Recycling carbon dioxide in the cement industry to produce added-value additives: a step towards a CO_2 circular economy

Deliverable 7.7
Final report on environmental assessment according to Life Cycle Analysis and REACH methods

WP 7 – Impact analysis

Version [1]

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1 Introduction

The present deliverable D7.7 reports the activities of task 7.1 which involves the evaluation of the environmental impact of the overall process of the RECODE project. The RECODE project aims at the recovery of the CO_2, present in the flue gas from a rotary kiln in cement manufacturing, to produce high added-value products.

The RECODE process is composed of 4 process units:

1. Unit 1 (PU-01) is the CO_2 capture by means of an absorption-desorption process using an ionic liquid as a CO_2 absorption promoter.
2. Unit 2 (PU-02) is the CO_2 conversion into nano$CaCO_3$ particles through a precipitation process.
3. Unit 3 (PU-03) includes the CO_2 compression-dissolution system and the electrochemical conversion into zinc oxalate.
4. Unit 4 (PU-04) is divided into two subunits: the oxalic acid reduction to glyoxylic acid and the CO_2 reduction to potassium formate.

The overall RECODE process is shown in Figure 1.

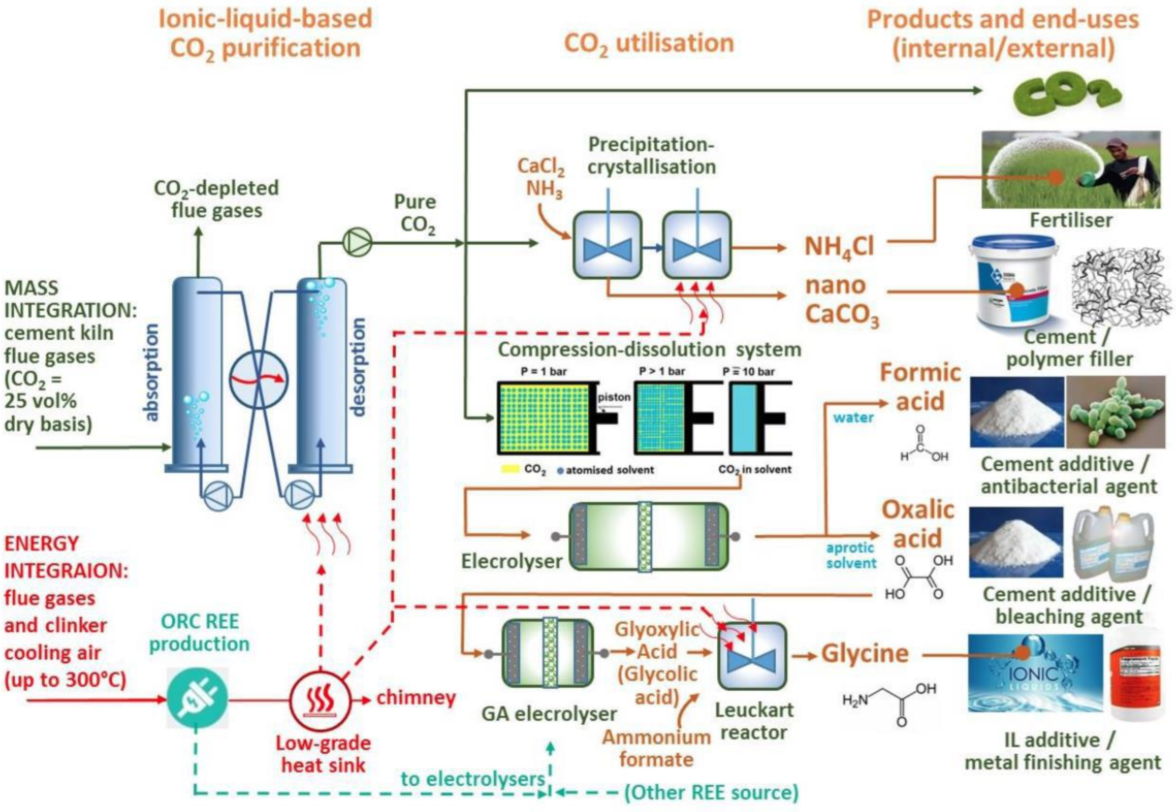

Figure 1: RECODE process

The RECODE project belongs to the field of carbon capture utilization (CCU) technologies. In the long term, CCU technologies must aim for a circular carbon economy which would be emission-neutral once implemented [1–3]. It is therefore necessary to evaluate the feasibility of this project from a sustainable point of view.

The Life cycle assessment (LCA) has been widely adopted to evaluate the potential environmental impacts or drawbacks of products and processes.[4] Thus, the entire life cycle of the process has been assessed with this methodology, including the raw materials collection, gas upgrading and purification and final processing through the RECODE concept.

Furthermore, a comparison between a standard cement production process with the one implemented in RECODE has been performed in order to evaluate the RECODE manufacturing routes' influence on the environmental impact of the cement industries.

Finally, all chemicals involved in the RECODE technologies (e.g. ionic liquids, solvents, catalysts, electrode materials, nanoparticles, etc.) have been checked against the REACH directives to avoid impact on production-workers health, and release of harmful chemicals into the environment.

2 Life cycle assessment

LCA is a technique to measure the environmental aspects and potential environmental impacts associated with a product over its life cycle. According to ISO 14040-44 standards, an LCA study consists of four stages:

1. Goal and scope definition.
2. Life cycle inventory analysis (LCI).
3. Life cycle impact assessment (LCIA).
4. Interpretation of the results.

2.1 Goal and scope definition

The aim is to quantify the potential reduction of the environmental impact that can be achieved by the processes of the RECODE project and to fill the gap in the literature on the key technology components by defining the main critical elements of each process unit.

Data were collected to create an appropriate database for the life cycle analysis (LCA) modelling the estimation of the environmental footprint. For this purpose, mass and energy balances were determined experimentally and via model calculations by the key component developers. The balances for TRL 6 Demo plant were used as an input. In this regard, this study takes the cradle-to-gate approach in which the system boundaries only encompass the product system from the extraction of raw materials to the final product leaving the factory gate [5].

The CO_2 emitted to the environment was considered as an elementary flow. Whilst, captured CO_2 is often treated intuitively as a consumed emission ($GW_{CO2} = -1\ kg_{CO2eq}/kg_{CO2}$), it is a product of human transformation, and so consequently CO_2 is a technical flow and a chemical feedstock for CO_2 utilization. Thus, treating CO_2 as negative emission is usually incorrect, and so the CO_2 captured from the rotary kiln flue gas was instead treated like any other feedstock. [5]

The RECODE process is divided into different units and the product of each process unit was considered as functional unit for the environmental impact evaluation. Calculations have been performed with the SimaPro 9.1 software by means of ILCD-Mid Point baseline method. The Ecoinvent 3.1 database was used to model the dataset in this work by considering the European context as geographical scope. For the multi functionality problems, the system expansion method was adopted according to ISO 14040-44 standards.

2.2 Life cycle inventory

2.2.1 Unit 1: Absorption-desorption unit

Unit 1 includes several gas-treating operations to supply purified CO_2 to downstream process units (PU-02, PU-03 and PU-04). As reported in D.3.4, Titan flue gas presents a variable flow rate and CO_2 composition. For this reason, a mean value of 94 Nm^3/h of flue gas with 10 vol% CO_2 content was considered as the basis for the LCA. The purification of the flue gas is carried out through activated carbon filters while the absorption and desorption of CO_2 are obtained by using the 1-ethyl-3-methylimidazolium acetate ([Emim][Ac]) ionic liquid.

This system should guarantee a production capacity of 8 Nm^3/h of purified CO_2 with a composition ≥ 97%. Considering an adsorbed power of 85% of the installed power, the electric power consumption of the unit 1 is 2.51 kWh/Nm^3 purified CO_2. A detailed description of the process containing mass and energy balances is reported in D6.5.

Nevertheless, an optimized version of the process was studied for the LCA, based on data provided by the partners. This version considers a 98% purified CO_2, lower ionic liquid and activated carbon amount. A batch of 600 Kg of activated carbon every 6 months is required for flue gas purification. 600 L of ionic liquid are required as a start-up with an estimation of 5% of make-up every year. Furthermore, lower electrical consumption (0.43 kWh/Nm^3) was considered which contributed significantly in the decrease of the environmental impact

Nowadays, specific LCA studies about ionic liquid are scarce. Alviz and Alvarez, (2017) evaluated the potential environmental impacts coming from the use of the ionic liquid 1-butyl-3-methylimidazolium bromide ([Bmim]Br) [6]. On this base, the authors of this research work modelled the ionic liquid in terms of LCA. The impact of the ionic liquid was evaluated by considering as input 3-methyl-1-butyl acetate because of their similar impact in terms of global warming potential (GWP).

Table 2-1 provides the life cycle inventory for unit 1.

Table 2-1: LCI of unit 1

INPUTS		
FEED GAS	Flowrate	94 Nm^3/h
	Flowrate	115.1 kg/h

	CO_2 content (% wt)	15 %
IONIC LIQUID	Startup	600 L
	Make-up (5%)	30 L/year
ACTIVATED CARBON	Batch	600 kg/ 6months
CHILLED WATER	Batch	350 kg
ELECTRICAL ENERGY		0.43 kWh/Nm^3 purified CO_2
OUTPUTS		
PURIFIED CO_2	Flowrate	8.8 Nm^3/h
	Flowrate	16 kg/h
	CO_2 purity (% wt)	98%
OFF GAS	Flowrate	91 kg/h
WASTEWATER	Flowrate	7,9 kg/h

2.2.2 Unit 2: Precipitation of calcium carbonate unit

Unit 2 consists of a technology that recycles the CO_2 emitted from cement manufacturing to produce nano-sized $CaCO_3$ particles that could be used as fillers in cement or polymers; The RECODE target of the demo plants for the production of $CaCO_3$ particles was considered as functional unit.

Mass and energy balances were provided by the partners of the WP4 and are presented in Table 2-2.

Table 2-2: LCI of PU-201

INPUTS		
PURIFIED CO_2	Flowrate	7 kg/h
	CO2 purity	98%
CALCIUM CHLORIDE	Flowrate	6.1 kg/h
AMMONIA	Flowrate	17.5 L/h
	Ammonia content (%wt)	24%
DEIONIZED WATER	Flowrate	0.125 m^3/h
ELECTRICAL ENERGY		10 KWh
OUTPUTS		
NANO $CaCO_3$	Flowrate	3.3 kg/h
	$CaCO_3$ purity (%wt)	90%
AMMONIUM CHLORIDE	Flowrate	1.67 kg/h
	NH_4Cl purity (%wt)	90%
WASTEWATER	Flowrate	0.1 m^3/h
WASTE CO_2	Flowrate	3.1 Nm^3/h
	Flowrate	6.1 Kg/h

A best-case scenario was considered in which the unreacted CO_2 is completely recycled and the ammonia recovery is 90%. The inventory is reported in Table 2-3.

Table 2-3: LCI of the best case-scenario of PU 201

INPUTS		
PURIFIED CO_2	Flowrate	7 kg/h
	CO2 purity	98%

CALCIUM CHLORIDE	Flowrate	6.1 kg/h
AMMONIA	Flowrate	17.5 L/h
	Ammonia content (%wt)	24%
DEIONIZED WATER	Flowrate	0.125 m^3/h
ELECTRICAL ENERGY		10 KWh
OUTPUTS		
NANO $CaCO_3$	Flowrate	3.3 kg/h
	$CaCO_3$ purity (%wt)	90%
AMMONIUM CHLORIDE	Flowrate	1.67 kg/h
	NH_4Cl purity (%wt)	90%
WASTEWATER	Flowrate	0.02 m^3/h
CO_2 RECYCLE	Flowrate	3.1 Nm^3/h
	Flowrate	6.1 Kg/h
NH_3 RECOVERY	Flowrate	3.14 kg/h

2.2.3 Unit 3: Compression- dissolution and zinc oxalate production unit

In unit 3 the purified CO_2 is dissolved at high pressure in a dry organic solvent by the compression dissolution system, after which this mixture is led through an electrochemical cell resulting in the reduction of CO_2 to zinc oxalate.

Compression-dissolution system

The compression-dissolution system provides a solvent-CO_2 solution as feedstock for the non-aqueous electrochemical conversion unit. The purified CO_2 deriving from the adsorption-desorption unit is simultaneously compressed and dissolved in a solvent in a piston compressor.

Mass and energy balances for the compression-dissolution unit are explained in detail in D5.2 ad reported in Table 2-4.

Table 2-4: LCI of PU-301

INPUTS		
PURIFIED CO_2	Flowrate	0.7 kg/h
solvent	Flowrate	5.6 L/h
co-solvent	Flowrate	0.96 kg/h
ELECTRICAL ENERGY		0.04 kWh
OUTPUTS		
CO2/solution	CO_2 Flowrate	0.7 kg/h
	Solution Flowrate	5.35 kg/h

CO_2 reduction to zinc oxalate

The electrochemical process PU-302 produces zinc oxalate and 100% faradic efficiency was considered. The process is described in D5.5.

2.2.4 Intermediate steps: From zinc oxalate to oxalic acid

The intermediate step to convert zinc oxalate to oxalic acid was not in the scope of the project but was considered in the environmental impact calculations.

2.2.5 Unit 4A: Glyoxylic acid synthesis unit

The electrochemical cell of PU-401A performs the oxalic acid reduction to glyoxylic acid, the process is illustrated in D5.5. A 100% Faradic efficiency was considered. .

2.2.6 Unit 4B: Potassium formate synthesis unit

The electrochemical cell of PU-401B performs the reduction of the purified CO_2 to potassium formate, this reaction takes place on the cathode of the electrochemical cell whereas on the anodic side in sulfuric acid the oxygen evolution reaction occurs. The process is extensively described in D5.1 and D 5.5. Data were collected based on 100% Faradic efficiency.

2.2.7 Comparison between Portland cement and the RECODE process

To state the potentially favorable effect of the RECODE project, a comparison of the impact of the conventional Portland cement, which is the most common type of cement in general use, and an improved Portland cement derived from the RECODE process was performed

Three different scenarios were considered.

Scenario I: Conventional production of Portland cement

The GWP of the conventional of the production of Portland cement was evaluated by considering the data reported in Table 2-5.

Table 2-5 LCI of commercial Portland cement

	INPUTS	
CLINKER	Flowrate	0.95 kg/h
GYPSUM MINERAL	Flowrate	0.05 kg/h
LIMESTONE	Flowrate	0.05 kg/h
CEMENT FACTORY	Flowrate	5.36E-11 kg/h
STEEL	Flowrate	1.1E-5 kg/h
ETHYLENE GLYCOL	Flowrate	1.9E-5 kg/h
ELECTRICAL ENERGY		0.00697 kWh
HEAT		0.135 MJ
	OUTPUTS	
COMMERCIAL PORTLAND CEMENT	Flowrate	1 kg/h

Scenario II: RECODE process with 80% CO_2 recovery from the rotary kiln flue gases

A second scenario was examined which considered the capture of 80% of the CO_2 emitted by the rotary kiln to produce nano particles of $CaCO_3$ and a 3 wt% addition of nano$CaCO_3$ to the clinker to produce a cement with improved mechanical properties, as proved in D7.5. In this case the CO_2 emitted by the clinker manufacturing was considered as avoided product. The mass and energy balances are listed in Table 2-6.

Table 2-6 LCI of the RECODE process with 80% CO_2 recovery

INPUTS		
CLINKER	Flowrate	0.95 kg/h
GYPSUM MINERAL	Flowrate	0.05 kg/h
LIMESTONE	Flowrate	0.05 kg/h
CEMENT FACTORY	Flowrate	5.36E-11 kg/h
NANO CALCIUM CARBONATE	Flowrate	0.029kg/h
STEEL	Flowrate	1.1E-5 kg/h
ETHYLENE GLYCOL	Flowrate	1.9E-5 kg/h
ELECTRICAL ENERGY		0.00697 kWh
HEAT		0.135 MJ
OUTPUTS		
COMMERCIAL PORTLAND CEMENT	Flowrate	1 kg/h
CARBON DIOXIDE FROM FLUE GAS	Flowrate	0.662 kg/h
CARBON DIOXIDE EMITTED TO AIR	Flowrate	0.155 kg/h

Scenario III: RECODE process with 100% CO2 recovery from the rotary kiln flue gases

Finally, a best-case scenario was estimated in which a total CO_2 capture is performed to synthesize nano$CaCO_3$ to be used as filler in the cement production. Balances are shown in Table 2-7.

Table 2-7 LCI of the RECODE process with 80% CO_2 recovery

INPUTS		
CLINKER	Flowrate	0.95 kg/h
GYPSUM MINERAL	Flowrate	0.05 kg/h
LIMESTONE	Flowrate	0.05 kg/h
CEMENT FACTORY	Flowrate	5.36E-11 kg/h
NANO CALCIUM CARBONATE	Flowrate	0.029kg/h
STEEL	Flowrate	1.1E-5 kg/h
ETHYLENE GLYCOL	Flowrate	1.9E-5 kg/h
ELECTRICAL ENERGY		0.00697 kWh
HEAT		0.135 MJ
OUTPUTS		
COMMERCIAL PORTLAND CEMENT	Flowrate	1 kg/h
CARBON DIOXIDE FROM FLUE GAS	Flowrate	0.777 kg/h

A similar study was conducted within the RECODE project that examined the environmental effect of including 2 wt% of $CaCO_3$ nanoparticles into the cement and compared it with the conventional Portland cement [7].

2.3 Life cycle impact assessment

In a Life Cycle Assessment, the emissions and resources consumed that are linked to a specific product are compiled and documented in the LCI. An impact assessment is then performed, considering human health, the natural environment, and issues related to natural resource use. The purpose of the impact assessment phase is thus to interpret the life cycle emissions and resource consumption inventory in terms of indicators for the Areas of Protection (AoPs). Impacts considered in a LCIA include climate change, ozone depletion, eutrophication, acidification, human toxicity (cancer and non-cancer related) respiratory inorganics, ionizing radiation, ecotoxicity, photochemical ozone formation, land use, and resource depletion. The emissions and resources are assigned to each of these impact categories. They are then converted into indicators using impact assessment models. Emissions and resources consumed, as well as different product options, can then be cross-compared in terms of the indicators [8].

A key driver for CCU is to lower both greenhouse gases (GHG) emissions and dependence on fossil resources, LCA studies for CCU technologies usually analyze midpoints indicator categories, such as global warming and fossil resource depletion which lie in the AoPs of 'Human Health' and 'Natural Environment' [8]. In this case emphasis was placed on evaluating the impact climate change category in terms of global warming potential GWP ($kgCO_{2eq}/kg_{product}$) because conventional production processes involve the intense use of fossil resources leading to a growth in carbon dioxide concentrations in the atmosphere and significant global warming caused by the anthropogenic greenhouse effect. Thus, in order to reduce GHG emissions and to access alternative carbon sources in the chemical industry, new approaches through CCU are being developed.

Even though such processes lead to lower CO_2 emissions compared to the status quo, they can't be considered as carbon-negative, but have net-positive CO_2 emissions over the life cycle. Nevertheless, such emissions can be lower than for competing conventional processes. In this case, the CCU process contributes to climate change mitigation [5].

For the impact evaluation, long term emissions were considered and medium voltage electricity from market group was chosen as energy source.

2.4 Interpretation of the results

2.4.1 Unit 1: Absorption-desorption unit

The GWP of PU-01 is equal to 0.287 $kg_{CO2eq}/kg_{purifiedCO2}$. The main contribution is given by the electricity, which accounts for the 40%, as shown in Figure 2.

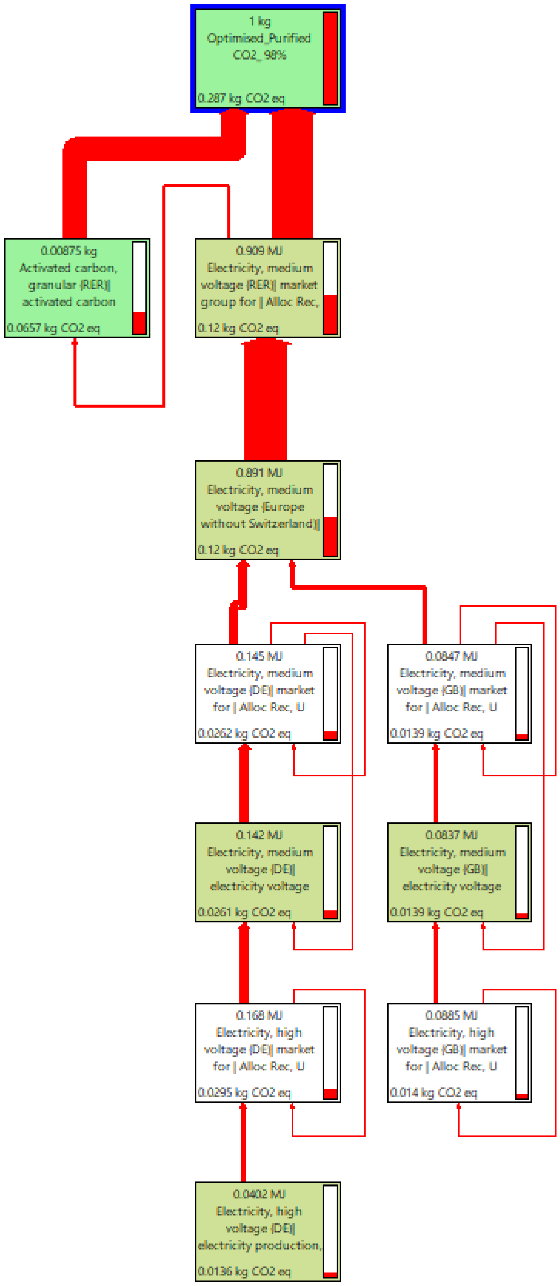

Figure 2 GWP of Unit 1

2.4.2 Unit 2: Precipitation of calcium carbonate unit

The impact of PU-201 is equal to 2.23 $kg_{CO2eq}/kg_{nanoCaCO3}$ (Figure 3). This value considers a 90% ammonia recovery however the large amount of ammonia required for this process is primarily responsible for this result. Further studies should be conducted by trying to lower the amount of ammonia in order to reduce the final impact.

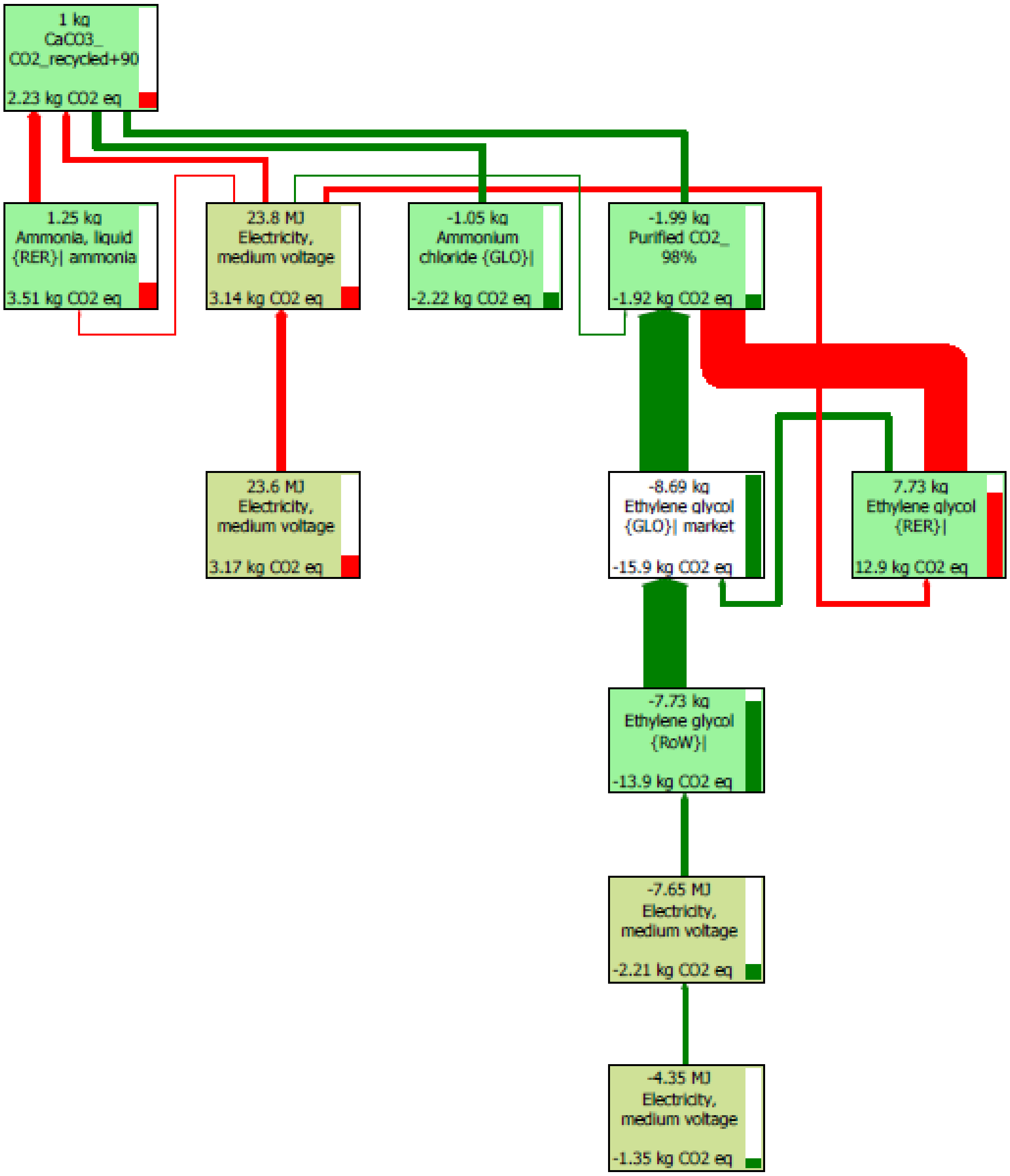

Figure 3 GWP of PU-201

2.4.3 Unit 3: Compression- dissolution and zinc oxalate production unit

Compression dissolution system

The compression-dissolution system has a high impact because of the high energy required for the compression, furthermore the use of the solvents contributes to an increase in the final GWP value.

CO_2 reduction to zinc oxalate

The zinc oxalate production process is affected for the 80% by the high contribution given by the electricity. As the electrical consumption of the unit was not known, the 85% value of the installed power was chosen as electrical energy input. Therefore, this impact could be overestimated and should decrease once the energy consumption is determined. A scenario in which renewable energy is used was not considered but seems to be an important prerequisite for reducing the environmental impact of this process.

2.4.4 Intermediate steps: From zinc oxalate to oxalic acid

The result of the LCA of this process unit highly affected by the impact of electricity.

2.4.5 Unit 4A: Glyoxylic acid synthesis unit

The GWP of the PU-401A is impacted by the foregoing units. In this case the impact of the previous process accounts for the 98% of the total impact. The final value could be largely reduced by optimizing the previous units.

2.4.6 Unit 4B: Potassium formate synthesis unit

The GWP of the PU 401B is could represent a viable route to mitigate the GHG emissions and could be more improved by considering a renewable energy scenario since also here the electricity has a high impact.

2.4.7 Comparison between Portland cement and the RECODE process

Scenario I: Conventional production of Portland cement

The environmental impact of the conventional Portland cement is equal to 0.891 kg_{CO2eq}/kg_{cement}. This value depends on various factors such as the relative amount of the cement components, but it usually varies from 0.7 to 0.9 kg_{CO2eq}/kg_{cement}. The main contribution is given by the clinker production, as illustrated in Figure 4. In this step calcination of calcium carbonate occurs at about 900 °C to form calcium oxide and lime, and it involves a high amount of heat required and a considerable release of CO_2 containing flue gas.

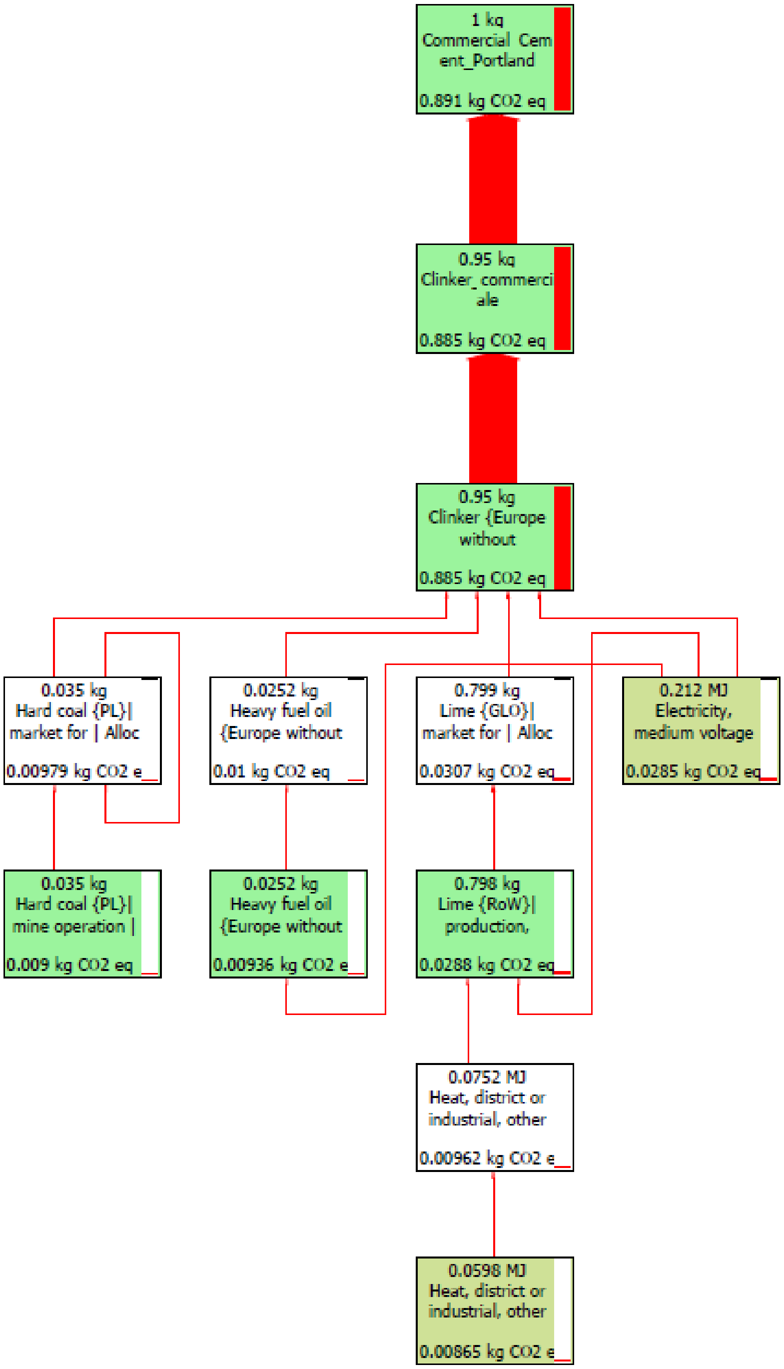

Figure 4 GWP of scenario I

Scenario II: RECODE process with 80% CO_2 recovery from the rotary kiln flue gases

Figure 5 shows the beneficial effect of capturing the CO_2 to produce valuable products. A reduction of the GWP of about 70% could be achieved through the carbon capture and conversion of the 80% of the CO_2 emitted by the rotary kiln.

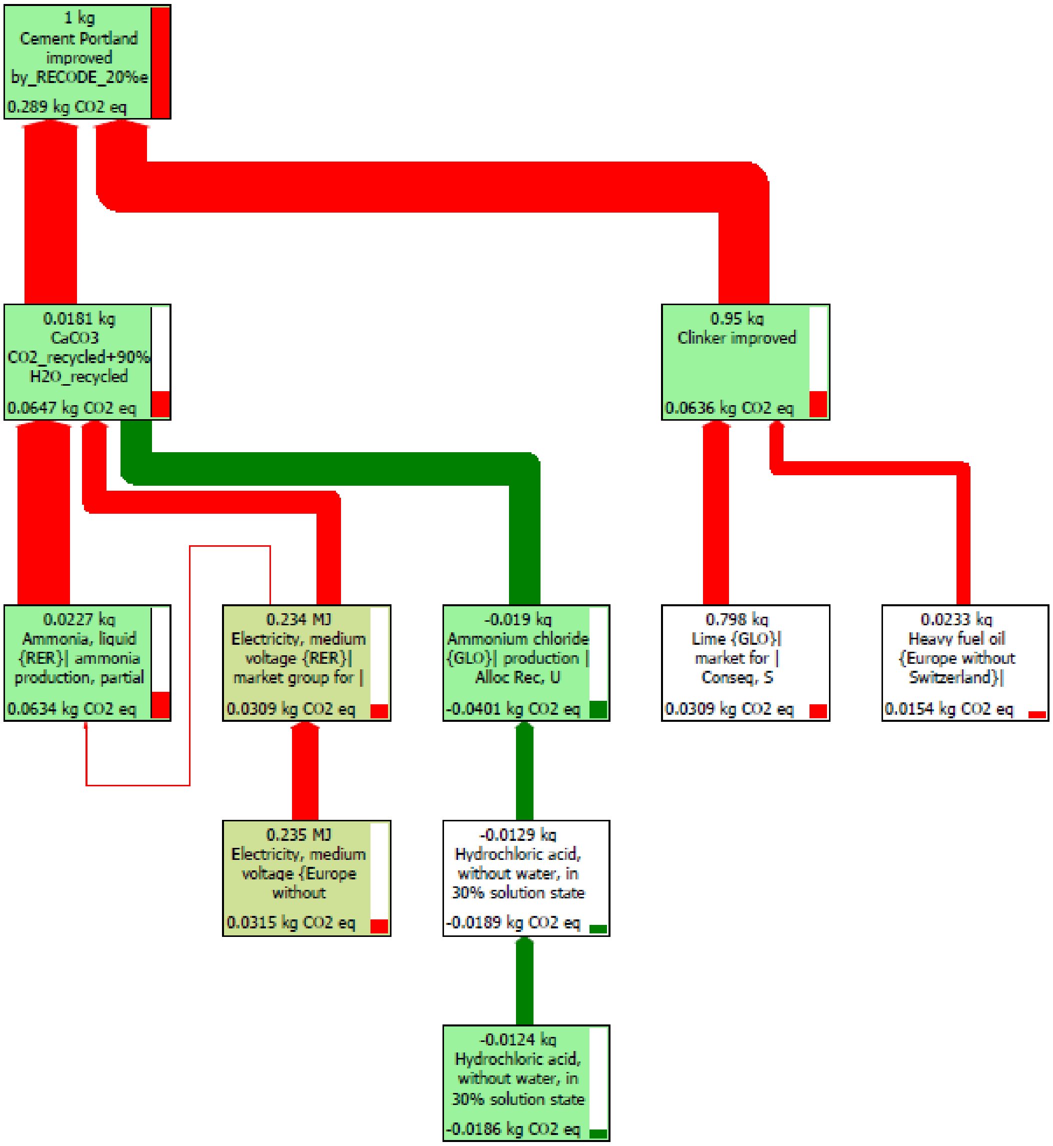

Figure 5 GWP of scenario II

Scenario III: RECODE process with 100% CO_2 recovery from the rotary kiln flue gases

Finally, a GWP reduction of 85% could be obtained by recovering all the CO_2 emitted by the cement manufacturing (Figure 6). The GWP value of 0.134 kg_{CO2eq}/kg_{cement} represents the best-case scenario, that is the theoretical lowest impact value that could be reached through CCU technologies in the context of Portland cement production.

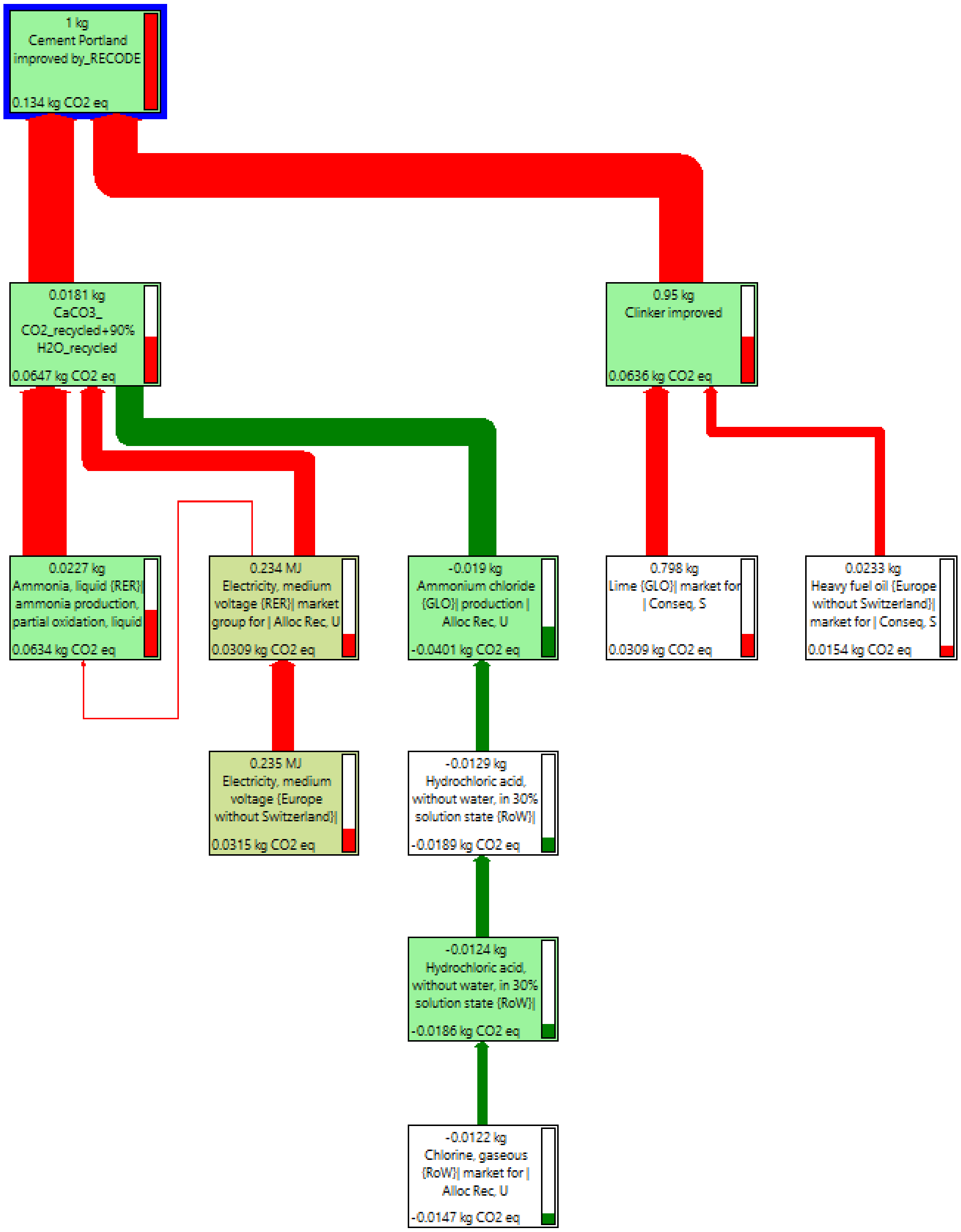

Figure 6 GWP of scenario III

Finally, the environmental impacts of all the units could be further improved by considering renewable energy sources as alternative energy service.

3 REACH analysis

The REACH regulation was adopted to assess hazards and risks of the substances produced within the RECODE project. The analysis was carried out for all the chemicals involved in the four units comprising the process (CO_2 purification, nano-$CaCO_3$ and electrochemical reactors units).
Information about properties and hazards of all substances involved in the project were collected and assessed, to manage the related risk and providing appropriate safety information for the consortium and other users. Additionally, the toxicity assessment of a specific product of the RECODE process, namely $CaCO_3$ nanoparticles, was performed through different in vitro and in vivo screenings. It was demonstrated the high biocompatibility in specific target cells of the $CaCO_3$ nanoparticles as well as their high biocompatibility in selected vertebrate systems (zebrafish, very similar to humans in terms of genome), allowing to predict the absence of health and safety effects of $CaCO_3$ NPs in humans.
The REACH regulation was studied and presented to the consortium during the first meetings. All the details regarding the REACH analysis are widely explained on the previous deliverable D7.1.
No further evaluation has been performed since no additional substances have emerged and used in the process.

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