

Recycling carbon dioxide in the cement industry to produce added-value additives: a step towards a CO₂ circular economy

Deliverable 7.6

Report on the definition of regulatory framework after coming in contact with key energy players

WP 7 – Impact Analysis

Version v1.0

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Revision History

Author Name, Partner short name	Description	Date
Christian Müller (DVGW)	Drafting of the deliverable	07/09/2022
Friedemann Mörs (DVGW)	Internal Revision	08/09/2022
Boyan Iliev (IOL)	Internal Revision	13/09/2022
Christian Müller (DVGW)	Final Version	21/09/22



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1 Introduction

This deliverable (D7.6) includes the work done by DVGW, along with help from different project partners, within Task 7.5 ‘Social, pre-normative and regulatory impacts’. Nevertheless, most of this task’s work was carried out within other work packages. From the outset, this task was connected to WP 8 (dissemination) and WP 7 (exploitation) as well as WP 1 (exploitation plan). The related results are reported within different deliverables. In terms of dissemination, this included the gathering of information of past and upcoming events that are related to the RECODE project. Due to delays in the demonstration campaign, the duties of this task focused on the exploitation plan and the final workshop to reach the task’s goals. Also because of increased effort in WP 3, DVGW’s originally budgeted person months for WP 7 were reduced from 5.5 to 3 in the second amendment accordingly.

2 Cross-cutting activities

In all cross-cutting activities within RECODE and between different work packages, the focus was the CO₂ recovery. It is the first step for all CCU applications. Moreover, the cost calculated for CO₂ captured or CO₂ avoided, as reported in Deliverable 7.3, is probably the most relevant number in preliminary considerations when defining a CCU project in industrial scale.


Therefore, additional tests of the ionic liquid used in the demo unit were conducted by DVGW and described in the final report within Task 3.5. These experiments aimed for a better understanding of the long-term stability of the IL which is a key parameter for an economically competitive performance of the process.

Moreover, considerable effort went into the exploitation plan on the Key Exploitable Result KER 1 of WP 1, the CO₂ recovery with ionic liquids, to push the further use of the technology. The outcome is reported in Deliverable 1.5.

3 Reaching generic public

One duty of this task was meant to share the outcome of the demonstration campaign at TRL 6 with Regulatory Authorities, stakeholders and public authorities. As it is the nature of a demonstration project, the major and most relevant outcome is the demonstration itself. Even though the project was extended twice, the operation of the units happened at the very end (July 2022). Some results were even generated after the end of the project (Sep 2022). Therefore, it was difficult to transfer the outcome of the demonstration period to the generic public earlier within the project.


During execution of this task DVGW tried to get in contact to other European CCU projects. A promising contact with a representative with EU wide organization CO₂Value lead to a pre-planning of a shared workshop with another European project CO₂IntBio. Unfortunately, the efforts were in vain, due to

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diverging interests. One outcome of these conversations was that we decided not to do the work of potent networks such as CO2Value in parallel.

Instead, DVGW focused on how it can contribute added value to the project and beyond. Therefore, we collected information to all four demo units. We got in contact with all partners responsible for the technology demonstration and produced fact sheets. The fact sheets include the CO₂ recovery with ionic liquids, the electro catalytic conversion of CO₂ and the conversion of CO₂ into nanoCaCO₃. Originally, it was planned to hand out the fact sheets at a face-to-face event on the demo site. Due to the late start of the demonstration campaign, Corona circumstances and the hurdle of an elaborate journey to the demo site, all partners decided to make an online event as the final workshop. This is why we changed again the layout of the flyers without reducing the content. The fact sheets were uploaded to the RECODE homepage and shared among the participants of the final workshop. Moreover, this info material can be used beyond the project to address stakeholders and policy makers or interested industry partners to increase the reach of the overall project.

The fact sheets point out the key messages of the project in form of the development of each technology and the construction of the demo units. The flyers are attached to this deliverable.

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Appendix A: fact sheet – CO₂ recovery with ionic liquids

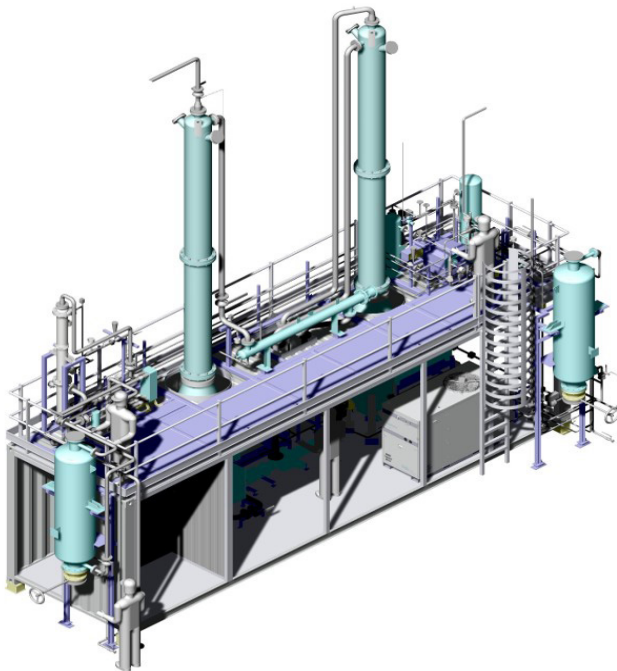
Partners involved in technology:

Process Technology:	DVGW
Engineering Construction:	Hysytech
Ionic Liquids:	Iolitec
Project Coordination:	IIT



CO₂ recovery with ionic liquids

a step towards a CO₂ circular economy



The RECODE project has received funding from the European Union's Horizon 2020
Research and Innovation Programme under Grand Agreement No. 768583



Background

Not the cement industry alone, many industries worldwide have the obligation to lower their CO₂ emissions. If their processes cannot be adjusted to suppress emissions, CO₂ needs to be captured. To do so, ionic liquids can be the key technology. Due to their extraordinary capabilities, the state-of-the-art-process for CO₂ separation – chemical scrubbing with amines – can be simplified and thus operated in an energy efficient and economically viable way.

Technology

Developed for an efficient upgrading of biogas, the CO₂ recovery technology with ionic liquids allow for large scale application in cement, steel or chemical plants. Even CO₂ recovery from ambient air is possible. The process is adapted to the special characteristics of the tailor-made solvents through which the energy required can be lowered by up to 50 %. Moreover, oxygen-resistant liquids ensure a long lifetime in post-combustion processes. Compared to conventional gas scrubbers, the technology facilitates a less substantial retrofit of the production plant since it requires a fraction of process heat for an economical use. The demo-unit is able to treat 100 m³/h of flue gas and delivers 16 kg/h of high-purity CO₂.

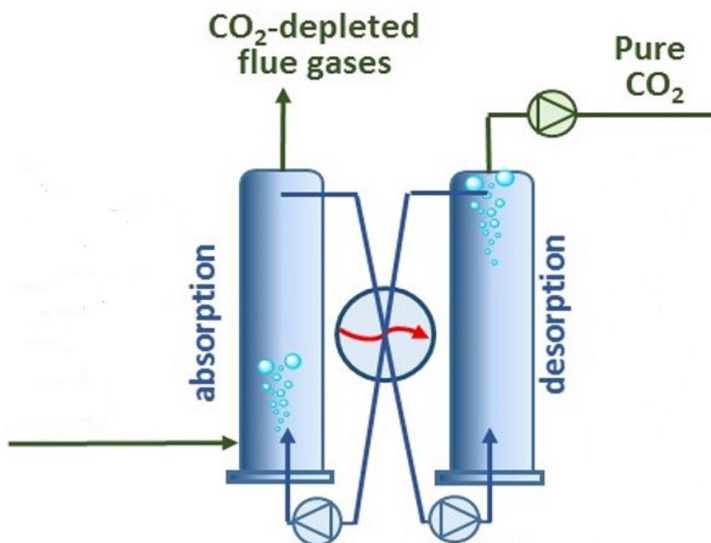


Process

The separation of CO_2 is done by chemical scrubbing using ionic liquids. These task-specific liquids are molten salts that are in liquid state at room temperature. Due to their ionic bond, the liquids do not evaporate and thus enable an energy-efficient regeneration by vacuum without discharge. Thereby, the energy demand is shifted from heat to electricity. The CO_2 separated reaches the high purity which is needed for the RECODE utilization paths.

CO_2 containing gas streams (flue gas, biogas, ambient air) are fed into the absorption column in which the liquid is loaded. Without feeding stripping gas, CO_2 is released from the liquid in the desorption column only by applying vacuum at 20 – 100 mbar. Liquid pumps and controllers ensure stable operation of the solvent cycle. Both columns operate at the same temperature level of 60 – 80 °C. This makes up for the low thermal energy required. A heat exchanger within the liquid cycle further economizes heat demand through the exchange of reaction heat of the absorption and desorption process. Within RECODE, the liquid is tailored for treating oxygen-rich flue gas streams to keep up operation of the absorption column at elevated temperature.

The process was developed by DVGW-Forschungsstelle (GER) in cooperation with chemical supplier IoLiTec (GER). The RECODE demonstration plant for separation of cement flue gas was designed and constructed by Hysytech (ITA).





Facts

- ❑ Up to 50 % lower energy consumption compared to amine scrubbing (benchmark)
- ❑ Lower life cycle cost compared to benchmark
- ❑ CO₂ separation efficiency of 80 %
- ❑ CO₂ purity of up to 99 vol-%
- ❑ Optimized degradation behavior
- ❑ No VOC (Volatile Organic Compounds) emissions
- ❑ Lower levels of request for heat integration at < 100 °C



Demo-unit for the treatment of 100 m³/h of flue gas



Project

The Recode project answers the question how the cement industry can lower their carbon footprint: by enabling a circular-economy-approach. The CO₂ produced by cement manufacturing is re-used in significant part within the plant to produce better cement-related products entailing less energy intensity and reducing related CO₂ emissions. Moreover, CO₂ 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 which then were upscaled 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.



Process
Technology




Engineering
Construction



Ionic
Liquids



Project
Coordination

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Appendix B: fact sheet - electrocatalytic conversion of CO₂

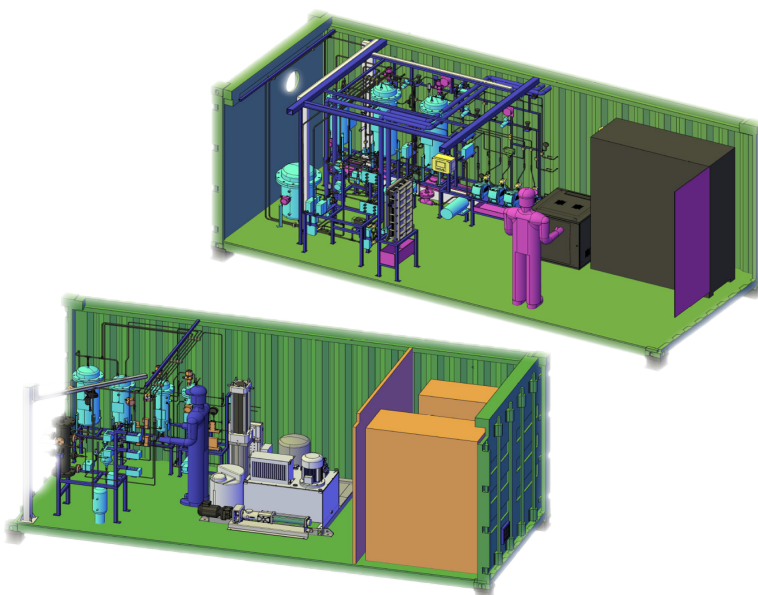
Partners involved in technology:

Electrochemical Synthesis:	Avantium
	University of Groningen
	ERIC
Compression Dissolution:	KIT
	Cubogas
Engineering Construction:	Hysytech
Project Coordination:	IIT



Electrocatalytic conversion of CO₂

a step towards a CO₂ circular economy



The RECODE project has received funding from the European Union's Horizon 2020
Research and Innovation Programme under Grand Agreement No. 768583



Background

To take the circular approach, the captured and purified CO₂ of the cement industry is converted to acid additives for cement formulations. To meet future challenges in terms of energy sources for industrial processes, electrochemical synthesis routes are targeted. Due to the significant cost impact of electricity, high Faradaic efficiencies are needed. High added-value products are coupled with high enough revenues for the company when the ratio of electrons needed per carbon atom is low.

Technology

The chemicals produced for re-use within the cement plant are formate, oxalate and glyoxylic acid. The basis of an efficient electrochemical synthesis are the key functional materials such as catalysts and electrodes. The development was carried out by Academia and SMEs which lead to the design of different electrochemical units. In addition, a new process for the combined gas compression and dissolution was developed. A scale-up of all sub-processes lead to a pre-pilot scale demonstration of the different products.



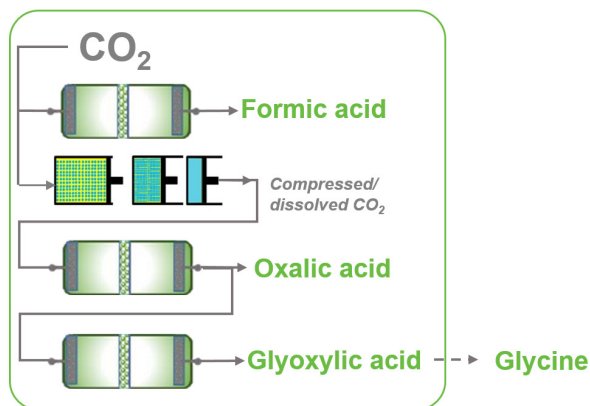
Process

For the synthesis of formate, CO_2 is directly reduced using Avantium's novel gas diffusion electrode technology and a highly selective electrocatalyst developed by the University of Groningen (NLD).

In parallel, the purified CO_2 stream is compressed and dissolved into a non-aqueous electrolyte which is fed to the electrochemical unit where the CO_2 reduction to oxalate takes place. The dissolution system resembles a conventional compressor in which liquid is injected. The simultaneous compression and dissolution enables a nearly isothermal and thereby energy efficient operation.

Oxalic acid – derived from oxalate – is reduced to glyoxylic acid through electrochemical reduction. This reaction is tested in the same unit as formate synthesis which is possible due to the fact that both reactions are carried out in aqueous electrolytes with the same oxygen evolution reaction. One of the container units is designed as a flexible dual nature reactor that is used for testing the two electrochemical processes. This concept brings technological innovation in terms of process and electrochemical cell design.

The compression-dissolution system was developed by Karlsruhe Institute of Technology (GER) and built by Cubogas (ITA). The electrochemical reactors were developed by Avantium (NLD). Hysytech (ITA) assembled all components in two containerized demonstration plants.





- ❑ Development of electrocatalytic routes with high Faradaic efficiency
- ❑ Formate production by electroreduction of CO_2 : Faradaic efficiency $> 90\%$ at $> 100 \text{ mA/cm}^2$
- ❑ Oxalate production by electroreduction of CO_2 : Faradaic efficiency $> 90\%$ at $> 50 \text{ mA/cm}^2$
- ❑ Development of an energy efficient system for the simultaneous compression and dissolution of CO_2 in the electrolyte solution
- ❑ Flexible dual pre-pilot scale unit able to produce 0.5 kg/h of formate or glyoxylic acid



Demo-unit for the production of 0.5 kg/h of formate and glyoxylic acid



Project

The Recode project answers the question how the cement industry can lower their carbon footprint: by enabling a circular-economy-approach. The CO₂ 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 CO₂ emissions. Moreover, CO₂ 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.



avantium



Electrochemical
Synthesis



Engineering
Construction



Compression
Dissolution

Academical partners



Compression
Dissolution



university of
 groningen



Electrochemical
Synthesis




Electrochemical
Synthesis



ISTITUTO
ITALIANO DI
TECNOLOGIA



Project
Coordination

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Appendix C: fact sheet - conversion of CO₂ into nanoCaCO₃

Partners involved in technology:

Membrane-Based Precipitator: CERTH

Packed Bed Reactor: POLITO

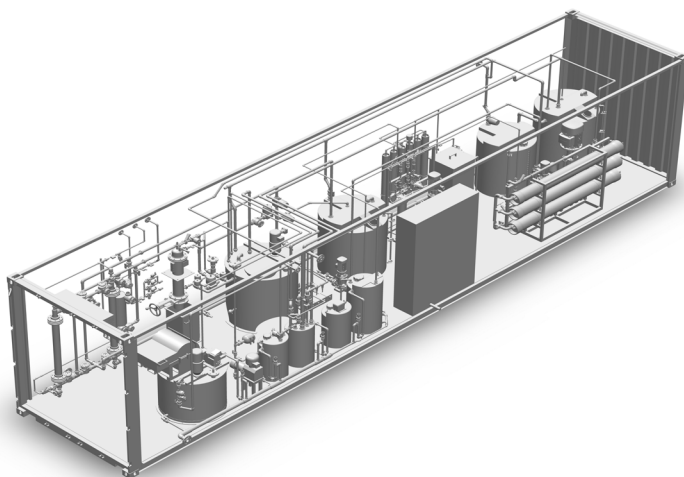
Engineering Construction: MET

Project Coordination: IIT



Conversion of CO₂ into nanoCaCO₃

a step towards a CO₂ circular economy



The RECODE project has received funding from the European Union's Horizon 2020
Research and Innovation Programme under Grand Agreement No. 768583



Background

The application of packed-bed reactor (PBR) and/or membrane-based precipitator (MBP) technologies for converting CO₂ 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 CO₂ emissions. NanoCaCO₃ 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 CO₂ conversion efficiency and a high product quality is achieved in both technologies employed.

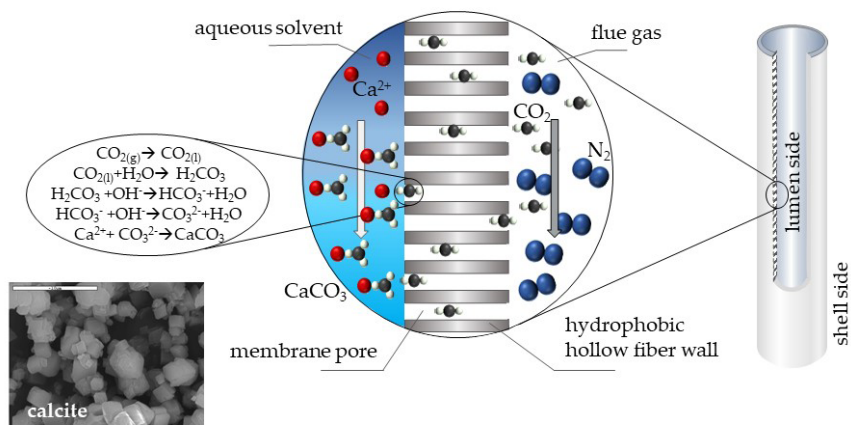
Technology

The technology developed in the RECODE project is used for the utilization of CO₂ by producing CaCO₃ nanoparticles of controllable size and crystallinity as additives for cement and other materials, as well as simultaneous production and crystallization of NH₄Cl. A PBR is used to produce CaCO₃ 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 CO₂, comparing with conventional techniques (i.e. continuously stirred bubbling reactor, CSBR). Similarly production of nano CaCO₃ particles from captured CO₂ using MBP leads to high CO₂ recovery and synthesis of CaCO₃ 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 CO₂ 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 CO₂ 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).





- ❑ CaCO_3 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 CaCO_3 nanoparticles
- ❑ Simultaneous production and crystallization of NH_4Cl
- ❑ Continuous product separation system



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



Project

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Membrane-Based
Precipitator



Engineering
Construction



Packed Bed
Reactor



Project
Coordination