quality is achieved in both technologies employed.

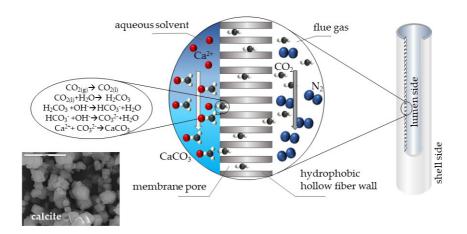
Technology

The technology developed in the RECODE project is used for the utilization of $\rm CO_2$ by producing $\rm CaCO_3$ nanoparticles of controllable size and crystallinity as additives for cement and other materials, as well as simultaneous production and crystallization of $\rm NH_4Cl$. A PBR is used to produce $\rm CaCO_3$ nanoparticles with easily tuneable properties for a wide field of applications. Optimal growth and agglomeration control are achieved and nanosized calcite cubic particles are synthesized with an increase in process conversions in terms of calcium and $\rm CO_2$, comparing with conventional techniques (i.e. continuously stirred bubbling reactor, CSBR). Similarly production of nano $\rm CaCO_3$ particles from captured $\rm CO_2$ using MBP leads to high $\rm CO_2$ recovery and synthesis of $\rm CaCO_3$ particles, with controllable crystalline structure (aragonite, vaterite, and calcite) and size under both contactor and bubbling modes. RECODE project is enabling the scaling up of the MBP process towards the establishment of Carbon Capture and Utilization via Mineralization (CCUM) for direct application in energy-intensive cement industries.

Process



Membrane-Based Precipitator (MBP): A gas-liquid hollow fiber membrane contactor – a well established technology in the field of gas separation/bubbling/extraction in industrial applications – is used for direct conversion of CO_2 to useful nanostructured calcium carbonates. Using a hydrophobic microporous membrane, an immobilized gas-liquid interface is formed at the pores' mouth in the liquid side (membrane contactor mode), or the gas enters in the liquid phase in the form of nano-bubbles (membrane bubbling reactor mode). The benefits of employing hollow fiber membrane contactor in carbonates' precipitation come from its distinct characteristics: no dispersion of the gaseous phase into the liquid solvent, large specific contact area, high surface area to volume ratio, high mass transfer rates, precisely controlled pore size. These contactors offer an ideal route for CO_2 mineralization with controllable morphological and structural properties of the generated particles. The MBP process was developed by CERTH (GRC). The RECODE demonstration plant for membrane-based precipitation was designed and constructed by MET (LTU).







- ☐ CaCO₃ nanoparticles are synthesized by gas-liquid carbonation reaction
- average crystal size of 50 nm (XRD), average nanoparticle diameter of 80 − 100 nm and average aggregates size of 1 − 5 μm (DSL and SEM)
- ☐ In the RECODE Pilot Plant two types of reactors are installed: Packed Bed Reactor (PBR) and Membrane-Based Precipitator (MBP)
- ☐ Production scale 3 kg/h of CaCO₃ nanoparticles
- □ Simultaneous production and crystallization of NH₄Cl
- Continuous product separation system



Demo-unit for the production of 3 kg/h of $CaCO_3$





The Recode project answers the question how the cement industry can lower their carbon footprint: by enabling a circular-economy-approach. The $\rm CO_2$ produced by cement manufacturing is re-used in significant part within the plant to produce better cement-related products entailing less energy intensity and reduction of $\rm CO_2$ emissions. Moreover, $\rm CO_2$ is used in various synthesis routes. Through electrocatalytic and catalytic pathways, formic acid, oxalic acid and glycine are produced to be used as hardening acceleration promoters or grinding aids.

For the past five years, the project consortium investigated all necessary sub-processes and scaled them up to technically relevant size. Dedicated pilot plants were developed for all technologies and are demonstrated within a TRL 6 integrated system campaign at Kamari cement plant in Greece.





Membrane-Based Precipitator





Engineering Construction





Packed Bed Reactor





Project Coordination